

Considerations on the application of miniaturized sample preparation approaches for the analysis of organic compounds in environmental matrices

Review Article

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Abstract: The miniaturization and improvement of sample preparation is a challenge that has been fulfilled up to a point in many fields of analytical chemistry. Particularly, the hyphenation of microextraction with advanced analytical techniques has allowed the monitoring of target analytes in a vast variety of environmental samples. Several benefits can be obtained when miniaturized techniques such as solid-phase microextraction (SPME) or liquid-phase microextraction (LPME) are applied, specifically, their easiness, rapidity and capability to separate and pre-concentrate target analytes with a negligible consumption of organic solvents. In spite of the great acceptance that these green sample preparation techniques have in environmental research, their full implementation has not been achieved or even attempted in some relevant environmental matrices.

In this work, a critical review of the applications of LPME and SPME techniques to isolate and pre-concentrate traces of organic pollutants is provided. In addition, the influence of the environmental matrix on the effectiveness of LPME and SPME for isolating the target organic pollutants is addressed. Finally, unsolved issues that may hinder the application of these techniques for the extraction of dissolved organic matter from environmental samples and some suggestions for developing novel and less selective enrichment and isolation procedures for natural organic matter on the basis of SPME and LPME are included.

Keywords: Miniaturization • Sample preparation • Microextraction • Environmental samples • Natural organic matter
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1. Introduction

A clear trend in analytical chemistry is the development of miniaturized systems. The term miniaturization is actually applicable to detection, separation and sample preparation techniques [1]. From the point of view of sample preparation, conventional pretreatment techniques are increasingly being replaced by miniaturized alternatives that show several benefits when compared with classical liquid-liquid extraction (LLE) or solid-phase extraction (SPE) techniques. Thus, solid-phase microextraction (SPME) and liquid-phase microextraction (LPME) can be considered as a greener new generation of sample preparation techniques characterized by their negligible extractant phase consumption, high potential to pre-concentrate target analytes, easiness and expeditiousness. Moreover, the volume of generated wastes can be reduced by several orders of magnitude. The broad applicability of these techniques to extraction and pre-concentration of analytes of very different

physicochemical properties has been feasible due to the development of different and complementary SPME and LPME modes. The selection of the most appropriate miniaturized technique is therefore a critical issue for the achievement of large enrichment factors.

A comprehensive description of the different miniaturized sample preparation approaches is not intended in this review. Hence, interested readers are directed to the relevant literature for further information. Specifically, theoretical and applied aspects of SPME and related techniques are addressed in many books and review papers [2-18]. As for LPME, a general book and several general and specific review papers have been published [19-32]. Additionally, some other reviews describing the application of sample preparation approaches to environmental samples can be found in the literature [33-40].

The purpose of this work is to provide an updated and critical overview of miniaturized sample preparation techniques (SPME and related methods and LPME)

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as powerful tools for the monitoring of relevant organic compounds in environmental samples. Finally, the potential implementation of miniaturized sample preparation approaches to the extraction and pre-concentration of relevant complex matrices, such as natural organic matter (NOM) in environmental samples, is suggested.

2. Miniaturization in sample preparation

Miniaturization of classical sample preparation approaches, such as LLE and/or SPE, has been an outstanding research subject since 1990, when Arthur and Pawliszyn first introduced a miniaturized technique named as SPME [41]. Some years later, Liu and Dasgupta [42] and Jeannot and Cantwell [43] published preliminary work of the LPME technique. Nowadays, hundreds of papers are published regarding the development of novel miniaturized sample preparation methodologies and/or their application to different analytical problems. Therefore, it is important to note that downsizing sample preparation still is a trend in analytical chemistry.

Several benefits are derived from the miniaturization of conventional sample pretreatment techniques, *i.e.*, related to the improvement of analytical aspects that affect the overall performance of an analytical method, such as potentially high enrichment factors, rapidity and easiness; and those related to green chemistry aspects, such as negligible consumption of organic solvents, reduced generation of wastes and relatively low sample consumption. Furthermore, the employment of green extractant phases, such as ionic liquids (ILs) or aqueous drops are then feasible. These techniques are prone to certain limitations. For instance, both SPME and LPME are, in general, non-exhaustive extraction techniques, and unlike the conventional LLE or SPE methods careful calibration is required. In addition, some microextraction approaches are not yet the best option when working with relatively complex matrices. The selection of the most appropriate miniaturized technique for a given analytical problem is therefore the first task that the analyst should solve. A concise overview of the available miniaturized sample preparation approaches (SPME and related methods and LPME) is provided on section 2.1 in order to make easier such selection. On the other hand, the understanding of how experimental parameters affect the microextraction processes is highly recommended. Given that most of such parameters are common for the different SPME and LPME modes, a joint description and evaluation

of the variables that play a key role when working with microextraction techniques is tackled on section 2.2.

2.1. Miniaturized sample preparation approaches

2.1.1. SPME and related techniques

The miniaturization of the SPE technique has been a hot topic over the last two decades. Several different miniaturized SPE approaches have been proposed to date. Among them, the SPME technique is the most widely accepted and employed. Introduced by Arthur and Pawliszyn in 1990 [41], SPME is based on the extraction of target analytes by a polymeric coating immobilized in a fused silica fiber. SPME can be performed by immersing the polymer-coated fused silica fiber directly in a sample solution for extraction of volatile and non-volatile analytes, or to the headspace above the sample for extracting volatiles present in the sample. Extraction of organic compounds present in atmospheric samples is also feasible with SPME. The nature of the polymeric coating defines the type of analyte retention (sorption or adsorption) and the type of analytes that may be pre-concentrated using SPME on the basis of their polarity. Currently, five polymers (polydimethylsiloxane (PDMS), divinylbenzene (DVB), polyacrylate (PA), carboxen (CAR) and carbowax (CW)) are available with commercial polymeric coatings. Thus, ten total SPME configurations are commercially available as a result of the combination of the above mentioned polymeric materials. In spite of the great acceptance of SPME, it should be highlighted here that SPME coating fibers show different drawbacks, including reduced lifetime of polymeric coatings, possible carryover, considerable fiber-to-fiber variability, and the above mentioned limited availability of commercial fibers. In the last few years, many researchers have focused their efforts on the development of novel SPME fiber coatings with improved properties (selectivity, mechanical strength, chemical and thermal stability) to overcome the weaknesses of commercially available SPME fibers and to expand even more the applicability of this sample preparation technique. An excellent critical review on the development of SPME coatings is highly recommended for interested readers [6]. Both liquid and thermal desorption can be performed at the end of the microextraction process. The selection of the most appropriate desorption mode depends to a high extent on the analytical instrument employed in combination with SPME.

