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Fabric phase sorptive extraction for environmental samples

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ABSTRACT

Fabric phase sorptive extraction (FPSE) has gradually become more widespread as a novel sorptive extraction technique since it has a number of advantages including a wide range of available materials, cheap and easy performance and highly efficient extraction. Because of this, FPSE has been applied in different fields to extract various types of analytes from different kinds of samples. In particular, it has been widely used in environmental applications.

This review covers the use of FPSE in environmental samples. It discusses the optimization of the variables involved during FPSE and presents novel FPSE approaches applied to environmental samples. It also reviews figures of merit obtained using the FPSE methods developed and summarizes data on the occurrence of contaminants in different types of environmental samples. This is done by looking at a selection of different studies in which FPSE is applied to analyze environmental samples.

1. Introduction

The development of analytical methods for the quantitative determination of contaminants in environmental samples is one of the aims of researchers today. Because contaminants are present in the environment at such low levels, extraction techniques are mandatory for most applications. As far as liquid samples or liquid extracts are concerned, sorptive extraction techniques such as solid-phase extraction, solid-phase microextraction and stir bar sorptive extraction are often used to extract contaminants from all kinds of environmental matrices [1,2]. The main reason for this is the versatility of the materials available to cover different types of interaction [3]. Other approaches that involve improvements to the material technology including novel devices or combining with magnetic components are continuously evolving [1,2].

Introduced in 2014 [4], fabric phase sorptive extraction (FPSE) incorporates the advantages of equilibrium based extraction, exploits the benefits of sol-gel coating technology for microextraction sorbents and increases the primary contact surface area (PCSA) for fast analyte sorbent interaction. Moreover, during desorption the fabric can be transformed into very small pieces, and therefore only a small volume of elution solvent is required [4–6], which is in line with the principles of Green Analytical Chemistry [7,8].

Since it overcomes most of the drawbacks associated with other microextraction techniques, FPSE has been applied to extract various types of compounds in different fields such as food, biological samples and environmental samples.

These fields of application have been already covered in some reviews [5,9–11], with this particular review being devoted specifically to environmental analysis. Indeed, the application of FPSE in environmental samples is so far one of its main fields of application and accounts for about half of the studies where this method is applied. Table 1 gathers together these studies and gives details of where environmental samples were extracted using FPSE. In summary, FPSE has been used to extract a wide range of compounds such as drugs, pesticides, personal care products, hormones, polycyclic aromatic hydrocarbons (PAHs) and brominated flame retardants (BFRs) from aqueous environmental samples of varying complexity including drinking and tap water, surface water and sewage samples. Most of the studies in which FPSE is applied in the environmental field follow the same procedure: firstly, the FPSE technique and its variables are optimized; secondly, the method involving FPSE followed by a chromatographic technique is validated; and finally, this method is applied to analyze different types of environmental samples. This is therefore the organization scheme used in this review, in which the following sections cover the steps mentioned above and review the FPSE environmental applications.

2. Fabric phase sorptive extraction variables

The conventional procedure for applying FPSE in a wide range of situations including environmental analysis is as follows. The clean 5 cm^2 FPSE fabric coated with the selected media is immersed in a glass vial containing the sample at the desired conditions (pH, ionic strength, volume, etc.) and stirred with the aid of a magnetic stirrer during the extraction time. After extraction, the compounds retained in the FPSE media are back-extracted into a suitable solvent system. This is done by immersing the dry FPSE fabric in a vial containing the minimum volume

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Table 1
Environmental applications of FPSE: details on the variables involved in the method development.

Compounds	Sample	Material (substrate) dimensions	Optimum FPSE conditions	% Recovery	Determination technique	Ref.
CONVENTIONAL FPSE						
Alkyl phenols	Ground water River water Effluent WWTP Soil Sludge	Sol-gel PTHF (cellulose) n.d.	E: 10 mL pH 6.5, 1000 rpm, 25 min D: 0.5 mL MeOH, immersed, 6 min → direct injection	74-78	LC-UV	[37]
PPCPs	River water Effluent WWTP Influent WWTP	PDMDPS PTHF PEG-PPG-PEG **Carbowax 20M** (cellulose) 2.5 cm x 2 cm	E: 10 mL pH 6.5, 5% NaCl, 900 rpm, 240 min D: 1 mL MeOH, sonication, 6 min → evap dryness and resuspention in 1 mL mobile phase	$\%R_{app}$: 9-80 (river) 14-59 (effluent) 27-93 (influent) %ME: -16-39 (river) -17-38 (effluent) -29-+48 (influent)	LC-MS/MS	[27]
Hormones	Tap water Effluent WWTP Hospital influent WWTP	Sol-gel PTHF (cellulose) n.d.	E: 10 mL pH 5.7, 0% NaCl, 1000 rpm, 20 min D: 0.75 mL MeOH, immersed, 3 min → direct injection	%RR: 73-120 (tap) 68-109 (effluent) 66-114 (influent) %ME: -10-+37 (effluent)	LC-MS/MS	[12]
UV stabilizers	Seawater	**PDMDPS** PTHF PEG (polyester) n.d.	E: 25 mL pH 6, 5% NaCl, 1000 rpm, 150 min D: 1 mL MeOH, immersed, 10 min → direct injection	$\%R_{app}$: 32-51	LC-MS/MS	[13]
UV stabilizers	Effluent WWTP	PDMDPS (polyester) 2.5 cm x 2 cm	E: 10 mL 5% NaCl, 1000 rpm, 30 min D: 1 mL MeOH, immersed, 5 min → direct injection	$\%R_{app}$: 43-99	LC-MS/MS	[22]
PAHs	Rain water River water Influent WWTP	Sol-gel C_{18} (cellulose) 2.5 cm x 2 cm	E: 15 mL 0% NaCl, 1000 rpm, 30 min D: 0.3 mL ACN, sonication, 5 min → direct injection	88-92	LC-FD	[20]
PAHs	River water Reclaimed water	PDMDPS (fiber glass) 1.5 cm x 2 cm	E: 5 mL 0% NaCl, 700 rpm, 50°C, 20 min D (thermal desorption in inlet IMS): vaporization at 160°C	80-105	IMS	[21]
Cytostatic drugs	Effluent WWTP Effluent WWTP Hospital influent WWTP	UCON Caprolactone **Carbowax 20M** CN-Carbowax 20M PEG 300 (cellulose) n.d.	E: 10 mL pH 8 or 10, 0% NaCl, 1000 rpm, 60 min D: 1 mL MeOH, immersed, 5 min → direct injection	$\%R_{app}$: 25-90 (ultrapure) %ME: -42-+29 (effluent)	LC-MS/MS	[14]
Multiclass emerging organic compounds (2 parabens, 3 plastic additives, 1 antimicrobial, 2 anesthetic drugs)	Tap water Ground water Effluent WWTP Water sludge	Sol-gel C_{18} PTHF **Carbowax 20M** (cellulose) 2.5 cm x 2 cm	E: 10 mL pH 3, 10% NaCl, 1200 rpm, 25 min D: 0.4 mL acetone, immersed, 10 min → direct injection	95-99	GC-MS	[28]
Parabens	Effluent WWTP	Carbowax 20M (cellulose) 1.5 cm x 1 cm	E: 3 mL pH 5 + 50 mL DI, 0% NaCl, 1000 rpm, 40 min D: 0.7 mL MeOH, vortex, 1 min → direct injection	94-106	LC-DAD	[35]
Fungicides	Tap water Spring water Fountain water Rain water Run off water River water	PDMS PCAP-PDMS-PCAP PTHF **Carbowax 20M** (cellulose) 2.5 cm x 2 cm	E: 20 mL pH 6, 0% NaCl, 1000 rpm, 20 min D: 0.5 mL EtAc, vortex, 3 min → direct injection	72-115	GC-MS/MS	[15]
Pesticides	River water Lake water Pound water	PCAP-PDMS-PCAP (cellulose) 1.5 cm x 1 cm	E: 50 mL, 1000 rpm, 30 min D: 0.4 mL MeOH/ACN (50/50, v/v), vortex, 0.5 min → direct injection	EF: 125	LC-DAD	[36]

