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Review

Applications of Fabric Phase Sorptive Extraction to the Determination of Micropollutants in Liquid Samples

Sarah Montesdeoca-Esponda, Rayco Guedes-Alonso, Sergio Santana-Viera, Zoraida Sosa-Ferrera and José Juan Santana-Rodríguez *

Instituto de Estudios Ambientales y Recursos Naturales (i-UNAT), Universidad de Las Palmas de Gran Canaria, 35017 Las Palmas de Gran Canaria, Spain; sarah.montesdeoca@ulpgc.es (S.M.-E.); rayco.guedes@ulpgc.es (R.G.-A.); sergio.viera@ulpgc.es (S.S.-V.) zoraida.sosa@ulpgc.es (Z.S.-F.)
* Correspondence: josejuan.santana@ulpgc.es

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Abstract: The occurrence of organic micropollutants (OMPs) in the environment is a global concern due to their potential ecological risks. Several studies have shown that some OMPs are widely detected in environmental matrices such as surface water and sewage. Wastewater treatment plants (WWTPs) have received international attention over past decades because they are considered the greatest source of aquatic environmental contamination by anthropogenic micropollutants. Intensive sampling and analysis have been globally made to improve understanding of the occurrence, behavior and fate of OMPs in WWTPs using different types of analytical approach. Recently, special awareness has been devoted to developing new effective strategies to extract the micropollutants of wastewater. In particular, microextraction protocols have gained popularity because of their simplicity, low cost and in-field application for environmental analysis. Among these, fabric phase sorptive extraction (FPSE) is reported as an excellent approach due to its properties, not only reducing the required time but also employing minor solvent volume. In this overview, we summarize the results obtained by the Research Group of Environmental Chemical Analysis of the University of Las Palmas de Gran Canaria (Spain) using this technique. Its aim is to show the potential of FPSE for the extraction of some micropollutants, such as personal care products (benzotriazole ultraviolet stabilizers (BUVSs)) and pharmaceuticals (steroid hormones and cytostatic compounds) in different liquid samples, prior to their determination by liquid chromatography.

Keywords: fabric phase sorptive extraction; organic micropollutants; wastewater treatment plants; sample preparation

1. Introduction

Aquatic ecosystems are affected by the introduction of organic micropollutants (OMPs) of different sources such as domestic, industrial and agriculture effluents. Although these OMPs may be present at trace levels, their adverse effects on aquatic life, animals and even humans are a growing concern. It has been considered that wastewater treatment plants (WWTPs) are the greatest entry of aquatic environmental pollution [1,2] and many of these compounds are polar and persistent and, therefore are not eliminated by conventional treatments.

Consequently, besides minimizing the use of and developing treatments for removing OMP, there is a strong need to increase knowledge of the occurrence of OMPs in wastewater effluents in order to reach an adequate assessment of their environmental impact. For that, the study of water quality is one of the current priority issues around the world.

The OMPs are also called "emerging contaminants", which are compounds that are not included in routine environmental monitoring programs and may be candidates for future legislation due to their adverse effects and/or persistency. OMPs include a diverse group of compounds, such as pharmaceuticals and personal care products (PCPs), drugs of abuse and their metabolites, steroids and hormones, endocrine-disrupting compounds, etc.

At present, an overwhelming number of chemicals are in use worldwide. Their inevitable entry into the environment affects all compartments. These compounds and their degradation products and/or metabolites must be monitored since their eco-toxicity can be comparable or more dangerous than those of the original compounds [3,4].

There is, for that reason, a clear need to reveal the qualitative and quantitative occurrence of OMPs in the environment, but this is only possible with the continual development of sensible and selective analytical processes. Thereby, the range of identifiable chemicals is extended and the quantification limits are lowered.

While nowadays liquid chromatography (LC) in combination with mass spectrometry (MS) represents the best option for the analysis of OMPs in liquid samples, due to their high selectivity and sensitivity, there is no agreement about the most adequate extraction method, and a variety of procedures have been reported.

Although many traditional sample-preparation methods are still in use, such as liquid–liquid extraction or solid phase extraction (SPE), these procedures have some disadvantages like the requirement of large amounts of sample and solvent volume and time. For that, efforts have been made in recent years to simplify the overall sample preparation, reducing the amount of organic solvents and the sample volume and also reducing the time necessary for extraction [5,6].

