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Liquid-phase microextraction of polycyclic aromatic hydrocarbons: A review

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Abstract: Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds comprised of two or more fused benzene rings, which arise from the incomplete combustion of organic materials. These compounds have been of concern as carcinogens and mutagens for the past 50-60 years. Lately, they are also receiving attention as endocrine-disrupting chemicals. Therefore, proper analytical methods are required for sampling and analyzing these compounds. In response to problems associated with the conventional methods like solid-phase extraction (SPE) and liquid-liquid extraction (LLE), many studies have focused on the miniaturization of different sample preparation techniques. In this regard, the use of different types of liquid phase microextraction (LPME) techniques has increased significantly during the recent few decades. LPME techniques are advantageous because they use single-step sample preparation and have shown a greater sensitivity, selectivity, and efficiency than the conventional methods. In addition, these techniques have good potential for automation, to reduce the time and cost of analysis. This review focuses on the most important configurations of LPME including single-drop microextraction (SDME), hollow-fiber liquid-phase microextraction (HF-LPME), and dispersive liquid-liquid microextraction (DLLME) techniques used for the sampling and determination of PAHs in different samples, along with their cons and pros, as well as their prospects.

Keywords: Polycyclic aromatic hydrocarbons; Liquid-phase microextraction; Review.

Abbreviations: PAHs, Polycyclic aromatic hydrocarbons; **SPE,** Solid-phase extraction; **LLE,** Liquid-liquid extraction; **LPME,** Liquid-phase microextraction; **SDME,** Single-drop microextraction; **HF-LPME,** Hollow-fiber LPME; **DLLME,** Dispersive liquid-liquid microextraction; **DI-SDME,** Direct-immersion SDME; **HS-SDME,** Headspace SDME; **HPLC,** High-performance liquid chromatography; **LOD,** Limit of detection; **LOQ,** Limit of quantification **RSD,** Relative standard deviation; **SPME,** Solid-phase microextraction; **GC-FID,** GC–flame ionization detection; **MSPE,** Magnetic solid-phase extraction; **MAE,** microwave-assisted extraction; **CE,** capillary electrophoresis; **AAS,** atomic absorption spectrometry; **ILs,** ionic liquids; **MILs,** magnetic ionic liquids; **DESs,** deep eutectic solvents; **SUPRASs,** supramolecular solvents.

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) constitute a large class of organic materials that are of global concern due to their stability in the environment and their carcinogenic effects [1]. These compounds are produced from anthropogenic and natural sources [2]. They are formed mainly as a result of the incomplete combustion of organic materials, such as coal, petrol, wood, garbage, and tobacco [3]. Sixteen PAHs are listed as priority organic pollutants by the United States Environmental Protection Agency (EPA) and the European Union due to their high toxicity and adverse effects on human health. In addition, one of the PAHs, i.e., benzo[a]pyrene, is considered as a marker for cancer [4, 5]. Due to the very low concentrations of PAHs and their distribution in complex environmental samples, proper sample preparation methods and sensitive analytical techniques are required to extract, isolate, and determine their trace and ultra-trace amounts in various samples [6]. To date, different extraction methods, including solid-phase extraction (SPE) and liquid-liquid

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extraction (LLE), have been used to preconcentrate samples and remove interferences before PAHs analysis [7-9]. However, these methods can be tedious and time-consuming and sometimes require large volumes of organic solvents. In response to these limitations, many studies have focused on the miniaturization of the sample preparation process [10, 11]. Sample preparation is a crucial step during the analytical process because it can dramatically affect the results. The primary objective of the analytical methods field is to develop reliable and efficient methods for the qualitative and quantitative analysis of different compounds [12, 13]. The development of extraction techniques that facilitate the removal of potentially interfering compounds and preconcentrate the analytes of interest in a single step will simultaneously increase selectivity and sensitivity during a trace analysis. More recently, methods known as microextraction techniques have been widely used for various sample analysis. These techniques reduce sample volume, cost, and solvent consumption while achieving higher enrichment factors [14, 15]. Liquid-phase microextraction (LPME) was introduced as a miniaturized sample preparation technique in 1996 [16]. This technique is based on the equilibrium between an aqueous sample and a micro-volume organic solvent as the extraction phase [17, 18]. LPME overcome the issues associated with the conventional LLE and is advantageous in terms of enrichment, excellent sample cleanup, low consumption of organic solvents, and ease of implementation and use [19]. Additionally, the LPME technique is compatible with a wide range of analytical instruments, such as gas chromatography (GC) and liquid chromatography (LC) systems [20, 21]. In recent years, the efforts towards improvement of the performance have led to the development of different new extraction media for LPME like ionic liquids (ILs) [22, 23], surfactants [24, 25], switchable hydrophilicity solvents [25], and deep eutectic solvents (DESs) [26, 27]. Hypotoxicity, low vapor pressure, easy synthesis, safety, and convenient phase-separation are the main properties of these extraction media [28]. LPME techniques can be mainly classified into three categories (Figure 1), including single-drop microextraction (SDME), hollow-fiber LPME (HF-LPME) and dispersive liquid-liquid microextraction (DLLME) [29]. Table 1 has summarized the advantages and the drawbacks of the LPME techniques described in this review. Due to the importance of PAHs and their adverse effects on human and environmental health, many articles have been published on the sampling of them from different matrices. One of the most widely used methods are LPME techniques. To the best of our knowledge, no review article summarizing this subject has yet been published. So, in this paper, for the first time, we reviewed the history and prospects of LPME techniques for the sampling of PAHs from different matrices.