(*continued on next page*)

Table 1 (*continued*)

Compounds	Sample	Material (substrate) dimensions	Optimum FPSE conditions	% Recovery	Determination technique	Ref.
Estrogens	Drinking water Ground water River water Effluent WWTP Hospital influent WWTP	PTHF (cellulose) 2.5 cm x 2 cm	E: 10 mL, 0% NaCl, 1200 rpm, 20 min D: 0.5 mL MeOH, immersed, 8 min + centrifugation 5 min → direct injection	EF: 14	LC-FD	[25]
NSAIDs	River water Effluent WWTP Influent WWTP	PDMDPS PTHF **PEG** (cellulose) 2.5 cm x 2 cm	E: 30 mL pH 2, 0% NaCl, 500 rpm, 120 min D: 1 mL EtAc, immersed, 15 min → evaporation and derivatization	RR: 82-116 EF: 162-418	GC-MS	[16]
Anthracyclines	WWTP	UCON PTHF250 Carbowax 20M CN-Carbowax 20M PEG 300 **PCAP-PDMS-PCAP** (cellulose) 1 cm x 1 cm	E: 20 mL pH 3, 1000 rpm, 15 min D: 2 × 1 mL 10% HCOOH in MeOH/ACN, (50/50, v/v), immersed 4 min → evap to dryness and reconstituted in 1 mL MeOH/ACN, (50/50, v/v)	39-60	LC-FL	[18]
Antidepressant drugs	Lake water Effluent WWTP	PEG-PPG-PEG **PEG** (glass fiber) Circle ○ 100 mm i.d.	E: 1 mL pH 2, 300 rpm, 30 min D: 1 mL MeOH, 10 min, 300 rpm → evaporation and resuspended in 100 μL	RR: 60-93	LC-DAD	[19]
Pharmaceuticals and acesulfame	Effluent WWTP Hospital effluent WW	PEG300 (glass fiber) Circle ○ 100 mm i.d.	E: 10 mL pH 3, 350 rpm, 30 min D: 1 mL 5% NH_3 in MeOH + 1 mL 5% HCOOH in MeOH, 10 min, 350 rpm → evaporation and resuspended	RR: 83.7-114.0 %R_{app}: 20-80 (ultrapure) %ME: -50.5-+54.7 (effluent)	UHPLC-LTQ-Orbitrap	[23]
UV-filters	River water Lake water Sea water	MOF (UiO-66-Zr-NH_2) (polyamide)	E: 150 mL pH 4, 3% NaCl, 400 rpm, 60 min D: 3 mL MeOH/H2O (75/25, v/v), vortex, 15 min → direct injection	28-72	LC-UV	[31]
RELATED FPSE APPROACHES						
Triazine herbicides	Stream water River water	Stir-FPSE PDMDPS PTHF **PEG** (cellulose) n.d.	E: 100 mL, 5% NaCl, 1100 rpm, 60 min D: 1 mL MeOH, stirring, 5 min → evaporation and resuspension (50 or 100 μL)	%R_{app}: 22-70 (ultrapure)	LC-DAD and LC-MS/MS	[17]
BFRs	Reservoir water Effluent WWTP	Stir bar-FPSE & magnetic stir-FPSE PDMDPS **PTHF** PEG (cellulose) n.d.	Stir bar-FPSE E: 10 mL, 15% NaCl, 300 rpm, 10 min D: 0.3 mL ACN, sonication, 10 min → direct injection Magnetic stir-FPSE E: 10 mL, 10% NaCl,400 rpm, 15 min D: 0.3 mL ACN, sonication, 15 min → direct injection FPSE E: 10 mL, 15% NaCl, 400 rpm, 20 min D: 0.3 mL ACN, sonication, 10 min → direct injection	87-96 (stir bar-FPSE) 85-95% (magnetic stir-FPSE) 82-89% (FPSE)	LC-DAD	[26]
PPCPs	River water Effluent WWTP Influent WWTP	DFPSE Carbowax 20M (cellulose) ○ 47 mm i.d. 3 disks	E: 50 mL (25 mL influent) pH 3, 10% NaCl, 10 min D: 10 mL EtAc → evaporation and resuspension (1 mL mobile phase)	%R_{app}: 10-76% (river) 5-64% (effluent) 3-45% (influent) %ME: -5-26% (river) +9-36% (effluent) -7-52% (influent)	LC-MS/MS	[39]
Benzoyl urea insecticides	Drinking water Mineral water Tap water River water Lake water	MI-FPSE **Carbowax 20M** (cellulose) Circle ○ 1 ″ i.d.	E: 100 mL, 800 rpm, 40 min D: 1 mL MeOH, 2 min → evaporation and resuspended in 100 μL	50-73 EF: 501-731	LC-DAD	[24]

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Table 1 (*continued*)

Compounds	Sample	Material (substrate) dimensions	Optimum FPSE conditions	% Recovery	Determination technique	Ref.
Fluoroquinolones	Reservoir water Lake water River water Wastewater	Stir-bar FPSE **PEG** PDMDPS PTHF (cellulose) n.d.	E: 10 Ml pH 6, 10% NaCl, 400 rpm, 10 min D: 0.3 mL Hac/ACN, sonication, 15 min → direct injection	28-32 RR: 90-100	LC-UV	[38]

ACN: acetonitrile; BFRs: brominated flame retandants; D: desorption; DAD: diode array detector; DFPSE: dynamic FPSE; E: extraction; EF: extraction factor; EtAC: ethyl acetate; FD: fluorescence detector; FPSE: fabric phase sorptive extraction; GC: gas chromatography; IMS: ion-mobility spectrometry; LC: liquid chromatography; ME: matrix effect; MeOH: methanol; MS: mass spectrometry; MS/MS: tandem mass spectrometry; n.d.: no data; NSAIDs: non-steroidal inflammatory drugs; PAHs: polycyclic aromatic hydrocarbons; PPCPs: pharmaceuticals and personal care products; PCAP: polycaprolactone; PDMS: polydimethyl siloxane; PDMDPS: poly(dimethyldiphenylsiloxane); PEG: polyethylene glycol; PPG: polypropylene glycol; PTHF: polytetrahydrofune; R_{app}: apparent recoveries; RR: relative recoveries; UV: ultraviolet; WWTP: wastewater treatment plant.