Currently, sample preparation is moving towards environmental friendly processes, which means miniaturization, automation and simplicity of the methods [7]. A large number of microextraction techniques have been demonstrated to be well-suited for simple and effective analysis of a broad range of compounds in different kinds of sample [8].

Among microextraction techniques, fabric phase sorptive extraction (FPSE) is a novel sample preparation procedure developed by Kabir and Furton [9] that offers unique benefits, such as a high pre-concentration factor for the target analytes, low cost, simplicity and combined use with almost all the analytical measurement techniques. The sorbent is covalently bonded to the substrate surface, offering high chemical, physical and thermal stability.

This paper provides an overview of the FPSE applications carried out by the Research Group of Environmental Chemistry Analysis of the University of Las Palmas de Gran Canaria, Spain, for the extraction of some OMPs in liquid samples prior to their determination by liquid chromatography. The overview includes personal care products (benzotriazole ultraviolet stabilizers (BUVSs)) [10,11] and pharmaceuticals such as steroid hormones [12] and cytostatic compounds [13].

Analysed Compounds

BUVSs are a group of substances extensively employed in PCPs as well as in a large diversity of industrial activities [14], and it has been reported that they could enter to the environment directly (through bathing in rivers or seas) or indirectly (through the effluents of WWTPs) [15]. Their continuous introduction in the marine ecosystem means that these compounds could be accumulated in fish [16,17] and other marine organisms [18,19], even reaching trophic levels as high as marine mammals through the food chain [18,20]. BUVSs have been described as mutagenics, toxics, pseudo-persistents and bioaccumulative and could also pose significant estrogenic activity. Limited information is available regarding the extent of the contamination of this class of ultraviolet (UV) stabilizers, especially the most lipophilic compounds [21].

Steroid hormones are a wide group of biologically active compounds that control many functions of endocrine systems. These compounds excreted by humans reach the aquatic environment daily via sewage systems, and several authors have stated municipal wastewaters as their main entry to

aquatic environments [3,22]. Moreover, industrial wastewaters are a source of hormonal contamination as well. Both natural and synthetic steroid hormones are excreted at very low concentrations, so, the environmental levels of this type of compound are usually in the range of ng or pg per litre [23,24]. Nevertheless, changes in aquatic biota such as hermaphroditism, feminization, inhibition of locomotion and aggressive behaviour or changes in fertility or vitellogenin, could be produced by steroid hormones at lower concentrations than $ng \cdot L^{-1}$ [25,26]. Considering these facts, many extraction, preconcentration and determination methods for steroid hormones have been developed to determine the presence of these compounds in different matrices [27].

Cytostatic compounds are used to fight cancer. These compounds attack the cells preventing their development, but attack both healthy and cancerous cells, so they are potentially carcinogenic [28]. They are considered to be emerging contaminants and there is little knowledge about their degradation products and their possible toxicity; however, some of them have low biodegradability in conventional WWTPs and are considered recalcitrant compounds [29]. Cytostatics are found at very low concentrations [30], reaching the WWTPs mainly through a patient's urine [31]. Despite lack of clarity about the possible damage of these compounds to the environment, it is necessary to establish the concentration value for a safe exposure due to the way these kinds of compound act. They could have genotoxic effects and, in addition, a mixture of them could be more dangerous that the single compounds [32–34].

2. Optimization of Fabric Phase Sorptive Extraction (FPSE) Methodology

FPSE is a simple sample preparation technique consisting of only two main steps: (1) sample extraction, in which the sample is put in contact with the FPSE media and analytes are retained in the sorbent; and (2) solvent desorption, where FPSE media is submerged in a small volume of organic solvent and analytes are back-extracted to this solvent. Figure 1 shows the general procedure applied in FPSE extraction.