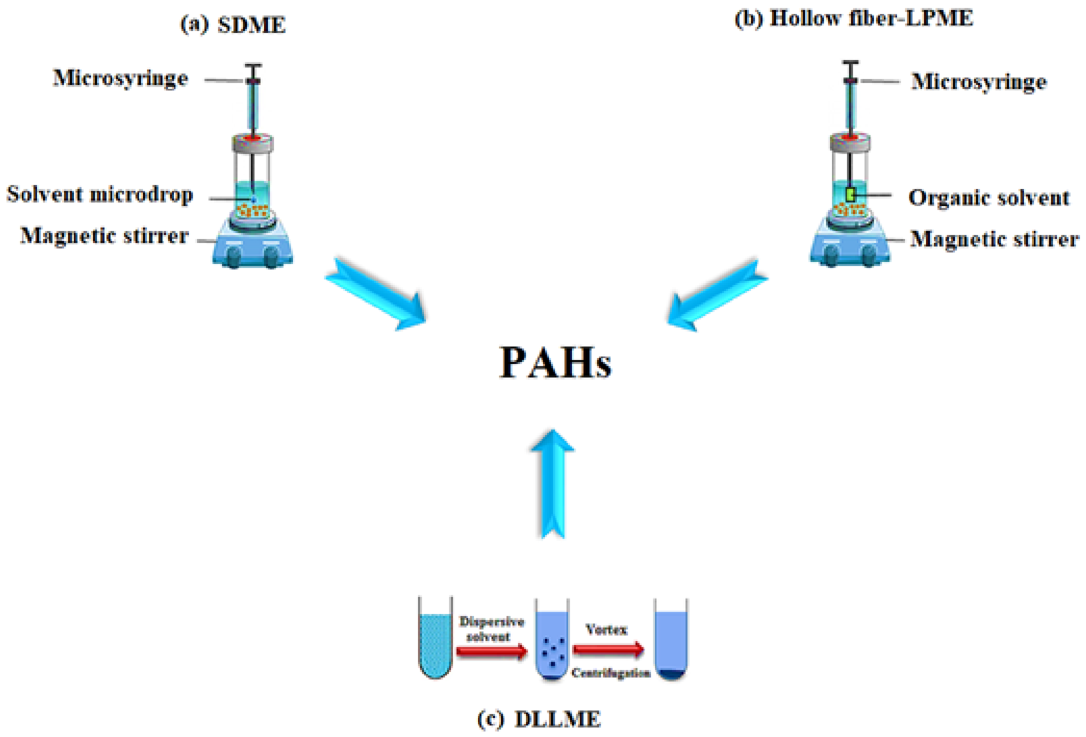


Figure 1 Schematic of different types of LPME techniques: (a) SDME, (b) HF-LPME, and (c) DLLME.

Table 1 Strengths and weaknesses of LPME techniques.

LPME Techniques	Advantages	Disadvantages
SDME	■ Easy to use ■ Fast ■ Inexpensive ■ Possibility of using various solvents (HS-SDME) ■ Good clean-up ability with a complex matrix composition (HS-SDME) ■ Possibility of extracting volatile and water-soluble analytes (HS-SDME) ■ Possibility of derivatization ■ Required small amount of organic solvents ■ Possibility of using various solvent ■ High enrichment factor	■ Impermanence of solvent drops (DI-SDME) ■ Limited solvent choice (DI-SDME) ■ Low sensitivity and precision
HF-LPME	■ Easy to use ■ good clean-up ability ■ Inexpensive ■ Protection of extraction solvent ■ Easy to automate and miniaturize ■ High repeatability Possibility of derivatization	■ Possibility of fiber pores getting blocked ■ Preconditioning of protection membrane ■ Long extraction time ■ Possibility of carryover when reusing membranes
DLLME	■ Easy to use ■ Fast ■ Required small amount of organic solvents ■ Required small amount of sample ■ Possibility of automation ■ High contact level between the extraction phase and sample ■ High recovery and high enrichment factor ■ The extraction efficiency does not depend on the time ■ Very short balance time is required	■ Limited solvent choice ■ Not appropriate for samples with a complex matrix composition ■ Requires the use of three solvents ■ Various steps such as centrifugation/freezing/auxiliary solvent/demulsifier are required