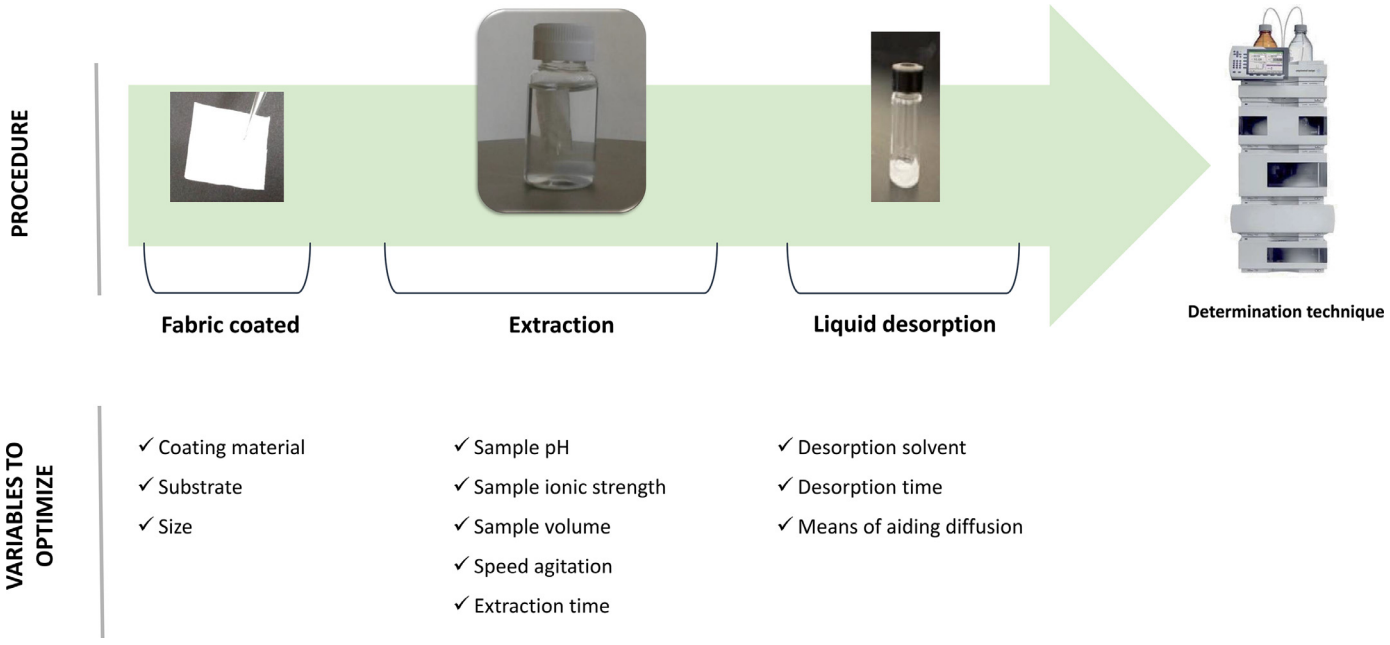


Fig. 1. Steps involved in the conventional FPSE procedure for the analysis of environmental samples and the main variables involved during the optimization.

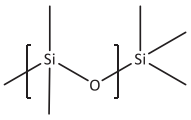
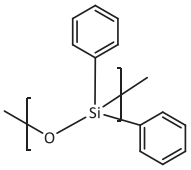
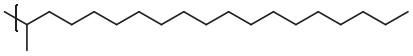
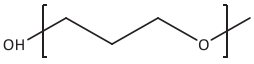
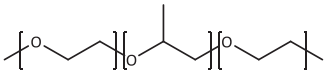
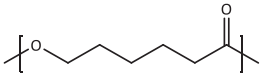
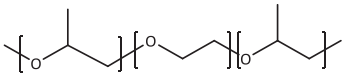
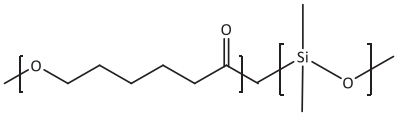
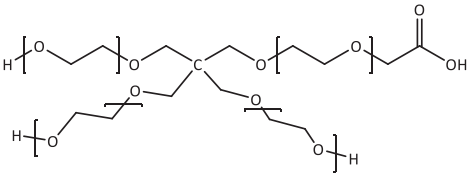
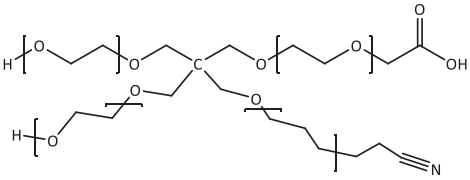
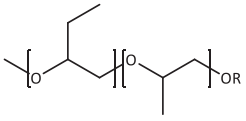
of the solvent system and leaving it in contact for the predetermined desorption time. The fabric is then removed and the extract solution directly injected into the chromatographic system or evaporated to either reduce the volume and increase the preconcentration or exchange the solvent. In order to reuse the FPSE fabric and avoid carryover, the fabric is cleaned with solvents and left to dry and then stored until it is next used. Fig. 1 shows the conventional procedure involved in a typical FPSE application.

In order to enhance the extraction efficiency of the FPSE, a number of variables involved in the extraction should be optimized. Fig. 1 also details a list of the most common variables to be optimized. They include the type of material, the extraction conditions (conditions and volume of the sample, extraction time, stirring speed, etc.), the desorption conditions (volume and desorption solvent, desorption mode, etc.) and the washing/restoring conditions. All these parameters along with the most common values selected for environmental samples are discussed in this section. Table 1 details the optimum extraction conditions and readers are redirected over the course of the review to follow these details in the text.

It should be noted that the optimization of the parameters was carried out either by using chemometric tools such as experimental design [12–19] or by changing one parameter at a time and evaluating the experimental results.

Like other sorptive extraction techniques, FPSE efficiency is closely related to the characteristics of the coating fabric material. Currently there are several coating materials with different chemical properties available in FPSE. Table 2 lists the most common coatings classified by polarity along with their chemical structure. The choice of extraction material in turn is closely related to the properties of the compounds to be extracted, i.e. if the compounds present non-polar features then the material should also present non-polar characteristics, whereas if the compounds present polar features, the material should also be polar. Table 1 lists the material selected in each example as well as the type of substrate – the entries in bold show when the material was selected from among the various different materials after they were compared. In short, the non-polar sol-gel poly(dimethyldiphenylsiloxane) (PDMDPS) and sol-gel C_{18} were selected to extract the most apolar compounds such as PAHs [20,21] and UV stabilizer [13,22] compounds, while the polar polyethyleneglycol (PEG)-based materials (PEG and Carbowax 20M) were selected for the extraction of more polar compounds such as pharmaceuticals [14,16,23], triazine herbicides [17] or benzoyl urea insecticides [24]. The medium-polar polytetrahydrofuran (PTHF) was used in the extraction of medium-polar analytes such as hormones [12,25] and BFRs [26]. When dealing with a wide range of compounds with different psychochemical properties, the choice of material should be a compromise, although polar/mid-polar materials such as PEG and

Table 2
List of the most common FPSE sorbent coating and its classification.