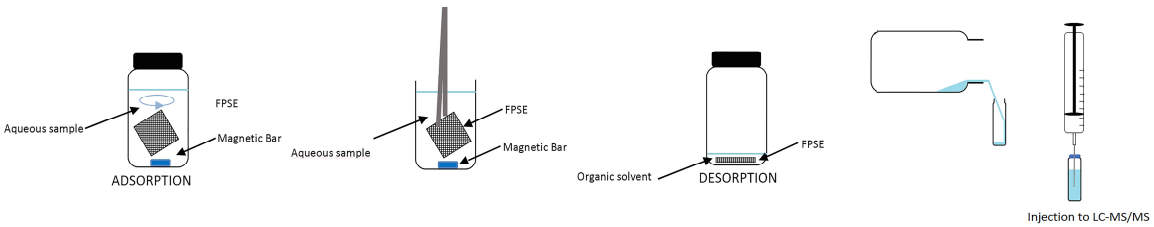

Figure 1. General procedure of fabric phase sorptive extraction (FPSE) methodology.

The efficiency of sorption primarily depends upon the characteristics of the sorbent material used as well as the physicochemical properties of the analytes. Due to the fact that FPSE is an equilibrium process, for the selection of a sorbent it is necessary to obtain good adsorption efficiency but also an adequate desorption of the target compounds.

Currently, there are several coating materials with different properties that could be used as extractants of emerging pollutants. When these compounds present similar physicochemical characteristics, only a coating with appropriate properties for the extraction of all the target compounds can be selected. For example, for the determination of non-polar compounds such as BUVSs, sol-gel-poly(dimethyldiphenylsiloxane) (PDMDPS) provides appropriate extraction capacity [10,11]. Regarding steroid hormones, we chose polytetrahydrofuran (PTHF) coating because it presents medium polarity which has been shown be effective for the extraction of polar, medium polar and non-polar analytes without any derivatization [35]. However, when we deal with a heterogeneous group of compounds with different physicochemical properties, a careful selection of the sorbent as a compromise is necessary. For the extraction of different cytostatic compounds with polar and non-polar characteristics in water samples, a study of different sorbent must be developed to choose

the most suitable coating for all of them. In this case, we chose a sorbent based on carbowax coating, which was appropiate for most of the target compounds.

To ensure the diffusion of the analytes from the sample to the surface of the fabric media during the extraction time, a teflon-coated magnetic stir bar is placed inside, stirring the sample at 800–1000 rpm. Once the extraction is complete, the device is taken from the vial containing the sample and submerged into the back-extracting solvent to recover the retained analytes.

Fabric media can be used several times, which means an important advantage in comparison with other extraction techniques. To eliminate carryover effects when fabric media are reused, after the back extraction step the FPSE device is washed with 2 mL of methanol/acetonitrile (1:1) and 2 mL of deionized water.

In order to not extend the procedure excessively, both extraction time and back-extraction time must be carefully optimized. Enough time should be taken to supply the maximum quantity of extracted analytes but avoid lengthening the procedure too much. On the other hand, long back-extraction times could provide lower efficiencies due to a resorption process onto the FPSE media [10].

Because FPSE is considered a microextraction technique and the sample volume used is small, the sample preparation steps are shorter and simpler. In fact, the extraction of BUVSs, steroid hormones and cytostatic compounds from wastewaters was developed using only 10 mL of sample. Only in the extraction of BUVSs from seawater, because of the difficulties faced for saline samples, was the required volume slightly higher (25 mL) as will be explained later. Higher volumes were not tested in order to achieve a good preconcentration [11].

There are several experimental parameters that must be considered to optimize the FPSE procedure and achieve the greatest efficiencies. The pH, ionic strength and volume of the sample are key variables that must be considered as well as the back-extraction solvent and its volume. In a first stage, a chemometric experimental design including three or four parameters at two different levels (2^3 or 2^4) can be used for a preliminary study into the influence of experimental conditions in the extraction process. These factorial designs allow an understanding of the influence of each variable on the extraction process and the presence of potential correlations among them, evaluating bivariate and partial correlations or Pareto charts of standardized effects. After that, another factorial design could be applied taking into consideration the variables that show strongest correlations. To do this, a 3^2 experimental design (two parameters at three different levels) could be used to build response surfaces where the contributions of each one to the extraction method can be seen. In the different studies developed to extract emerging pollutants from liquid samples, extraction time has been revealed as a key parameter of the process. In this step the physicochemical properties of the target analytes are decisive in the optimization of the extraction, because they define the sorption capacity of the analytes over fabric devices.