Non-equilibrium multiple-SPME, based on successive sorption-desorption cycles, can be used to achieve an extraction efficiency equivalent to that of SPME under equilibrium conditions in a reduced sampling time.

The potential of multiple-SPME is based on the exponential relationship between the extraction time and the amount of analyte extracted by the SPME fiber. Furthermore, matrix effect-errors can be avoided with multiple-SPME when dealing with complex matrices [44,45].

Even though SPME is widely recognized as an efficient sample preparation technique, other related miniaturized techniques such as stir bar sorptive extraction (SBSE), needle trap device (NTD) and microextraction in a packed syringe (MEPS) provide complementary analytical information and are therefore included in this discussion.

SBSE was introduced by Baltussen *et al.* in 1999 [46]. In SBSE, a 10-40 mm length stir bar is coated with up to 219 μL of PDMS, and the polymer-coated stir bar is exposed to the sample, or to the headspace above it for extraction and pre-concentration. Keep in mind that PDMS is used as a polymer coating in SBSE [47], the principles that govern the analyte retention are analogous to that of the SPME when this sorbent is used. Nevertheless, the greater coating volume used in SBSE (up to two orders of magnitude when compared with SPME) gives rise to enhanced extractability of analytes showing partition coefficients (K_{ow}) below 10^5 , which can be quantitatively extracted onto the PDMS coating with SBSE unlike SPME. As in SPME, both liquid and thermal desorption can be performed in SBSE. However, a thermodesorption system is needed when applying SBSE in combination with a GC due to the large differences between the dimensions of the polymeric coated-stir bar and the injection port of the GC instrumentation.

NTD was presented by Pawliszyn's group in 2001 with the aim of achieving sampling and analysis of airborne particulate matter and aerosols [48]. The proposed system was designed to obtain the merits of active sampling and SPME. In the NTD technique, the different coatings are immobilized inside the needle, including, PDMS, DVB and CAR [49], Carbo-pack X [50], and carbon nanotubes (CNTs) [51]. Both analytes and particles present in a sample can be trapped onto the coated needle. After that, thermal desorption is easily performed by introducing the needle to the injection port of a GC instrument, liquid desorption may be also performed if necessary. The NTD system is characterized by its high sorption capacity, which allows the achievement of exhaustive extractions. In addition, calibration is easily performed with the NTD system, since quantitative extractions can be obtained [10,17].

MEPS is a miniaturized SPE system introduced by Abdel-Rehim in 2004 [52]. MEPS is based on the same principles that govern SPE, and shares many

aspects with syringe cartridge SPE, but at a reduced scale. Hence, MEPS involves the four common steps described for conventional SPE: sorbent conditioning, loading of the sample, washing the sorbent, and elution of analytes. In MEPS, the sorbent material is packed as a plug in the barrel or located in a small container between the barrel and the needle of a 100-250 μL syringe. A large variety of sorbents can be used in MEPS, including C8, C18, C2, silica and C8 + strong cation exchanger (SCX - commercially available). MEPS has been mainly employed with bioanalytical applications [18], although its use in environmental analysis has been recently proposed [53], (in special cases when only scarce sample amounts are to be analyzed). In addition, pre-concentration and subsequent injection in the corresponding analytical technique can be performed in an automated manner using MEPS [54].

2.1.2. LPME techniques

Many LPME techniques are available for the extraction of target analytes. Even though LPME approaches have been derived from conventional LLE, 'two and three-phases' LPME systems can be used. Thus, miniaturized 'two phases' LPME systems are commonly employed for the direct extraction of neutral (volatile or non-volatile) analytes, while 'three-phases' LPME systems are used for the extraction of ionizable analytes (when using the 'liquid-liquid-liquid' approach), and volatile and semivolatile analytes (when using the 'liquid-gas-liquid' approach').

In 'two-phases' systems, the extractant phase must be immiscible with the sample solution and show low water solubility. The way in which the extractant phase is exposed to the sample defines the different LPME approaches. Thus, in direct-single-drop microextraction (direct-SDME) [55], a microdrop of immiscible extractant phase hanging from the tip of a microsyringe is directly exposed to the stirred sample solution. The limited stability of the drop in the presence of high concentrations of organic matter and/or in the presence of solid particles, or when relatively high stirring rates or extended extraction times are used, restricts the applicability of direct-SDME to clean samples. As it will be described later, both the extraction time and the stirring of the sample solution are key to achieving a large enrichment factor. In this sense, this technique is also limited.

To minimize these limitations, the use of polymeric hollow fibers (HFs) have been proposed [56]. The extractant phase presents cylindrical configuration in hollow-fiber liquid-phase microextraction (HF-LPME). When HFs are used, the extractant phase is protected inside the lumen of the HF, and the extraction of target

analytes is produced by means of the extractant phase that fills the pores present in the walls of the HF. HFs protect the extractant phase from particles during the extraction, and higher stirring rates and extended extraction times can be successfully employed. HF-LPME is, however, more elaborate than direct-SDME and several steps are needed to perform the extraction process.

The use of a microsyringe as a miniaturized separation funnel has also been proposed under the denomination of dynamic-LPME [57]. In this system, the extractant phase is kept inside the barrel of the syringe during the entire extraction process, and the extraction is produced when the extractant phase is exposed to the sample by repeated up and down movements of the plunger (sample draw-eject). It is not advisable to use dynamic-LPME with complex samples owing to the potential damage that sample particles could produce on the syringe.

Several two-phases LPME approaches have been recently proposed where the syringe is only employed to retract back the extract at the end of the extraction process. Thus, exploitation of different physicochemical properties of the extractant phase, such as density and/or melting point, has given rise to the emergence of directly suspended droplet microextraction (DSDME) [58], vortex-assisted liquid-liquid microextraction (VALLME) [59], solidification of a floating organic drop microextraction (SFOME) [60] and dispersive liquid-liquid microextraction (DLLME) [61]. In these systems, the extractant phase is not held during the extraction process but directly exposed to the sample solution. Strong agitation is allowed by these systems, thereby enhancing the extraction kinetics and reducing the required extraction time. Complete dispersion of the extractant phase in the sample can be performed by vortex agitation [59], by the application of ultrasound energy [62], and by addition of a disperser solvent [61]. When the extractant phase is dispersed during the extraction process, a subsequent centrifugation step is necessary to allow the separation of the enriched extract.