Polarity	Name of the sorbent coating	Structure	Abbreviation
Non-polar	Sol-gel poly(dimethylsiloxane)		PDMS
	Sol–gel poly(dimethyldiphenylsiloxane)		PDMDPS
	Sol–gel octadecyl		Sol-gel C_{18}
Medium polar	Sol–gel poly(tetrahydrofuran)		PTHF
	Sol–gel poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol)		PEG-PPG-PEG
	Sol-gel polycaprolatone		PCAP
	Sol–gel poly(propylene glycol)-poly(ethylene glycol)-poly(propylene glycol)		PEG-PPG-PEG
	Sol–gel poly(caprolactone)-poly(dimethylsiloxane)-poly(caprolactone)		PCAP-PDMS-PCAP
Polar	Sol-gel Carbowax 20M		Carbowax 20M
	Sol-gel cyanopropyl Carbowax 20M		CN-Carbowax20M
	Sol-gel polyalkylene glycol		UCON

PTHF are commonly the material of choice. For instance, in the extraction of a group of pharmaceutical and personal care products (PPCPs) that have a $LogK_{ow}$ ranging from −0.6 to 6.1, different materials including PDMDPS, PTHF, PEG-polypropyleneglycol-PEG and Carbowax 20M were evaluated [27]. In the comparison the non-polar compounds presented similar recoveries in all tested materials, but the most polar compounds were only retained in the most polar material (Carbowax 20M), which was therefore selected [27]. Similarly, Carbowax 20M was also selected for the extraction of cytostatic drugs [14], multiclass emerging organic compounds [28] and fungicides [15]. Activated carbon cloth is an alternative fabric material obtained by pyrolysis of the phenolic polymer fibers that has been successfully applied to the extraction of lead [29] and iridium [30] from tap water [29,30] and soil [30]. Recently, zirconium metal organic framework (UiO-66-Zr-NH_2) was immobilized on polyamide cotton fabric as sorbent for the FPSE of a group of UV-filters (model compounds) [31]. This material was tested as both under stirring and under flow-through conditions with successful results.

Regarding the substrate used to perform the sol-gel process, in most cases this was cellulose, the hydrophilic nature of which encourages water molecules to approach the extraction device and allows the extraction of non-polar compounds such as PAHs [20]. Nevertheless, in other instances, polyester (hydrophobic) [13,22], which also contains terminal hydroxyl groups that may participate in the polycondensation during the sol-gel process, and silica fiber glass [21,32], which is a suitable substrate for the subsequent thermal desorption, are used.

As for the size of the fabric medium, this is usually 2.5 cm × 2 cm [15,16,20,27,28,33,34], which involves 10 cm^2 of exposure medium (both sides are exposed to the target analytes) and contains a sorbent loading from ~20 mg in PDMDPS medium to ~87 mg in PEG medium [5]. In some cases the size of the fabric is smaller (1 cm × 1.5 cm [35,36]

or 1.5 cm × 2 cm [21]), which works in detriment to capacity. Circle [19,23] and formats other than the square one were adapted in line with the relevant approaches (see Section 3).

As mentioned earlier, the extraction conditions are usually optimized to achieve the greatest efficiency. The optimum sample pH is linked to the pK_a of the target analytes and is usually optimized. In the extraction of a group of NSAIDS (pK_a <5), better efficiency was obtained in acidified samples [16,23]. In another study [14] in which seven cytostatic drug compounds were determined by FPSE (PEG) followed by LC-MS/MS, two extraction pHs (8 and 10) were selected due to the wider range of pk_a values of the target compounds. Nevertheless, in other studies the sample pH is not optimized [17,20–22,25,26,36] and the environmental sample is extracted without adjusting the pH.

As regards ionic strength, this is optimized through the addition of different proportions (from 0% to 20%) of NaCl. The addition of salts is not recommendable in the extraction of the more polar compounds since it encourages the movement of analytes to the surface of the water and minimizes interaction with the sorptive material. It also increases the viscosity and has a negative influence on the extraction kinetics. In correlation with this, most of the studies dealing with environmental water did not add salt [14,15,20,22,24,25,35] or added it at lower percentages (ca. 5–10%) [13,17,27,28,31] after optimization of this parameter. As for seawater, the salt content is only adjusted to the natural concentration in this type of sample [13]. For instance, in one of the studies [13], the concentration of salt in seawater taking into account both the environmental conditions and the sampling sites was calculated as 5% NaCl (w/v), and this was the concentration of salt added to the standard solution during FPSE optimization.

Since FPSE can be considered a microextraction technique, the sample volume extracted is small, with 10 mL being the usual volume for environmental samples. Nonetheless, Gouna et al. [31] assayed larger sample volumes (up to 750 mL). They observed that the extraction efficiency decreased as the sample volume increased, which attributed to an inadequate contact time of the sorbent rather than sorbent saturation. Another feature is that the sample volume is fixed despite the fact that samples with different complexities are analyzed in the same study. For instance, 10 mL was adopted as the optimum sample volume to be extracted from less complex matrices such as drinking and tap water to more complex matrices such as effluent and influent sewage [12,25,28]. This strategy is not followed in other extraction techniques such as SPE, where the volume of sample percolated is in agreement with the complexity of the sample.

Different extraction times are usually assayed to identify the time needed for the analytes to reach equilibrium (t_{95}) and to work under these conditions and decrease the variability. In most of the environmental applications, the extraction time is usually fixed at 15-30 minutes [12,20,22,25,28,34,36,37], although in some studies it is longer (60 min [14,31], 120 min [16] or even 240 min [27]). Despite presenting long extraction procedures, most authors decided to work under equilibrium conditions as many parallel extractions can be performed at the same time, which reduces the total analysis time.

The diffusion of the analytes reduces the time needed to reach extraction equilibrium, and this process is aided by the stirring, sonication or heating of the sample. Magnetic stirring by means of a Teflon-coated stir bar is usually selected at 800–1000 rpm speed after the optimization procedure.

For the back-extraction step, parameters such as type and volume of solvent as well as desorption time are often tested to select the optimum values. In this step the diffusion of analytes is aided in only a few examples by stirring [17,19,23], sonication [20,26,27,38], centrifugation [25] or vortex [31,35,36], with most of them simply submerging [12–14,16,22,24,25] the fabric material in the selected back solvent during the desorption time. As far as the type of solvent is concerned, usually methanol, acetonitrile or a mixture of the two are evaluated [13,14,16,18,27], with methanol [12–14,17,19,22,24,25,27,35,37] being the most frequently selected. In other instances, less polar solvents such as ethyl acetate or hexane are also evaluated when the compounds are less polar or to adjust to the conditions of the subsequent determination technique. In the determination of NSAIDs by FPSE and GC-MS, for instance, only ethyl acetate was considered because of its good compatibility with the derivatization reaction [16]. In other instances, however, different solvents were evaluated during the desorption process. In the extraction of three parabens, for example, acetonitrile, water, methanol, water/methanol (50/50, v/v), ethanol, isopropanol and buffer solution at pH 3 or pH 10 were compared [35]. In the end methanol was selected since it provided the best signal for the tested compounds. In another study [23] where pharmaceuticals owing different pK_a were evaluated, two consecutive elution steps by adding 5% of NH_3 and 5% of HCOOH in the methanol were adopted to enable the satisfactory desorption of all pharmaceuticals. Volumes from 0.3 mL to 1.5 mL are usually tested, with the lowest volume (Table 1 lists the values) that provided the best extraction efficiencies being selected to favor the preconcentration factor as well as the alignment with Green Chemistry principles. However, in some studies low volumes are not enough to back extract the compounds, as for example with the back extraction of a group of UV stabilizers for which 1 mL of solvent provided better recoveries than 0.5 mL [22]. Generally speaking, this low volume extract is directly injected into the chromatographic system [12–15,20,25,26,28,35–37] unless it presents incompatibility or shows bad performance. In this case the extract is evaporated to dryness and redissolved in the appropriate solvent [16,17,27,39]. Desorption times within the range of 2–15 min are usually investigated, with the optimum values being detailed in Table 1. A shorter desorption time may arise due to insufficient desorption of the compounds, whereas a longer desorption time may cause re-adsorption of the compounds into the fabric material. This latter explanation was adopted when, in the extraction of a group of UV stabilizers, the efficiencies were worse when the desorption time was 10 and 15 min than when it was 5 min [22].