Table 1 shows the optimized FPSE conditions for the determination of different OMPs. For example, steroid hormones studied present an optimum extraction time of 20 min [12] while BUVSs and cytostatic compounds need longer times to reach the equilibrium between solid and liquid phases [10,11,13]. Matrix properties could also influence the optimum extraction time. For example, in the determination of BUVSs from seawater samples, 150 min was taken as the extraction time [11], which is longer in comparison with the extraction time used for wastewater samples for the same compounds (60 min) [10]. This different behavior could be due to a slower diffusion of the analytes in a more viscous medium as saline water.

Regarding sample pH, optimum values of this variable are related to pKa of the target compounds. For steroid hormones and BUVSs for example, several pH values were studied and it was observed that extraction efficiencies were higher when it was performed at pH values in which molecules were in neutral form (close to pH 6 for BUVSs and steroid hormones). For cytostatic drugs, it was observed that basic pH values offered a better extraction, but we had to use two different pH (8 and 10) for two

subgroups of target analytes, since the simultaneous extraction of all of them at the same pH provided worse results.

Table 1. Optimum FPSE conditions and method detection limits (MDLs) for the determination of ultraviolet (UV) stabilizers, hormones and cytostatic compounds.

	Benzotriazole Ultraviolet Stabilizers (BUVSs) in Sewage [a]	BUVSs Stabilizers in Seawater [b]	Steroid Hormones in Sewage and Urine [c]	Cytostatic Compounds in Sewage [d]
Type of FPSE	Sol-gel PDMDPS	Sol-gel PDMDPS	Sol-gel PTFH	M-CW20M
Extraction time	60 min	150 min	20 min	60 min
Sample Volume	10 mL	25 mL	10 mL (20 mL urine)	10 mL
pH	6	6	5.7	8 and 10
Ionic strength	0%	5%	0%	0%
Elution volume	1 mL	1 mL	0.75 mL	1 mL
Elution solvent	MeOH	MeOH	MeOH	MeOH
Elution time	5 min	10 min	3 min	5 min
MDLs	1.06–8.96 ng·L^{-1}	6.01–60.7 ng·L^{-1}	1–264 ng·L^{-1} (sewage) 8.9–132 ng·L^{-1} (urine)	0.20–80 ng·L^{-1}

[a] Montesdeoca-Esponda, S. et al. (2015) [10]; [b] García-Guerra R.B. et al. (2016) [11]; [c] Guedes-Alonso, R. et al. (2016) [12]; [d] Santana-Viera, S. et al. (2016) [13].

With respect to the ionic strength of the sample, the addition of salts is not recommendable for the extraction of non-polar compounds because it can reduce the extraction efficiency of compounds with log K_{ow} > 3.5, as for example some BUVSs [36–38] or steroid hormones. The increase of ionic strength probably promotes the movement of the analytes to the water surface and minimizes the interaction with the sorption phase [39]. For instance, for the determination of several BUVS compounds in wastewater samples, different ionic strength conditions between 0 and 10% of salt were tested [10]. As expected, values of 5% and 10% made the extraction less efficient. Something similar happened with the steroid hormones and cytostatic compounds extraction. The study of ionic strength for these compounds showed that the presence of salt cause lower extraction efficiencies. For example, to determine BUVSs in seawater samples, some modifications in respect of the optimized method for sewage samples must be included in order to overcome the problems related with the presence of salt (seawater contains approximately 3.5% of salts) [11]. As we stated above, 10 mL was the optimum sample volume used for wastewater samples while 25 mL was necessary to extract the target BUVSs from seawater samples.

Back-extraction time is also a parameter with a relative importance in the whole procedure. For BUVS determination it was observed that the required back-extraction time was higher for seawater samples (10 min) [11] than for wastewater samples (5 min) [10]. Regarding pharmaceutical compounds, 3 min was long enough for steroid hormones [12], while 5 min was the optimum back-extraction time for cytostatic compounds [13].