'Liquid-liquid-liquid' LPME approaches allow the extraction and pre-concentration of ionizable analytes by an appropriate pH adjustment of both the sample (donor solution) and the extractant phase (acceptor solution). In these systems, analytes are first extracted into a microvolume of organic solvent, and subsequently back-extracted into the pH-adjusted aqueous extractant phase. The pH is adjusted in such a way that the analytes are in their neutral form in the sample, and in their ionized form in the acceptor solution. Three different 'liquid-liquid-liquid' LPME approaches have been described to

date, namely liquid-liquid-liquid microextraction (LLLME) [63], hollow-fiber liquid-liquid-liquid microextraction (HF-LLLME) [64] and membrane assisted liquid-phase microextraction (membrane assisted-LPME) [65]. The 'liquid-liquid-liquid' LPME approaches allow for a high degree of cleanup as a result of two separation processes involved in such systems and the filtration effect provided by the porous polymeric fibers when HF-LLLME or membrane assisted-LPME are used. It is remarkable that the final extract is of aqueous nature, thereby being compatible with high performance liquid chromatography (HPLC) and capillary electrophoresis (CE). However, the achievement of high enrichment factors is subject to an efficient mass transfer in both the extraction and the back-extraction processes.

As for 'liquid-gas-liquid' LPME approaches, the most widespread and successfully applied LPME mode for the extraction and pre-concentration of volatile or semivolatile compounds is headspace-single-drop microextraction (HS-SDME) [66]. In this system, a microdrop of extractant phase is exposed to the headspace above the continuously stirred sample solution by means of a microsyringe. The analytes are transferred to the headspace by stirring and, subsequently, extracted by a drop of extractant phase showing appropriate physicochemical properties. Thus, apart from a polarity similar to that of target analytes, the extractant phase must also show a high boiling point, and a low vapor pressure for being applicable in HS-SDME. Both the mass transfer of analytes from the sample to the headspace, and from the headspace to the microdrop, are crucial for the achievement of high enrichment factors. A high degree of cleanup is also achieved with HS-SDME, since non-volatile compounds are not extracted, and the extraction of high molecular weight compounds is kinetically hindered.

2.2. Parameters that influence the extraction efficiency

2.2.1. Mode of extraction

The mode of extraction should be selected by the analyst bearing in mind the physicochemical properties of the analytes, the available analytical instrumentation, and the type of samples to be analyzed. Thus, neutral (volatile or non-volatile) analytes are commonly extracted and pre-concentrated using an 'immersed' microextraction mode, while volatile and semivolatile, and ionizable compounds can be subjected to headspace microextraction/HF-LPME modes and liquid-liquid-liquid LPME, respectively.

The compatibility of the extractant phase with the analytical technique must, nevertheless, be taken into account. In general, SPME and related techniques

can be combined with GC, HPLC and CE by choosing the most appropriate (thermal or liquid) desorption conditions. As for LPME, “two phases” approaches and HS-SDME are compatible with GC and HPLC, while ‘liquid-liquid-liquid’ LPME or HS-SDME (when aqueous drops are used) are recommended for analysis by CE.

The selection of the most appropriate microextraction mode may also depend on the type of sample to be analyzed. Thus, some ‘two phases’ LPME modes such as direct-SDME or dynamic-LPME are not recommended for complex sample matrices.

2.2.2. Extractant phase

The properties of the extractant phase can have a high impact on the extractability of target analytes. Hence, the selection of the most appropriate extractant phase must be done taking into account the physicochemical properties of the interest compounds.

In SPME and related techniques, the available commercial extractant phases are quite limited in some cases, as described in section 2.1.1. For instance, up to very recently, PDMS was the only coating polymer commercially available for SBSE, and this aspect restricted the applicability of SBSE to extraction and pre-concentration of nonpolar to moderately polar compounds. In the last few years, several researchers have focused on the development of coating materials with improved properties valid for SPME and related techniques [6,67-71]. The development of coating polymers with improved physicochemical properties, including increased specific surface areas as well as physical and chemical stabilities is therefore key to expand the applicability of these miniaturized techniques to different types of compounds.

As for LPME, the selection of the extractant phase is commonly performed keeping in mind the extraction efficiency, selectivity and level of toxicity [26]. Furthermore, the physical properties of the extractant phase, such as water solubility, vapor pressure, boiling point, density or even melting point, should be controlled for optimum performance. Depending on the analytes to be extracted, the LPME mode and the analytical technique combined with it, different extractant phases, namely, organic solvents, ILs, supramolecular solvents and even aqueous drops may be employed [23].

2.2.3. Extractant phase volume

Extraction efficiency (EE), as shown in Eq. 1, is defined as the percentage of the extracted amount of analyte with respect to its original amount in the sample:

$$EE = \frac{K \left(\frac{V_{extr}}{V_s} \right)}{1 + K \left(\frac{V_{extr}}{V_s} \right)} \quad (1)$$

where, V_{extr} and V_s are the extractant phase and sample volumes, and K is the corresponding partition coefficient.

As can be deduced from Eq. 1, exhaustive recoveries are less likely to occur under equilibrium conditions when the extractant phase volume is reduced, especially when K is not particularly large.

In PDMS-coated SPME fibers, the extractant phase volume is extremely low (0.5 μ L) and, therefore, exhaustive recoveries are only achieved under equilibrium conditions when K is larger than 10^5 [15]. Thus, the reduced extractant phase volume makes this SPME process an example of a non-exhaustive extraction technique, in which the only limited and difficult to control portion of the analytes present in the sample are extracted by the coating fiber. Unlike SPME, the extractant phase volume employed in SBSE is significantly larger than in SPME, then being capable of exhaustively extract (under equilibrium conditions) analytes showing less favorable K values.