2 Polycyclic aromatic hydrocarbons

PAHs are a group of over 100 different compounds that generally are produced during the incomplete combustion of organic materials. PAHs have been classified into two main categories including (1) compounds with a low molecular weight that has fewer than four rings and (2) compounds with a high molecular weight that has four or more rings [30]. Various factors associated with PAHs, such as their molecular weights and structures, resulting in their having different physical properties. For example, PAHs with low molecular weights have high vapor pressures [31]. The physical properties and structural formula of 16 PAHs defined as the priority pollutants by the US EPA are presented in Table 2. These compounds are measured in the atmosphere for air quality assessment, in biological matrices for monitoring health effects, in sediments for environmental monitoring, and in foods for safety purposes [32]. Understanding the sources of PAHs and level of their pollution are important in conducting environmental studies, especially in determining their background concentrations [33]. PAHs released into the atmosphere from various sources, such as industrial processes, exhausts of vehicles, incineration of waste materials, and domestic heating. In addition, there also are some natural emissions of these compounds [34]. Overall, anthropogenic sources of PAHs can be classified into two main categories, i.e., petrogenic and pyrogenic. Petrogenic sources are petroleum products, such as kerosene, gasoline, diesel fuel, lubricating oil, and asphalt.

Table 2 Physical properties and structural formula of 16 PAHs defined as priority pollutants by the US EPA [170].

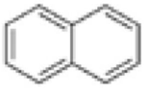
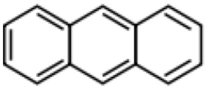
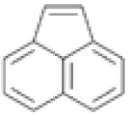
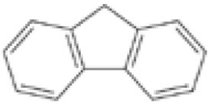
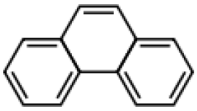
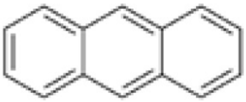
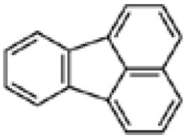
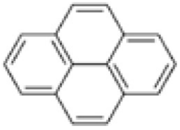
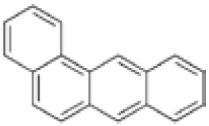
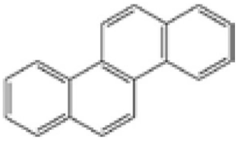
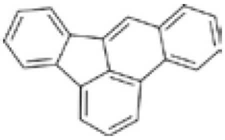
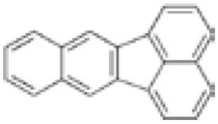
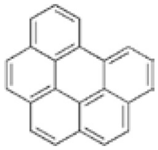
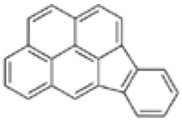
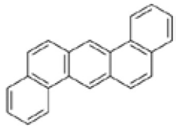
NO	PAH	Abb.	Mw	B.P. (°C)	Structure	Vp (Pa)	Log (K_{ow})
1	Naphthalene ($C_{10}H_8$)	Na	128	218		10.4	3.37
2	Acenaphthene ($C_{12}H_{10}$)	Ac	154	278		3.0	3.92
3	Acenaphthylene ($C_{12}H_8$)	Acn	152	265		0.9	4.00
4	Fluorene ($C_{13}H_{10}$)	Fl	166	295		0.09	4.18
5	Phenanthrene ($C_{14}H_{10}$)	Phe	178	339		0.02	4.57
6	Anthracene (C_{14}H10)	An	178	340		0.001	4.54
7	Fluoranthene ($C_{16}H_{10}$)	Fa	202	375		0.0012	5.22
8	Pyrene ($C_{16}H_{10}$)	Py	202	360		6.0×10^{-4}	5.18
9	Benz[a]anthracene ($C_{18}H_{12}$)	B[a]A	228	435		2.8×10^{-5}	5.91
10	Chrysene ($C_{18}H_{12}$)	Chr	228	448		5.7×10^{-7}	1.65
11	Benzo[b]fluoranthene ($C_{20}H_{12}$)	B[b]F	252	481		NA	5.80
12	Benzo[k]fluoranthene ($C_{20}H_{12}$)	B[k]F	252	481		5.2×10^{-8}	6.00