Finally, for this back-extraction step, the selected solvent must provide a good desorption of the target analytes and the volume of this solvent must be small enough to reach great preconcentration factors. For the back-extraction of BUVSs, methanol, acetonitrile and a mixture of them were tested in order to check which of them provides better efficiencies. Non-polar solvents like acetone or n-hexane were not tested because they could have an undesirable influence on the shape of the chromatograms, sometimes providing wide and not well-defined peaks that make it difficult to separate chromatographically very similar compounds. Although similar responses were obtained for methanol and acetonitrile, methanol was chosen due to its better resolution of the chromatographic peaks [10]. Regarding cytostatic compounds, methanol and acetonitrile were also tested, and the methanol was found to be the most effective [13].

For the extraction of steroid hormones, it was observed that the recoveries using 1.5 or 0.75 mL of methanol were practically similar, so a volume of 0.75 mL of methanol was established as the optimum

to reach greater preconcentration factors. However, sometimes low volumes are not enough to recover the total amount of analytes retained in the sorbent. For example, for BUVSs, higher signal responses were obtained using 1 mL than using 0.5 mL, despite bigger dilution. Using this back-extraction volume, the enrichment factors achieved for BUVS determination were 10 times for wastewaters samples [10] and 25 times for seawater samples [11]. 1 mL of methanol was also selected for the back extraction of cytostatic compounds [13].

FPSE has been revealed as a powerful analytical tool not only to extract analytes from aqueous samples, but also in biological liquid samples as serum or urine. In clinical fields, it is mandatory to develop analytical methods that permit the quantification of analytes in order to know the progression of an illness or the effectiveness of a medical treatment. To extract target analytes from biological samples, different authors have used extraction procedures that present several pretreatment steps and are usually time-consuming [40,41] because it is necessary to eliminate the interferences, which are present in these types of sample. Nevertheless, FPSE could be used directly in raw samples, with simple pretreatment as filtration or centrifugation. As could be seen in Tables 2 and 3, in other microextraction techniques such as stir bar sorptive extraction (SBSE) or solid phase microextraction (SPME) there are extra steps such as dryness of the extraction device or the evaporation of extracts, as well as longer extraction times than in FPSE.

Table 2. Comparison of microextraction techniques used to extract steroid hormones from urine samples.

Stir Bar Sorptive Extraction (SBSE) [a]	Solid Phase Microextraction (SPME)–Molecularly Imprinted Polymer [b]	FPSE [c]
Dilute 5 mL of urine to 30 mL	Conditioning of the fibre during 5 min	Conditioning of the FPSE media for 10 min
Insert stir bar and extract for 2–4 h.	Centrifuge urine for 15 min	Centrifuge urine for 10 min
Dry stir bar using lint-free tissue	Immerse the fibre into 20 mL of sample during 30 min	Dilute 10 times centrifuged urine
Ultrasound desorption for 15 min with 1.5 mL of solvent	Air-dried the fibre for 3 min	Immerse FPSE media for 20 min
Evaporate to dryness	Thermally desorption at 240 °C for 1 min	Desorption using 750 uL of MeOH for 3 min
Redissolve in 100 uL of CAN/H_2O		
Total extraction time: up to 5 h	Total extraction time: 1 h approximately	Total extraction time: 45 min approximately
MDLs: 300–1000 ng·L^{-1}	MDLs: 8–20 ng·L^{-1}	MDLs: 8.9–132.3 ng·L^{-1}

[a] Almeida, C. & Nogueira, J.M.F. (2006) [40]; [b] Qiu, L. et al. (2010) [41]; [c] Guedes-Alonso, R. et al. (2016) [12].

Table 3. Comparison of microextraction techniques used to extract BUVSs from sewage samples.

SBSE [a]	SPME [b]	FPSE [c]
	Sample vessel was equilibrated in a water bath at 100 °C for 5 min	Conditioning of the FPSE media for 10 min
Insert stir bar and extract for 120 min	Exposed the fiber in head space way for 30 min	Immerse FPSE media for 60min
Dry stir bar using lint-free tissue		
Ultrasound desorption for 20 min with 1.5 mL of solvent	Thermally desorption at 270 °C for 3 min	Desorption using 1 mL of MeOH for 5 min
Total extraction time: 150 min approximately	Total extraction time: 40 min approximately	Total extraction time: 80 min approximately
MQLs: 61.5–184 ng·L^{-1}	MQLs: <2 ng·L^{-1}	MQLs: 20.0–202 ng·L^{-1}

[a] Montesdeoca-Esponda, S. et al. (2013) [42]; [b] Carpinteiro, I., et al. (2010) [43]; [c] Montesdeoca-Esponda, S. et al. (2015) [10].