The above discussion is also valid for LPME techniques. It is also important to introduce the concept of enrichment factor (EF), which is defined as the ratio between the concentrations of the analyte in the extractant phase to the initial concentration in the sample. EF can be expressed as:

$$EF = \frac{K}{1 + K \left(\frac{V_{extr}}{V_s} \right)} \quad (2)$$

From Eqs. 1 and 2, an increase of the V_{extr} gives rise to the enhancement of EE, at the expenses of decreasing potential EFs.

In addition to EE and EF, the extractant phase consumption per analysis is also of importance, especially when toxic organic solvents are employed. Reduced consumption of extractant phase volumes shows a positive impact on the reduction of wastes, thereby contributing to the greening of the analytical method [23,72].

2.2.4. Sample volume

In general terms, the sample volume also affects the extraction efficiency of target analytes when using microextraction techniques. According to Eq. 2, the larger the sample volume the larger the potential EF that can be achieved. For instance, enrichment factors of up to 25000 have been reported in the literature by using a sample volume of 1100 mL [73]. However, it should be taken into account that such large sample volumes are not always available. In most cases, the analysis of environmental samples using microextraction techniques involves sample volumes in

the range 1 to 50 mL, although the available volumes of some environmental samples may be reduced to a large extent, even to a few microliters [74,75].

In SPME systems, the amount of extracted analyte at equilibrium can be described as follows [76]:

$$n = \frac{KC_0V_sV_f}{V_s + KV_f} \quad (3)$$

where C_0 is the initial concentration of the analytes in the sample solution, and V_f is the volume of the coating fiber. It can be concluded that when V_s is large enough or K very low, Eq. 3 can be reduced to:

$$n = KC_0V_f \quad (4)$$

Thus, under these conditions, the amount of extracted analyte does not depend on the sample volume, but on the initial concentration of the analytes in the sample. This is important for field sampling using SPME [2].

2.2.5. Agitation of samples

An intense agitation of the sample under analysis allows the enhancement of the extraction kinetics, since it affects the convective-diffusive mass transfer of analytes, reducing the thickness of the Nernst diffusion film through which the analytes migrate from the sample solution to the extractant phase by steady-state diffusion [43]. The stronger the agitation the higher the analyte concentration extracted, which means that equilibrium conditions are achieved in shorter extraction times. In headspace techniques, the agitation of the sample is also employed to improve the mass transfer of volatile and semivolatile analytes from the sample to the headspace. In addition, the agitation induces the convection in the headspace, therefore improving the mass transfer from the headspace to the extractant phase (coating fiber or microdrop) [66].

2.2.6. Temperature control

Temperature control is commonly recommended when working with microextraction techniques, since mass transfer coefficients rise as a result of increasing temperatures. The effect that temperature produces on the extraction efficiency of analytes is especially noticeable in headspace microextraction modes due to its impact on the sample-headspace and headspace-extractant phase coefficient partitions [20]. This is particularly true for semi-volatile analytes, since the use of high sample temperatures yields increased concentrations of analytes in the headspace. It has been reported that at very high temperatures, however, the effect of this variable may be counterproductive, yielding lower extraction efficiencies, and such a negative

effect has been attributed to the exothermic process involved in the sorption of analytes [2,77]. Furthermore, in HS-SDME the use of high sample temperatures may bring about the evaporation of the extractant phase.

2.2.7. Extraction time

Sorption techniques are characterized by being time dependent. Thus, even though some microextraction techniques enable exhaustive extraction of analytes, the extraction kinetics may be low. Long extraction times may therefore be needed to achieve the highest extraction efficiency, then affecting the overall analysis time. Reaching an agreement among the analytical sensitivity achievable and the sample throughput needed is highly recommended. Practical non-equilibrium microextraction times are commonly selected by matching the extraction time with the chromatographic run [26]. The employment of multiple sorption-desorption cycles under non-equilibrium conditions allows the achievement of acceptable extraction yields using relatively short extraction times [44,45]. A strict control of extraction time is mandatory to achieve an acceptable precision when working under non-equilibrium conditions. In some LPME modes, the use of large extraction times may affect the stability of the extractant phase due to its increased solubilization or evaporation.

2.2.8. Derivatization

Derivatization is performed in analytical chemistry to obtain derivative products with appropriate physicochemical properties for sample preparation, detection, and improving sensitivity. In microextraction techniques, derivatization is performed in order to enhance the extraction efficiency by the formation of derivatives that can be extracted more easily than original analytes. These compounds are more compatible with the corresponding technique. Derivatization is a common practice in SPME and related techniques, partly due to the limited availability of fiber coatings. In this sense, the PDMS coating restricts the applicability of the SBSE technique to non polar or weakly polar analytes, unless polar analytes are converted into less polar derivatives by appropriate derivatization reactions.

In general, there are three different possibilities to carry out derivatization in microextraction techniques: derivatization in the sample solution, derivatization in the extractant phase (coating fiber or microdrop), and derivatization in the injection port of the GC [78,79]. In addition, any combination of the above mentioned possibilities can be performed. Thus, derivatization in the sample solution is commonly performed when dealing with a two phase microextraction system. A simple pH

adjustment of the sample can be enough to give rise to the formation of a highly extractable derivative [53]. In addition, derivatization may be carried out in both the sample and the extractant phase when a three phase microextraction system is used. For instance, non volatile analytes may be converted into volatile derivatives that can be extracted and pre-concentrated onto a microdrop containing a second derivatizing agent which brings about another compound with suitable properties for detection [80,81]. It can be deduced from these examples that it is possible to expand the applicability of the different microextraction techniques by making use of appropriate derivatization.

2.2.9. Impact of the environmental matrix

The environmental matrix can give rise to anomalous extraction recoveries when using miniaturized sample preparation approaches under non-controlled conditions. The evaluation of matrix effects is therefore necessary when a novel analytical method is developed in order to clarify the true applicability of the method. As for the evaluation of matrix effects in environmental matrices, several researchers have assessed the effect of NOM and salts on the extraction efficiency of target analytes when using LPME or SPME and related approaches.