Like other microextraction techniques, thermal desorption can also be performed to elute the compounds from the FPSE. This desorption mode was used when FPSE was directly analyzed using ion-mobility spectrometry (IMS) for the determination of PAHs [21]. After retention of the PAH analytes in FPSE, the fabric was directly inserted into the IMS inlet and the sample vaporized at 220 °C and detected by IMS (prior to optimizing the parameters).

The FPSE medium is usually reused a number of times (up to 30) because carryover after the back extraction step is effectively eliminated by washing with 2–3 cycles of solvents such as methanol, acetonitrile, water or combinations thereof. Nevertheless, due to the low cost of each FPSE medium, a single use is cheaper than the solvent consumption (achieving greenness in sample treatment) [34,37].

3. Different FPSE approaches

Variations on the classical FPSE have been developed and applied to environmental samples. In an attempt to increase the contact surface area and improve the diffusion of the extraction process, some approaches include the simultaneous stirring of the whole extraction system. This procedure was pioneered by Roldán-Pijuán et al. [17] with the stir-FPSE, which integrates the FPSE medium with a magnetic stirring mechanism. Fig. 2.i shows the mode of extraction. The stir-FPSE was applied to the extraction of triazine herbicides in environmental samples (Table 1 details the conditions) and achieved recoveries in the range of 22–70%. The improvement in analyte diffusion and the high contact surface area are responsible for the enhanced extraction efficiency and reduction in analysis time. Huang et al. [26,38] proposed the stir-bar FPSE (FPSE cut into a house shape, clamped and fixed by using a stir-bar) and the magnetic stir-FPSE (a similar approach to that presented in the stir-FPSE). Fig. 2.ii shows a diagram of the two approaches. Both of these techniques along with the conventional FPSE were compared for the extraction of BFRs from environmental samples. An interesting feature is that the optimum conditions were slightly different depend-

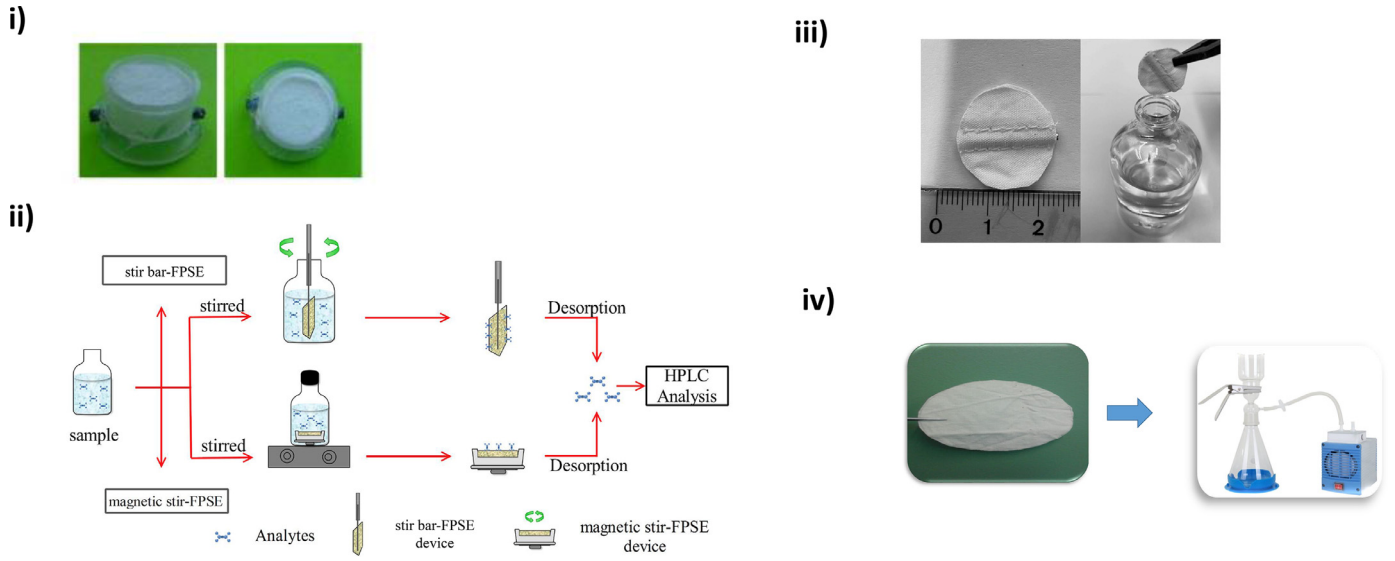


Fig. 2. Configuration of different FPSE approaches: (i) stir-FPSE, (ii) stir-bar FPSE and magnetic stir-FPSE, (iii) magnetic integrated-FPSE and (iv) dynamic FPSE, reproduced from [17] (i) [26] (ii) and [24] (iv) with permission of Elsevier.

ing on the technique (Table 1 for details). Nevertheless, both the stir-bar FPSE and the magnetic FPSE had better extraction efficiency and shorter extraction times than FPSE. Recently, magnet integrated (MI)-FPSE that assembles the coating fabric and the magnet in a single device (Fig. 2.iii) was presented [24]. This approach was successfully applied to the extraction of a group of benzoyl urea insecticides from different environmental samples.

To reduce the long FPSE extraction time, a new mode of FPSE known as dynamic FPSE (DFPSE) was proposed [39]. This uses a 47 mm disk of FPSE medium in a filtration assembly (Fig. 2.iv), with the sample being loaded through this and then the analytes eluted by passing the desorption solvent though it. The dynamic mode decreased the total extraction time considerably. Thus in the comparison of DFPSE and FPSE for the extraction of a group of PPCPs using Carbowax-20M as FPSE medium, the FPSE extraction time was 240 min whereas with DFPSE it was only 10 min, even though the volume percolated was higher (50 mL in DFPSE and 10 mL in FPSE) [27,39]. Nevertheless, the desorption volume (ethyl acetate) was ten times higher in the DFPSE mode than FPSE; thus, the DFPSE is less green as sample extraction technique than FPSE.

On-line flow injection fabric disk sorptive extraction (FI-FDSE) was proposed to automatize the system and reduce the extraction time [40]. The FDSE consisted of a mini column mode with a polypropylene syringe body (1.5 × 4 mm i.d.) being packed in series with the FPSE medium and cut into 38 to 40 disks with the same diameter (4 mm). No frits or glass wool were necessary at either end of the column to block the fabric disks. Fig. 3.i shows the preparation of the FI-FDSE technique. The prepared mini column provided limited back pressure because of the permeation of the FPSE substrate. Therefore, a high flow rate can be applied, resulting in a shorter analysis time with high extraction efficiencies. This approach was successfully applied to the extraction of cadmium and lead from river, coastal and ditch water samples. A similar on-site approach was prepared for the analysis of air samples [32], although in this case a holder accommodated the FPSE medium (Fig. 3.ii shows the device and its sizes). Other approaches in the future are expected to enhance the results and adapt to other determination conditions.

4. Application

4.1. Types of sample

Different types of aqueous environmental samples of varying complexity are analyzed. They mainly comprise effluent (primary, secondary and/or tertiary treatments) and influent sewage samples, but also surface waters such as river, sea and lake water and less complex samples such as drinking, tap, pound, rain and spring waters, among others. Table 1 shows the different types of sample analyzed in each study. Following conventional procedure, these samples are collected randomly (or as grab samples in the case of sewage) in an amber glass container, filtrated using 0.45 μm or/and 0.22 μm nylon filters to remove particulate matter, adjusted to acidic pH to inhibit microbial activity and stored in the fridge at 4 °C until analysis. Due to the nature of the fabric material the filtration step can be omitted that simplifies the analytical procedure approaching to green analytical chemistry principles, but most authors included it to facilitate reproducibility. Only in the case of the stir-FPSE approach was this step avoided [17]. Regarding the solid samples, few studies dealt with soil and sludge [30,37]. In this case the samples were dried and sieved, after which compounds were first solid-liquid extracted; and, then,the conventional FPSE procedure carried out.