3. Environmental Applications of Fabric Phase Sorptive Extraction

The optimization and development of different FPSE methodologies followed by ultra-high performance liquid chromatography with tandem mass spectrometry detection (UHPLC–MS/MS) has allowed their application to the determination of several families of OMPs in very varied liquids matrices, such as seawater, wastewater or urine samples.

Analytical parameters depend on the complexity of the matrices and the characteristics of the target compounds. For example, limits of detection (LODs) (calculated from the signal/noise quotient, S/N of the individual peaks assuming minimum detectable S/N levels of 3), differ considerably for BUVSs if the determination is carried out in seawater or in sewage samples. LODs obtained for BUVSs in seawater samples were in the range 1.06–8.96 ng·L^{-1} [11], while for the same BUVSs in sewage samples they vary between 6.01 and 60.7 ng·L^{-1}) [10], approximately 6 times higher in the last case. This is probably due to the higher complexity and content in interferences of this matrix, and also due to the differences in the preconcentration factor reached in each case (10 times for sewage samples and 25 times for seawaters).

Steroid hormones showed limits of detection in the range of 1 to 60 ng·L^{-1} (except for dehydroepiandrosterone, which showed a LOD of 264 ng·L^{-1}) for sewage samples and from 8.9 to 132 ng·L^{-1} for urine samples [12]. In the case of the determination of cytostatic compounds in sewage, LODs between 0.20 to 80 ng·L^{-1}, in the same order of magnitude that those achieved with solid phase extraction, were obtained [13].

For precision, intra-day and inter-day tests (expressed as relative standard deviation, % RSD) were undertaken. For BUVSs in both matrices, the values obtained were quite similar (1.76–10.9% and 7.72–29.2% for sewage [10] versus 3.97–10.0% and 5.71–20.8% for seawaters [11]); however, higher absolute values were obtained for the most complex matrix. The inter-day precision values were higher than the intra-day ones, probably because after 24 h variations owing to adsorption or degradation processes can appear. Regarding steroid hormones, the RSDs obtained in "clear samples", tap and osmotized waters, were lower than 10% while in more complex matrices such as sewage samples, the RSDs were between 10–20%. These differences could be caused by the interferences present in complex samples, which produce more undesired extraction effects [12]. For cytostatic compounds, despite being a heterogeneous group, good reproducibility values were obtained for sewage samples, with RSDs lower than 15% for almost all the compounds [13].

Calibration curves can be built through different approaches. Matrix-matched calibration curves were used for BUVS compounds in order to overcome the possible ionic enhancement or suppression that occurred in mass spectrometry detection, offering satisfactory linear ranges with correlation coefficients greater than 0.990 for all compounds in both type of samples, sewage and seawater [10,11]. As for steroid hormones, two deuterated internal standards were used to compensate the matrix effect. For this reason, external curves in methanol were built and the linearity was evaluated using the relationship between areas and concentrations of compounds and internal standards, achieving correlation coefficients higher than 0.997. The extraction of cytostatic drugs by FPSE in sewage did not present an important matrix effect, external curves with correlation coefficients greater than 0.998 were constructed [13].

The influence of the matrix is clearly observed when the recoveries or extraction efficiencies are calculated for different samples. This comparison was made for the extraction of BUVSs in samples from three WWTPs applying different treatments. For a WWTP that only had primary and secondary treatments, the recoveries were slightly worse (35–83%) than for other WWTPs including tertiary treatment (in the range of 42–99%). Between these last WWTPs, despite the fact that they apply distinct tertiary treatments (microfiltration process and osmosis), the differences in the recoveries are smaller. In this case, in addition to interferences, efficiencies of the methodology could be hindered by the behavior of non-polar compounds [10]. If we compare the extraction efficiencies achieved for the most non-polar BUVSs using FPSE with those obtained employing another techniques such as SBSE or on-line SPE, for which the recoveries were in the range 18–20%, it can be observed that FPSE provides

better yields [42,44]. It is probable that improvement is due to a better desorption of the compounds from the media after being retained.