NOM can be present in all the different compartments of Earth, showing an important effect on the complexation of trace elements. The interactions that NOM establishes with some specific organic analytes may give rise to decreased free analyte concentration [82-85]. Furthermore, the presence of NOM in the sample solution may affect the mass transfer of analytes when microextraction is performed under non-equilibrium conditions. In fact, depending on the properties of the organic compounds, the extraction kinetics may be retarded or even accelerated in the presence of NOM. These negative and positive effects have been explained according to barrier or shuttle effect mechanisms, respectively [86,87]. The evaluation of the impact of NOM presence in the sample solution should be therefore performed to assess the effect on the extraction efficiency of a target analyte, and subsequently define the applicability of a given microextraction method. Even though few works have reported enhanced extraction kinetics of organic compounds in the presence of NOM [87,88], the presence of high concentrations of NOM commonly yields a decrease on the extraction efficiency of organic compounds [89-94]. In the latter case, the use of the standard addition method allows the analysis of environmental samples showing high amounts of NOM but at the expense of a lower sensitivity. On the other hand, other procedures have been reported as being unaffected by the presence of NOM

[95]. Accordingly, the effect of NOM on the extraction of individual organic compounds must be evaluated and taken into account when complex environmental samples are analyzed by microextraction techniques.

The ionic strength of the sample solution may also have great importance on the extraction efficiency of target analytes. The presence of salts in the sample can diminish the solubility of analytes in the sample, then increasing their partition into the extractant phase. This phenomenon is known as "salting-out" effect. However, the presence of salts in the sample can also give rise to a decrease on the extraction efficiency, since it affects the physical properties of the Nernst diffusion film adjacent to the interface and, therefore, the extraction kinetics [19]. The net effect of the ionic strength on the extraction efficiency depends on the physicochemical properties of the analyte (hydrophobicity, diffusion molar volume, molecular diameter and hydrophobic surface area) [96], and on the microextraction conditions used. Therefore, this parameter should be carefully evaluated prior to any particular application.

3. Application of microextraction techniques to the determination of relevant organic compounds in environmental samples

Table 1 and Table 2 show selected applications of, respectively, SPME related techniques and LPME, to the extraction and pre-concentration of organic compounds in liquid (aqueous) samples, solid (soils and sediments) samples, and air samples. Relevant analytical information, such as the advanced analytical technique employed for the quantitative determination of target compounds, and the microextraction mode employed, type and volume of extractant phase, as well as the analytical characteristics achieved under optimal conditions (enrichment factor, limit of detection (LOD), precision and microextraction time), are included on the Tables.

It is noteworthy that the LPME technique has been primarily applied to the extraction and pre-concentration of organic compounds in aqueous samples, while the analysis of solid and, specially, air samples has been scarcely described in the literature. In general, this is mainly due to several factors. First, environmental water samples are interesting and readily-available matrices where organic compounds can be present at trace or ultratrace levels; therefore a pre-concentration step is crucial to achieve appropriate sensitivity for environmental monitoring. Second, the matrix complexity of environmental water samples is much

Table 1. Selected applications of SPME and related techniques to the determination of organic compounds in environmental samples.

Environmental sample(s)	Analyte(s)	SPME mode	Analytical Technique	Extractant phase (thickness)	LOD	Precision (RSD %)	Time (min)	Ref
Aqueous samples								
Tap, river and lake water	OPs	Direct-SPME	GC-MS	PDMS (100 μm); PA (85 μm); CW/DVB (65 μm); PDMS/DVB (65 μm)	7-50 ng L ⁻¹	6.0-15.0	30	[89]
River water and wastewater	PBDEs	Direct-SPME	GC-ECD	MWCNTs (~40 μm)	3.6-8.6 ng L ⁻¹	6.9-8.8	30	[160]
Lake water	Hydroxyaromatic compounds	Direct-SPME	HPLC-UV	CW-templated resin (50 μm) PDMS-DVB (60 μm)	660-3200 ng L ⁻¹ 990-4200 ng L ⁻¹	2.0-10.0 1.0-10.0	20	[161]
Sediment porewater	Pyrethroids	Direct-SPME	GC-MS-MS	PDMS (7 μm)	1-5 ng L ⁻¹	<20.0	40	[94]
Snow water	Phenyl compounds	HS-SPME	GC-MS	PDMS (100 μm)	300-3000 ng L ⁻¹	<5.0	8	[162]
Surface and groundwater	MTBE	HS-SPME	IMS	CAR/PDMS (75 μm)	5000000 ng L ⁻¹	8.3	1.5	[163]
Drinking water and chlorinated secondary effluent	Chlorinated VOCs	HS-SPME	GC-ECD	CAR/PDMS (85 μm)	0.08-23.8 ng L ⁻¹	0.1-10.8	30	[164]
Wastewater	BTEX	HS-SPME	GC- μ FID	PDMS/DVB (65 μm)	440-1400 ng L ⁻¹	5.8-8.3	1	[165]
Samples from a water treatment plant	N-nitrosamines	HS-SPME	GC-MS-MS	CAR/PDMS (75 μm)	3.2-15.2 ng L ⁻¹	--	60	[166]
Seawater	PAHs	SBSE	GC-MS	PDMS (500 μm)	0.14-14.6 ng L ⁻¹	1.0-48.0	60	[167]
Surface water, groundwater and precipitation water	PAHs	SBSE	HPLC-FLD	PDMS (500 μm)	0.2-2 ng L ⁻¹	4.7-13.5	60	[168]
Wastewater	Parabens, TCS, MeTCS	MEPS	GC-MS	C-18	1-590 ng L ⁻¹	2.0-7.1	15	[169]
Soils and sediments								
Marine sediments	Antifouling biocides	Direct-SPME	GC-MS	PDMS (100 μm)	0.5-6 ng g ⁻¹	4.0-11.0	30	[91]
Sediments	OCPs	Direct-SPME	GC-MS	PDMS/DVB (65 μm)	0.11-15 ng g ⁻¹	5.0-18.0	45	[170]
Marine sediments	PAHs	Direct-SPME	GC-MS	PDMS/DVB (65 μm)	0.4-15 ng g ⁻¹	3.3-9.6	60	[98]
Soils	Tetracycline antibiotic residues	Direct-SPME	CE-MS	CW-DVB; 65 μm	2.9-3.2 ng g ⁻¹	5.3	20	[171]
Estuarine sediments	OCPs	HS-SPME	GC-ECD	PDMS (100 μm)	0.029-0.301 ng g ⁻¹	3.7-9.6	60	[172]
Estuarine sediments	OCPs	HS-SPME	GC-MS; GC-ECD	PDMS (100 μm)	0.005-0.11 ng g ⁻¹ ; 0.01-0.26 ng g ⁻¹	7.0-17.0 6.0-18.0	60	[97]
Soils	BTEX	Multiple HS-SPME	GC-FID	CAR/PDMS (75 μm)	0.2-1.0 ng	3.2-6.9	60	[173]
Soils	OCPs, PCBs, PAHs and PBDEs	SBSE	GC-MS	PDMS (500 μm)	0.01-2.0 ng g ⁻¹	10.0-18.0	840	[99]
Air samples								
Indoor air	VOCs	SPME	GC-FID GC-MS	CAR/PDMS (75 μm)	380-5260 ng m ⁻³ 50.0-500.0 ng m ⁻³	4-20; 6-12	4; 180	[174]
Air samples from field-scale swine mortality composting units	VOCs	SPME	GC-MS	CAR/PDMS (85 μm)	0.011-572 ppbv	0.24-14.8	60	[175]
Indoor air	Fragrance allergens	SPME	GC-MS	DVB/CAR/PDMS (50/30 μm)	0.047-12.0 ng m ⁻³	0.5-15	20	[176]
Indoor air	Toluene	SPME	GC-FID	CAR/PDMS (75 μm)	110.0 ng m ⁻³	16	180	[177]