The impact of the matrix is clearly marked in the recoveries or extraction efficiencies. However, most studies report relative recoveries, which compensate for this effect. The relative recoveries obtained for a group of steroid hormones in tap water (73–120%) were similar to those found for secondary and tertiary effluent (68–109%) and influent sewage samples (66–114%) [12]. Similarly, the relative recoveries for a group of estrogens were similar in drinking water, ground water, river water, and effluent and influent sewage samples [25]. In the extraction of 100 mL of sample using stir-FPSE (PEG) followed by LC-MS/MS for the determination of the herbicide triazine, the apparent recoveries (of the whole method) reported in ultrapure water ranged from 22 to 70%, while the relative recoveries calculated for stream water were between 75 and 126% [17]. In those determinations that result from mass spectrometry detection, the matrix effect encountered during ionization of the compounds should also be considered. For instance, the matrix effect reported in the determination of a group of PPCPs in river, effluent and influent sewage samples using FPSE (Carbowax 20M) followed by LC-MS/MS ranged from 29% in the form of ion suppression to 49% in the form of ion enhancement [27]. Moreover, the matrix effect has an impact on the apparent recovery. In the same example for the determination of PPCPs [27], the apparent recoveries achieved in river water (27–93%) were similar to those reported in ultrapure water, while the recoveries in sewage samples were slightly lower (9–80% for effluent and 14–59% in influent) [27]. These decreases in recovery were attributed to both the matrix effect and the efficiency of the extrac-

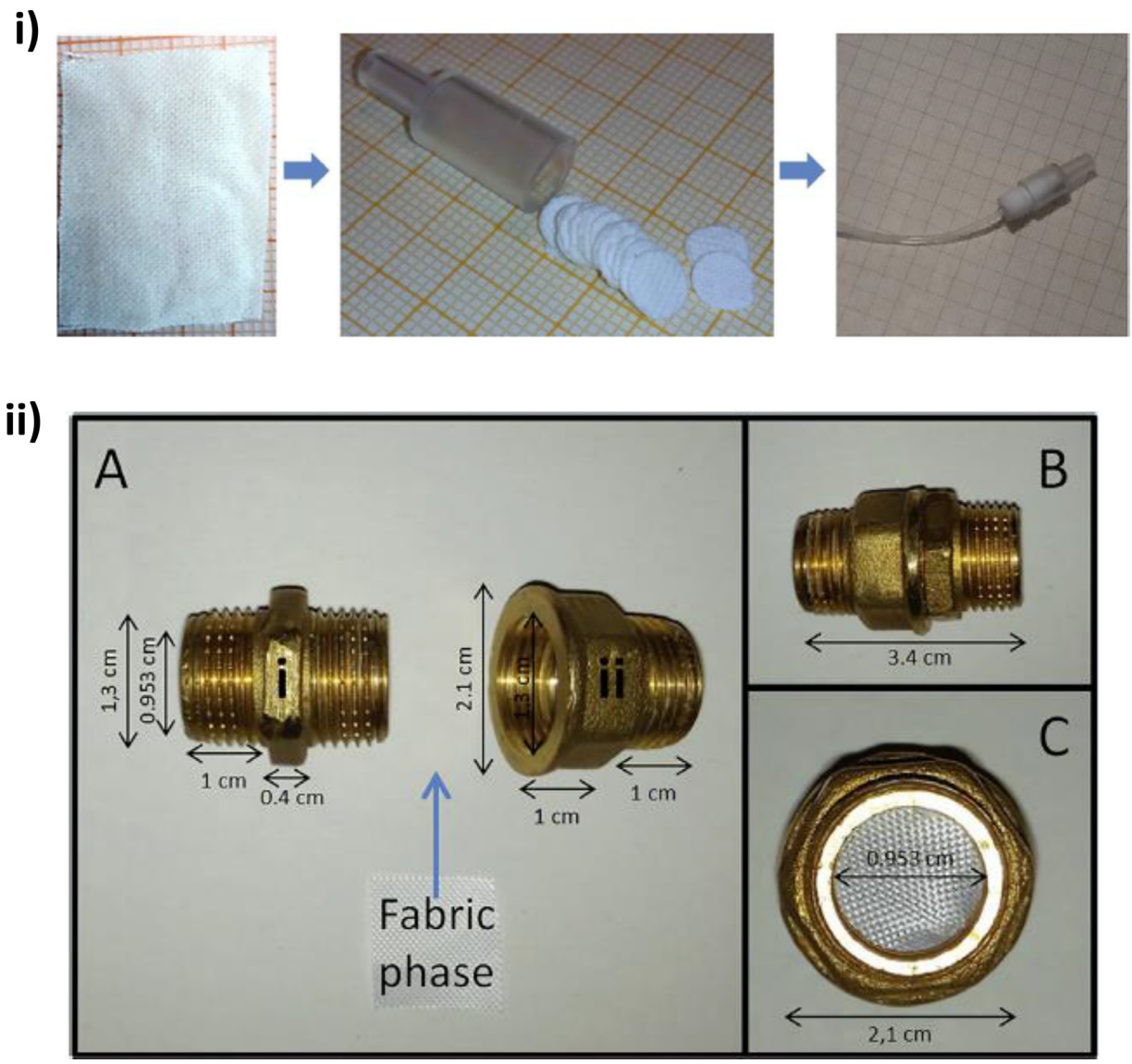


Fig. 3. Configuration of on-line FPSE approaches: i) on-line flow injection fabric disk sorptive extraction (FI-FDSE), and ii) fabric phase holder for air sampling, reproduced from [40] (i) and [32] (ii) with permission of Elsevier.

tion in more complex samples [27]. A similar situation was encountered when determining a group of cytostatic drugs using FPSE/LC-MS/MS [14]. The recoveries in ultrapure water ranged from 37 to 92%, whereas the relative recoveries in effluent sewage samples were between 45 and 200%. The matrix effect values ranged from 42% in the form of ion suppression to 29% in the form of ion enhancement. Fig. 4 details, as an example, the apparent recoveries obtained in ultrapure water and the relative recoveries and matrix effect reported in this study [14] when three different effluent sewage samples from three WWTPs were spiked at 10 $\mu g\ L^{-1}$ with the target compounds.

4.2. Validation parameters

Once the FPSE parameters have been optimized, the analytical parameters of the methods are evaluated in terms of linear range, limits of detection (LODs) and limits of quantification (LOQs), precision and accuracy, among others. Table 3 shows the analytical parameters reported in the various studies dealing with environmental samples in which FPSE is the extraction technique. In most cases the validation is performed in standard solution (or ultrapure water) and only the accuracy is evaluated in environmental samples.

Linearity is usually assessed by preparing 5–10 different concentration levels and plotting the signal versus the concentration of the analytes. Satisfactory linear ranges are reported with determination coefficients greater than 0.998 in all instances (see Table 3 for details). External calibration curves were constructed when the validations were conducted in standard solution [13,14,16,18,20,23–26,31,35–38], whereas calibration curves compensated by internal standard were used to minimize the volume variability that occurs in GC [12,15] and matrix-matched calibrations were conducted to compensate the matrix effect that occurs in LC-MS/MS determination [13,22,28,38].