Regarding steroid hormones, the recoveries obtained in the different analyzed samples showed similar behavior. Relative recoveries were in the range of 80–110% in tap water and slightly lower for treated and untreated sewage (from 65–100%). The differences between these types of sample are possibly because of the interferences present in sewage samples. Even though FPSE is considered as an equilibrium extraction technique, the recoveries obtained are similar to exhaustive extraction techniques such as SPE which uses larger sample volumes and extraction times [45]. For urine samples, the relative recoveries were better than in sewage samples (in the range of 80 to 100%). This could be explained by the dilution step performed with urine samples which is done to minimize the interferences [12].

Relative recoveries for target cytostatic drugs in sewage ranged from 40–100% in most cases. The physicochemical properties of such a studied group vary a lot, so sometimes a compromise solution must be adopted but the results probably will not be the best for some compounds [13]. If we compare our results with those obtained by other authors using SPE [30] and working also with cytostatic compounds from different families, similar recoveries were obtained [46–48]. A comparison with another microextraction technique can not be made because to the best of our knowledge there is no work in which cytostatic compounds are studied using these types of methodology.

The application of the FPSE–UHPLC–MS/MS methodology developed for the determination of BUVSs in samples from WWTPs allowed the measurement of two target BUVSs: UV-328 in the range 0.017–0.061 ng·L^{-1} and UV-360 between 0.069 and 0.099 ng·L^{-1}. The highest concentrations were found in the WWTPs that only applied primary and secondary treatments [10]. In the case of the seawater samples, only the UV-360 was detected among the studied BUVSs, in concentrations between 41.12 and 544.9 ng·L^{-1} [11]. Regarding steroid hormones, the optimized method was applied to tap water, raw sewage from a hospital, treated sewage and urine samples in order to validate the methodology. No hormones were detected in tap water samples, while only testosterone and progesterone were detected in sewage samples from WWTP at concentrations from 28 to 227 ng·L^{-1}. As for urine samples, endogenous steroid hormones (testosterone, progesterone and androstenedione) were detected at higher concentrations than in sewage samples (concentrations were in the range of 1100 to 3500 ng·L^{-1}). The cytostatic drug etoposide was also detected in the effluent of a hospital at 2600 ng·L^{-1}, however no cytostatic drugs were detected in sewage samples from WWTP.

4. Conclusions

Growing awareness of the presence of organic micropollutants in the environment has made it necessary to develop adequate tools for their analysis. Sample preparation is a crucial step in the development of analytical methods for environmental analysis. For that reason, it is important to develop novel analytical processes which should be characterized by a short time of analysis, adequate sensitivity and relatively low cost.

The determination of organic micropollutants in environmental samples is generally performed by liquid or gas chromatography, according to the volatility, polarity and thermal stability of the target analytes. Mass spectrometry is usually the selected detection technique due to its specificity and sensitivity and, consequently, its undoubted power of identification and quantification with very low limits of detection. However, the complexity of environmental matrices and the low concentrations of the pollutants require a sample preconcentration step and removal of the interferences before chromatographic analysis.

Nowadays, the implementation of microextraction techniques is essential to reduce solvent volumes, wasted materials, time and cost. Among them, fabric phase sorptive extraction has been revealed as a very promising technique, which is constantly evolving to fulfil the needs of novel preparation sample requirements in various fields of study.

Sample preparation using fabric phase sorptive extraction coupled to LC–MS has been demonstrated to be a highly efficient methodology for the determination of organic micropollutans in different kinds of sample. This innovative procedure is in accordance with green analytical chemistry concepts, which are oriented towards the development of new analytical technologies able to do direct analysis, using miniaturized equipment, reduced amounts of solvents, and time, and reducing energy costs and waste. However, few of these techniques are implemented in routine environmental analysis because of the lack of commercialization in some cases and the need for validation in others. It is evident that FPSE is a simplified sample preparation procedure that can provide similar or better quantification than other extraction methods, and it can be easily adapted for any type of analytes in any kind of sample.

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