lower than observed in solid samples, such as soils or sediments. In addition, some microextraction modes are not suitable for their direct application to complex samples, and are commonly restricted to clean water samples. Finally, calibration is easy to perform for water samples analysis, but it becomes a difficult task when dealing with air samples.

When SPME and related techniques are directly performed on very complex matrices that are rich in organic matter, the polymeric coating may be degraded and the desorption efficiency deteriorated [97].

As for the LPME technique, the complex nature of solid samples may avoid or limit their applicability. Thus, when soils and sediments have to be analyzed, a pre-extraction is commonly performed before the application of microextraction techniques to reduce the complexity of solid samples. Furthermore, the pre-extraction step allows the sample to achieve, in combination with microextraction techniques, an appropriate selectivity. Thus, pre-extraction with methanol or acetone [91], hot water extraction [98], microwave assisted extraction [97] or ultrasound

Table 2. Selected applications of LPME to the determination of organic compounds in environmental samples.

Environmental sample(s)	Analyte(s)	LPME mode	Analytical technique	Extractant phase (volume)	EFs	LOD	Precision (RSD %)	Time (min)	Ref
Aqueous samples									
Tap, river and lake water	OPs	Direct-SDME	GC-MS	Toluene (1.5 μ L)	--	10-73 ng L ⁻¹	8.6-16.0	15	[89]
River, seawater and swimming pool water	UV filters	Direct-SDME	HPLC-UV	[C ₈ MIM][PF ₆] (10 μ L)	8-98	60-3000 ng L ⁻¹	2.8-8.8	37	[178]
Tap and reservoir water	OPPs	Direct-SDME	GC-ECD	n-Hexane (3 μ L)	20-95	5-200 ng L ⁻¹	3.2-10.7	25	[179]
Drainwater	Phenols	HS-SDME	CE-DAD	NaOH 1 mol L ⁻¹ (5 μ L)	106-528	1000-3000 ng L ⁻¹	3.45-7.71	15	[180]
Tap, well, spring, pool and wastewater	PAHs	HS-SDME	GC-FID	1-Butanol (3 μ L)	9-159	4000-38000 ng L ⁻¹	0.7-19.5	12	[181]
Tap, lake and treated wastewater	Phthalate esters	DLLME	HPLC-UV	[C ₈ MIM][PF ₆] (50 μ L)	--	10600-28500 ng L ⁻¹	7.8-15.0	~5	[182]
River, well and farm water	OPPs	DLLME	GC-FPD	Chlorobenzene (12 μ L)	789-1070	3-20 ng L ⁻¹	1.2-5.6	~2	[183]
Tap, well and wastewater	PAHs	HF-LPME	GC-MS	Toluene (3 μ L)	--	5-11 ng L ⁻¹	2.7-11.3	15	[184]
Rainwater	OCPs and PAHs	HF-LPME	GC-MS	Toluene (5 μ L)	46-167	2-59 ng L ⁻¹	1.3-13.8	35	[185]
Tap and surface water	Aromatic amines	HF-LLLME	HPLC-UV	Di-n-hexyl ether/ HCl 0.1 mol L ⁻¹	240-510	50-100 ng L ⁻¹	3.84-4.83	30	[186]
River water	Nerve agent degradation products	LLLME	CE-C'D	1-Octanol (200 μ L)/ Tri-n-butyl amine 0.1 mM (2 μ L)	--	100-850 ng L ⁻¹	9.3-13.8	45	[187]
Tap, well and river	Phenylurea herbicides	DLLME	HPLC-DAD	Chloroform (73 μ L)	128-198	2.3-18 ng L ⁻¹	0.6-2.0	~6	[188]
Soils and sediments									
Soils	CBs	HS-LPME	GC-ECD	Toluene (2 μ L)	--	6-14 ng g ⁻¹	5.7-17.7	4.2	[189]
Soils	Dichlorobenzene isomers	HS-SDME	GC-FID	[C ₈ MIM][PF ₆] (4 μ L)	--	1-2 ng g ⁻¹	4.4-14.6	30	[190]
Soils	PBDEs	HF-LPME	GC-ICP-MS	Decane (4 μ L)	30-83	15.2-40.5 ng L ⁻¹	5.1-9.1	20	[191]
Soils	Carbamate and OPP	DLLME	HPLC-FLD	Tetrachloroethane (50 μ L)	--	0.014-0.11 ng g ⁻¹	1.96-4.24	3	[192]
Soils	PCBs	DLLME	GC-ECD	Chlorobenzene (30 μ L)	--	0.2-0.5 ng g ⁻¹	2.2-6.4	3	[193]
Soils	Pesticides and metabolites	DLLME	HPLC-FLD	[C ₈ MIM][PF ₆] (~90 μ L)	--	0.02-90.2 ng g ⁻¹	0.7-3.7	~18	[194]
Air samples									
Air samples	Formaldehyde	HS-SDME	UV-vis	Chromotropic acid 0.08% (m/v) (15.5 μ L)	--	<2 ppbv	--	7	[195]
Air samples	Nitrophenols	HF-LLLME	HPLC-UV	NaOH 0.1 M (20 μ L)/ dihexyl ether	~2000- 3500	3.6-41.7 ppbv	2.5-4.2	60	[196]

assisted extraction [99], among others, have been reported in the literature prior to different SPME or LPME modes. Unlike immersed microextraction modes, headspace sampling enables the direct extraction and pre-concentration of volatiles and semivolatiles in such complex matrices without the drawbacks described for direct modes, and with the advantage of increased selectivity.