The sensitivity of the method is assayed by determining the LODs and LOQs experimentally. In most studies the limits were defined on a signal-to-noise (S/N) basis, i.e. S/N ≥ 3 for LODs and S/N ≥ 10 for LOQs. However, when the limits are calculated using environmental samples, this approach is useless if the target analytes are naturally occurring. This was the case when calculating the LODs of a group of PPCPs in sewage samples, which were estimated on the basis of the instrumental LODs and the apparent recovery [39]. Table 3 presents the LODs and LOQs obtained in each study. It should be borne in mind that the sensitivity of a method is influenced by the detector used in the instrumental

Table 3
Environmental applications of FPSE: details on validation parameters.

Compounds	Sample	Determination technique	LODs (ngL^{-1})	LOQs ($ng\ L^{-1}$)	Linear range ($ng\ L^{-1}$) R^2	Repeat. (%RSD)	Reprod. (%RSD)	Accuracy (%RR)	**Ref.**
Alkyl phenols	Ultrapure water	LC-UV	161-192	531-640	5,000-500,000 $R^2 > 0.992$	0.9-1.2	1.2-1.5	89-96% (ground, river, effluent, soil, sludge)	[37]
PPCPs	Effluent WWTP	LC-MS/MS	1-10	10-50	20-10,000 Matrix matched $R^2 > 0.998$	6-15	8-18	-	[27]
PPCPs	Effluent WWTP	LC-MS/MS	2-20	20-100	20-1000 Matrix matched $R^2 > 0.993$	<19	<20	-	[39]
Hormones	Effluent WWTP Hospital influent WWTP	LC-MS/MS	2-264	30-440	500-400,000 Internal stand $R^2 > 0.9997$	<20	<20	-	[12]
UV stabilizers	Seawater	LC-MS/MS	1-9	4-30	n.d. range Matrix matched $R^2 > 0.9932$	4-10	6-21	-	[13]
UV stabilizers	Effluent WWTP Effluent WWTP	LC-MS/MS	6-60	20-200	1,000-500,000 Matrix matched $R^2 > 0.990$	<11	<29	-	[22]
PAHs	Ultrapure water	LC-FD	0.1-1	0.4-3.4	10-10,000 $R^2 > 0.9983$	1-6	2-5	86-93 (ultrapure)	[20]
PAHs	Ultrapure water	IMS	5,000-10,000	15,000-25,000	25,000-250,000 $R^2 > 0.991$	<15	n.d.	river reclaimed water	[21]
Cytostatic drugs	Effluent WWTP	LC-MS/MS	0-5-80	2-267	1,000-500,000 (ultrapure water) $R^2 > 0.998$	<12	<12		[14]
Fluoroquinolones	Ultrapure water	LC-UV	20-50	60-150	250-200,000 $R^2 > 0.99$	2-4	4-3	87-98 (wastewa-ter) 92-99 (reservoir water) 91-101 (river water) 91-99 (lake water)	[38]
Multiclass emerging organic compounds (2 parabens, 3 plastic additives, 1 antimicrobial, 2 anesthetic drugs)	Effluent WWTP	GC-MS	3-20	9-69	50-500,000 $R^2 > 0.9992$	2-4	3-5	>90	[28]
Pharmaceuticals + acesulfame	Ultrapure water	UHPLC-LTQ-Orbitrap	3.1-149.4	9.3-447.7	LOQ-10XLOQ $R^2 > 0.99$	<8	<11	>95 (wastewa-ter)	[16]
Parabens	Ultrapure water	LC-DAD	2,750-3,000	9,150-9,850	5,000-900,000 $R^2 > 0.9952$	<4	<4	>94	[35]
Fungicides	Ultrapure water	GC-MS/MS	1-50	1-165	200-10,000,000 Internal standard $R^2 > 0.9917$	<4	<12	70-115 (river)	[15]
Pesticides	Ultrapure water	LC-DAD	3010-3180	9140-9930	1,000-5,000 in μgL^{-1} $R^2 > 0.9984$	n.d.	<2	95-107 (river, lake, pound)	[36]
Benzoyl urea insecticides	Ultrapure water	LC-DAD	60	200	200-10,000 $R^2 > 0.9914$	<6.1	<8.2	81.5-107.0 (mineral, tap, river, lake)	[24]

(*continued on next page*)

Table 3 (*continued*)

Compounds	Sample	Determination technique	LODs (ngL^{-1})	LOQs ($ng\ L^{-1}$)	Linear range ($ng\ L^{-1}$) R^2	Repeat. (%RSD)	Reprod. (%RSD)	Accuracy (%RR)	**Ref.**
Estrogens	Ultrapure water	LC-FD	20-42	66-139	1,000-500,000 $R^2 > 0.9920$	<2	n.d.	88-98 (drinking, ground, river, effluent (2ari), hospital influent)	[25]
NSAIDs	Ultrapure water	GC-MS	0.8-5	3-15	LOQ-20 No IS $R^2 > 0.998$	<18	n.d.	82-116 (river, effluent, influent)	[16]
Triazine herbicides	Ultrapure water	LC-DAD and LC-MS/MS*	80-470 16-27*	260-1500	n.d.	1.4-4.8	6.8-11.8	75-126 (stream, river)	[17]
BFRs	Ultrapure water	LC-DAD	10-50	100	100-200,000 $R^2 > 0.9981$	<5.1	<6.8	90-99 (reservoir, effluent)	[26]

BFRs: brominated flame retandants; DAD: diode array detector; FD: fluorescence detector; GC: gas chromatography; IMS: ion-mobility spectrometry; LC: liquid chromatography; LODs: límits of detection; LOQs: límits of quantification; MS: mass spectrometry; MS/MS: tandem mass spectrometry; NSAIDs: non-steroidal inflammatory drugs; PAHs: polycyclic aromatic hydrocarbons; PPCPs: pharmaceuticals and personal care products; RR: relative recoveries; RSD: relative standard deviation; UV: ultraviolet; WWTP: wastewater treatment plant.

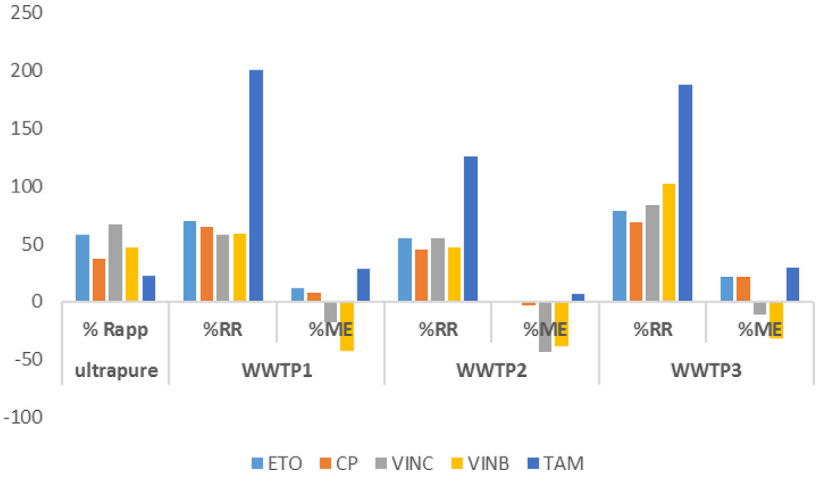


Fig. 4. % Apparent recoveries ($\%R_{app}$) obtained in ultrapure water and relative recoveries (%RR) and matrix effect (%ME) obtained for effluent sewage water from three different waste water treatment plants (WWTP) when a group of cytostatic drugs spiked at 10 $\mu g\ L^{-1}$ were determined by FPSE/LC-MS/MS. Compounds: etoposide (ETO), cyclophosphamide (CP), vincristine (VINC), vinblastine (VINB) and tamoxifen (TAM). (WWTP1 and WWTP2 treat the water of 290,000 and 180,000 equivalent population respectively with conventional activated sludge treatment, while WWTP3 treats the water of a rural area of 7000 equivalent population using membrane bioreactor technology). Data reproduced from [14] with permission of Elsevier.