As for the analysis of air samples, the number of publications concerning the employment of microextraction techniques for the monitoring of volatile organic compounds still is relatively scarce. Nevertheless, SPME is being considered a powerful passive method for the isolation and enrichment of volatile organic compounds (VOCs) when compared with conventional methods used for passive air

sampling [9,10,100-104]. When SPME fibers are used as passive samplers, both storage and preservation of fibers are of great importance to achieve accurate field measurements of VOCs. Sealing septa available commercially are commonly used to overcome this obstacle. However, they lack airtightness and have been reported to give rise to contamination by silicon by-products [105]. Some alternative systems have been proposed, and for instance, a home-made storage system containing activated carbon has been proposed to avoid analyte contamination and analyte losses before and after SPME sampling [105]. Furthermore, two different hermetic preservation systems, namely Tuff syringe™ and SafePorter™ are commercially available from Field Forensics. Unlike SPME, quite few applications can be found

in the literature regarding the use of the LPME technique. Future contributions of LPME techniques to this kind of matrices are therefore expected. In fact, the first work where a liquid microdrop was employed to extract target analytes was directed to the uptake of volatiles (specifically, ammonia and sulfur dioxide) in air samples [42]. HS-SDME has been widely applied to the extraction and pre-concentration of volatile and semivolatile analytes with a high degree of success. The application of the LPME technique in this mode to the pre-concentration of organic analytes in air samples, taking the sampling devices developed for SPME as a starting point, is to be expected.

4. Microextraction techniques: promising alternatives to conventional methods for isolating NOM?

NOM is a variable complex mixture of organic compounds, and such extreme complexity is the reason why there are continuing research efforts in the area of NOM characterization despite non breakthrough advancements. NOM has an impact on different environmental processes, including sorption and degradation of pollutants, modification of organic carbon production and release, and affects the natural cycles, namely the carbon, nitrogen and oxygen cycles [106-113].

Sample preparation techniques applied to NOM separation should fulfill some requirements to provide representative extracts from which obtain unbiased conclusions. An ideal sample preparation technique should provide quantitative extraction of the different NOM fractions, keep unmodified the physicochemical properties of the original sample, show reduced extractability of interferences (especially from inorganic salts, which interfere with advanced analytical techniques) and being expeditious [110]. The representativeness of the extract is of paramount importance for the subsequent analysis. However, the heterogeneity of NOM in environmental samples hinders the possibility to fully isolate NOM under the ideal conditions described above.

A variety of extraction and isolation procedures have been described in the literature prior to NOM characterization and/or quantification in the different environmental compartments. The extraction of different NOM fractions has been mainly performed by conventional SPE using a large variety of resins. In fact, the standard method adopted by the International Humic Substances Society (IHSS) to isolate

and purificate humic and fulvic acids in aqueous and solid samples involves the use of a polymethyl methacrylate Amberlite XAD-8 resin [114-119]. XAD-8 resin has recently been replaced by Supelite™ DAX-8, even though slight differences in the composition of the extract have been reported when using XAD-8 or DAX-8 resins, especially when considering the content of aliphatic carbons [120,121]. Other XAD type resins have also been employed to extract NOM fractions, including XAD-1 [122], XAD-2 [122,123], XAD-4 [122] and XAD-7 [122]. Apart from XAD type resins, a C-18 stationary phase [124-127] and a weak anion exchanger (diethylaminoethyl (DEAE) cellulose) [118,128] have been used for separation and fractionation purposes. Furthermore, different SPE resins in tandem have been employed to obtain additional NOM fractions as well as to achieve a further refinement of the extract, including XAD-8 and XAD-4 resins [129-134] or C-18 and strong anion exchanger SAX resins [128,135]. Other sample preparation techniques have also been proposed with the aim of separating the NOM. Thus, ultrafiltration using a series of membranes [136,137], a passive sampler consisting of a molecular weight selective membrane and a DEAE-cellulose resin [138], LLE [139] and cloud point extraction (CPE) [140,141] can be found in the literature. In addition, the employment of different materials has been proposed for the extraction or removal of NOM, including a mesoporous β -cyclodextrin-silica-4% material [142], β -cyclodextrin polyurethane [143] or polypropylene [144]. In general terms, none of these methods fulfill the initial requirements described above. In fact, the representativeness of the extract is compromised by the selected sample preparation technique. In addition, large amounts of sample and relatively large volumes of organic solvents are usually needed for sensitive analysis. Furthermore, contamination by monomer bleeding from the resins during the elution step, irreversible adsorption of organic matter or size-exclusion effects are specific drawbacks of commonly employed XAD resins [107,129].

As discussed in previous sections, microextraction techniques are mainly non-exhaustive techniques, and this feature could make some of the miniaturized approaches unsuitable for representative extraction of NOM from environmental samples, especially when working under non-equilibrium conditions. Nevertheless, microextraction techniques may be powerful for extraction and pre-concentration of NOM. Specifically, the use of such miniaturized systems would include several benefits when compared with conventional sample preparation techniques commonly employed for NOM isolation, *i.e.*, high potential enrichment factors,

sensitive reduction (or suppression) of organic solvents consumption and waste generation, easiness and economy.

Very few works concerning the employment of microextraction techniques have been published so far for extraction and pre-concentration of different operationally-defined fractions of NOM in environmental samples. An automated MEPS system (consisting of 4 mg of C-18 coating) was coupled on-line to an ion cyclotron resonance Fourier-transform mass spectrometer for extraction and desalting of marine dissolved organic matter (DOM) [53]. In this work the sample preparation is performed using a 2.2 mL of sample and a total volume of 1.4 mL of methanol (including condition of the cartridge, elution and cleaning) per analysis. Recovery values were not provided in this study.

The application of microextraction techniques has been mainly directed to the extraction of less complex NOM fractions. For instance, SPME [145-148], SBSE [148] and DLLME [149] have been applied to the determination of dissolved (short and long) chain fatty acids. In addition, SPME has been applied to the qualitative analysis of 86 VOCs and semivolatile organic compounds (SVOCs) present in atmospheric particulate matter [150], and SBSE has also been employed in combination with microwave assisted extraction for the extraction and pre-concentration of VOCs present in atmospheric aerosols [151].

The combination of SPME and NTD has been recently proposed for the quantitative determination of gaseous and particle-bound compounds in atmospheric samples, where SPME is used for extraction of volatile compounds and NTD for collection of VOCs and SVOCs from gaseous and particle-bound fractions [152].

In some publications, microextraction techniques are not employed for extraction and pre-concentration of NOM, but as a tool for studying different parameters that are affected by either the presence or the absence of NOM. For instance, SPME has been employed for evaluating freely dissolved concentrations and/or partition coefficients of different organic compounds in the presence of NOM [87, 153-158]. The only work focusing on the application of an LPME mode to these types of studies has been recently published [159]. In this study, a HF-LPME method has been employed to evaluate the effect of humic acid on the freely dissolved concentration of imidazolium-based ILs. The authors studied the sorption of humic acid onto two different ILs ([C₄MIM] and [C₈MIM]-based ILs), and concluded that both ILs associate strongly with humic acid, with partition coefficients comparable to those obtained for non polar organic compounds.

5. Conclusions and future research

Microextraction techniques have attracted much attention in the last two decades, and they are becoming widely used for extraction and pre-concentration of different organic compounds. Their application for environmental sampling is, however, not homogeneously distributed, being mainly employed to the analysis of water samples. Further efforts should be directed to the analysis of complex samples such as soils and sediments and, more importantly, to the analysis of air samples, where only SPME and NTD have been demonstrated to be efficient alternatives to conventional passive samplers.

As for NOM isolation and fractionation, it is apparent that advances are expected in this field, in spite of the recognized merits of the sample preparation approaches that are currently used for this aim. Nevertheless, it is foreseen that miniaturized techniques will play a predominant role in the development and implementation of novel sample preparation methods for NOM extraction and isolation. Their implementation will drastically reduce organic solvent consumption and waste generation, thereby providing greener alternatives for extraction and pre-concentration of NOM from environmental samples. In addition, sample volumes would also be significantly reduced without a loss of sensitivity. Novel materials with improved physicochemical properties have demonstrated a suitability for extraction of different organic compounds. The use of such materials as adsorbents in microextraction techniques may be a turning point in the development of ideal sample preparation approaches for the extraction and pre-concentration of NOM in environmental matrices.

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Abbreviations

[C₄MIM]: 1-Butyl-3-methyl-imidazolium ion;
[C₄MIM][PF₆]: 1-Butyl-3-methyl-imidazolium hexafluorophosphate;
[C₆MIM][PF₆]: 1-Hexyl-3-methyl-imidazolium hexafluorophosphate;
[C₈MIM][PF₆]: 1-Octyl-3-methyl-imidazolium hexafluorophosphate;
[C₈MIM]: 1-Octyl-3-methyl-imidazolium ion;
BTEX: Benzene, toluene, ethylbenzene and xylene;
C⁴D: capacitively coupled contactless conductivity detection;
CAR: Carboxen;
CBs: Chlorobenzenes;
CE: Capillary electrophoresis;
CE-MS: Capillary electrophoresis-mass spectrometry;
CNTs: Carbon nanotubes;
CPE: Cloud point extraction;
CW: Carbowax;
DAD: Diode array detection;
DEAE cellulose: diethylaminoethyl cellulose;
DLLME: Dispersive liquid-liquid microextraction;
DOM: Dissolved organic matter;
DSDME: Directly suspended droplet microextraction;
DVB: Divinylbenzene;
EE: Extraction efficiency;
EF: Enrichment factor;
GC: Gas chromatography;
GC- μ FID: Gas chromatography-microflame ionization detector;
GC-ECD: Gas chromatography-electron-capture detection system;
GC-FID: Gas chromatography-flame ionization detector;
GC-FPD: gas chromatography-flame photometric detection;
GC-ICP-MS: gas chromatography-inductively coupled plasma-mass spectrometry;
GC-MS: Gas chromatography-mass spectrometry;
GC-MS-MS: Gas chromatography-tandem mass spectrometry;
GC-NPD: Gas chromatography-nitrogen-phosphorus detector ;
HF: Hollow fiber;
HF-LLLME: Hollow fiber-liquid-liquid-liquid microextraction;
HF-LPME: Hollow fiber-liquid-phase microextraction;
HPLC: High performance liquid chromatography;
HPLC-FLD: High performance liquid chromatography with fluorescence detection;
HPLC-UV: High performance liquid chromatography with ultraviolet detection;
HS-SDME: Headspace single-drop microextraction;
HS-SPME: Headspace solid-phase microextraction;
IHSS: International Humic Substances Society;
IMS: ion mobility spectrometry;
LLE: Liquid-liquid extraction;
LLLME: liquid-liquid-liquid microextraction;
LOD: Limit of detection;
LPME: Liquid-phase microextraction;
MEPS: Microextraction in a packed syringe;
MeTCS: Methyl triclosan;
MTBE: methyl tert-butyl ether;
MWCNTs: Multiwalled carbon nanotubes;
NOM: Natural organic matter;

NTD: Needle trap device;
 OCPs: Organochlorine pesticides;
 OPPs: Organophosphorous pesticides;
 OPs: Organophosphorous insecticides;
 PA: Polyacrylate ;
 PAHs: polycyclic aromatic hydrocarbons;
 PBDEs: polybrominated diphenylethers;
 PCBs: Polychlorinated biphenyls;
 PDMS: Polydimethylsiloxane;
 RSD: Relative standard deviation;
 SBSE: Stir bar sorptive extraction;
 SCX: Strong cation exchanger;
 SFOME: Solidification of a floating organic drop microextraction;
 SPE: Solid-phase extraction;
 SPME: Solid-phase microextraction;
 SVOCs: Semivolatile organic compounds;
 TCS: Triclosan;
 UV: Ultraviolet detection;
 UV-vis: Ultraviolet-visible spectrophotometry;
 VALLME: Vortex-assisted liquid-liquid microextraction;
 VOCs: Volatile organic compounds.

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