technique, the preconcentration factors achieved (in this case in FPSE) and the type of matrix. Regarding the detector, for instance, in the determination of a group of triazines using both LC-DAD and LC-MS/MS, the LODs reported were 80–470 ng L^{-1} and 16–27 ng L^{-1}, respectively, which means an improvement in sensitivity in the range of between 5 and 18 times depending on the analyte [17]. As for the preconcentration factor and matrix, the Santana-Rodríguez research group reported limits approximately 6 times lower in seawater [13] than in sewage water [22] when determining the same group of UV stabilizers. This was attributed to the complexity of the sample, but also to the preconcentration factor (25 in the method developed for seawater [13] and 10 in that for sewage samples [22]). The preconcentration factors achieved in environmental applications generally range from 10 to 50, although in some studies they are greater. For example, in the extraction of a group of triazines using stir-FPSE, the preconcentration factor achieved was 2000 and 1000 when the extract was analyzed by LC-DAD and LC-MS/MS, respectively [17]. These large preconcentration factors were obtained because the sample volume was fixed at 100 mL and the extract was evaporated to dryness and re-dissolved in 50 μL of methanol or 100 μL of methanol/5 mM aqueous ammonium acetate (50/50, v/v) to improve chromatographic separation [17]. As it is well-known, evaporation to dryness and reconstitution with a lower volume is a strategy for improving preconcentration factors. In FPSE, however, because the extract volume is usually low (i.e. 0.5–1 mL), this strategy is not often adopted and thus the lengthening of the total analysis time is avoided.

Precision, expressed as a percentage of the relative standard deviation (%RSD) of the methods developed, is evaluated through the repeatability (intra-day variation) and reproducibility (inter-day variation) of usually three or five replicate samples at generally two different concentration levels. Table 3 shows the maximum %RSD values reported for precision in the environmental studies. As expected, these %RSD remain low when dealing with ultrapure water, while higher values are reported as the samples become more complex. For example, in the determination of a group of hormones in tap water, effluent sewage using tertiary treatment and influent sewage, the %RSD ($n = 3$) for inter-day variations ranged from 4.4 to 10% for the tap water, whereas those for the influent were 14.5–19.3% [12].

In those studies, in which the validation parameters were only evaluated in ultrapure water or standard solution, the accuracy of the method is also calculated (through the calculation of relative recoveries) with the environmental samples analyzed. These relative recoveries are generally adequate at values greater than 90% (for details see Table 3). In the determination of estrogens using FPSE followed by LC-FL [25], for instance, the method was validated in standard solution and accu-

racy determined in the form of relative recoveries for ground water (94–95%), drinking water (96–98%), river water (92–94%), effluent sewage (89–92%) and untreated hospital sewage (89–95%), which were the samples that the method was applied to. However, when FPSE/GC-MS was applied to determine NSAIDS from surface, effluent and influent sewage, the accuracy showed more variability because the sample was more complex. Thus relative recoveries were 96–109% for surface water, 92–94% for effluent sewage and 82–116 for influent sewage [16].

4.3. Occurrence

Most of the studies [12–16,18–20,22–24,26–28,35,36,39] applied the methods that include FPSE to analyze different kinds of environmental samples and determine the occurrence of the target compounds in them. In some studies, despite sample analysis, none of the analytes were present or were at concentrations lower than LOQs [18,19,24,28,36]. In the determination of cytostatic drugs in effluent sewage and untreated hospital sewage, just one of the cytostatic drugs (etoposide) was quantified at 2.6 μg L^{-1} at one of the two points of hospital sewage sampled [14]. A similar scenario was found when determining a group of UV stabilizers from seawater, since just one of them (UV 360, which is widely used in sunscreen formulations) was quantified (at concentrations ranging from 41 to 545 ng L^{-1}) at nine sampling points, while the other target compounds were not detected [13]. UV 360 was also found in sewage samples in which the same UV stabilizers were monitored. In this case UV 328 was also quantified (17–60 ng L^{-1}), but at lower concentrations than UV 360 (69–99 ng L^{-1}). Moreover, the highest concentrations of these UV stabilizers were measured in sewage treatment plants that had only primary and secondary treatments, while lower values were reported in the plant with tertiary treatment [22].

The method based on FPSE/GC-MS/MS was applied to determine a group of fungicide herbicides in different samples including five rainwater, one river water and three run-off water samples [15], revealing the presence of eleven out of seventeen of the fungicides in concentrations ranging between 0.01 and 584 μg L^{-1}. In general, the highest number of fungicides was found in rainwater, since these samples were collected from beneath vineyard leaves that had been treated 1–2 weeks previously. Similarly, the river and run-off samples were collected close to the vineyard crop and the presence of some of the fungicides demonstrated the transfer of these contaminants into the aquatic environment.

A similar group of PPCPs was determined in river, effluent and influent sewage samples using either FPSE [27] or DPSE [39] followed by LC-MS/MS. In both studies [27,39], only some compounds in some samples were detected in river water. However, in the case of effluent and influent sewage samples, all the target compounds were found in concentrations ranging from below LOQ levels up to 344 ng L^{-1} for carbamazepine or 776 ng L^{-1} for diclofenac [27,39]. Moreover, in both studies the concentrations generally found in effluent sewage were lower than those reported in influent, although in some cases this did not happen, which could be attributed to the fact that the samplings of effluent and influent were not carried out in the same period.

Bearing all this in mind, FPSE can be considered a worthwhile green extraction technique for contaminant monitoring in environmental samples since it enables enhanced extraction factors to be achieved which involves low detection limits in the analytical methods to determine contaminants at low concentration levels. In addition, it avoids sample manipulation and time consuming that leads to simplification of the techniques as well as reduction of the solvent consumption, in accordance with the Green Sample Preparation directives

5. Conclusions and future perspectives

FPSE and its related approaches are emerging extraction techniques framed in green sample preparation principles that are being increasingly applied in different fields to extract a wide range of analytes. This is mainly due to the great variety of materials available that covers a wide range of polarity as well as strong chemical bonding between the sol-gel materials and the fabric substrates that provides excellent stability.

Environmental water is one of the field of application, in which the introduction of FPSE as an extraction technique followed by determination techniques has involved the development of suitable green analytical methods to determine various contaminants from different types of environmental samples. These analytical methods present good figures of merit such as appropriate sensitivity to determine contaminants at low concentration levels, thanks to the preconcentration factors achieved in FPSE. In addition, FPSE gathers simplification because it might avoid the preliminary sample filtration step and it is easily handled. Analytical methods including FPSE can be therefore successfully applied to monitor contaminant occurrence in different environmental compartments.

Future research in FPSE envisages the development of novel FPSE media, which probably would include green solvents or reagents to further endorse the Green Chemistry Principles. Automation of the method for further application in throughput analysis in the environmental field is another pending issue that should be explored in future. Moreover, on-site analysis using FPSE as passive samplers might be totally feasible. Thus, the FPSE technique has still different unexplored fields.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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