Table 2 *Continued.*

NO	PAH	Abb.	Mw	B.P. (°C)	Structure	Vp (Pa)	Log (K_{ow})
14	Benzo[ghi]-perylene ($C_{22}H_{12}$)	B[ghi]P	276	N/A		6.0×10^{-8}	6.50
15	Indeno[1,2,3-cd]-pyrene ($C_{22}H_{12}$)	IP	276	536		NA	6.58
16	Dibenz[a,h]-anthracene ($C_{22}H_{14}$)	D[ah]A	278	524		3.7×10^{-10}	6.75

Pyrogenic sources include power plants that use fossil fuels, smelting, garbage incinerators, and forest fires. In addition, there are natural sources of PAHs, such as oil leaks, the erosion of ancient sediment, and early diagenesis [35-37]. Due to their stable structures, most of PAHs have high boiling points and low vapor pressures [38-41]. PAHs can also persist and accumulate in the environment; therefore, the characterization of PAHs in the environment has been an important focus of research for decades [42]. PAHs found in the environment often contain two or more fused benzene rings [42], and many PAHs are considered to be environmental pollutants that can have destructive effects on flora and fauna. The uptake and accumulation of toxic chemicals in the food chain can result in health problems and/or genetic defects in humans [43]. However, different PAHs have different effects on health, and some PAHs are more heavily studied due to their highly adverse effects on humans [44, 45]. Human exposure to PAHs occurs through a variety of methods including direct inhalation of polluted air or tobacco smoke, dietary intake of smoked foodstuffs and polluted water, direct contact with polluted soil, and dermal contact with soot and oils. In addition, PAHs are found with high concentration in the environment and have been shown to have mutagenic and carcinogenic effects [44, 45]. PAHs are highly lipid-soluble and can be rapidly distributed to a wide variety of tissues through body fat. The metabolites of some PAHs have the ability to bind to cellular proteins and DNA with toxic effects, and the damage that is caused to the cells can result in mutations and cancer. The microsomal mixed-function oxidase (MFO) system is an enzyme system that primarily is responsible for the metabolism of PAHs. Some enzymes convert the nonpolar PAHs into polar hydroxyl and epoxy derivatives [37]. The epoxides that are formed are metabolized to other compounds, such as dihydrodiols and phenols. The hydroxylated metabolites of PAHs can be found in human urine, both as free hydroxylated metabolites and as hydroxylated metabolites conjugated to glucuronic acid and sulfates [46, 47]. The main factor that contributes to the toxicity of PAHs in tissues and organs is their biotransformation to reactive intermediates. The components of the human body in the order of their metabolizing capacities are liver, lungs, intestinal mucosa, skin, brain, hair follicles, erythrocytes, platelets, leukocytes, placenta, and uterus. The enzyme systems that metabolize PAHs are distributed extensively in people's cells and tissues [48, 49]. The embryotoxic effects of PAHs have been investigated in many studies, and the results have shown that exposure to PAHs during pregnancy can result in adverse birth outcomes [50]. In addition, the results of several studies have indicated that exposure to PAHs is associated with low IQ at the age of three, behavioral problems among children whose ages are in the range of 6 to 8 years, and childhood asthma [51, 52]. Several factors can contribute to the acute effects of PAHs including extent of exposure, concentrations of the PAHs during exposure, route of exposure (e.g., inhalation or direct contact), as well as the health conditions and age of the people who are exposed [53-55]. In workers exposed to PAHs and other workplace chemicals, health problems, such as skin, lung, bladder, and gastrointestinal cancers, have been reported. Therefore, PAHs pose serious threats to human health [56-60]. In recent years, the application of LPME techniques during PAH analysis has increased remarkably [61-64]. Table 3 gives a list of various LPME techniques that have been reported in the literature for PAHs analysis.

Table 3 Applications different types of LPME techniques in the determination of PAHs in various matrices

Technique	Matrix	Separation technique	Concentration range (µg L^{-1})	R^2	LOD (µg L^{-1})	LOQ (µg L^{-1})	Refs.
SDME	Aqueous sample	HPLC-FLD	0.01–50	0.992–0.997	0.004–0.247	–	[74]
SDME	Aqueous sample	GC-MS	0.02–10	0.9912 – 0.9995	0.0012–0.0101	0.0041–0.0336	[76]
SDME	Aqueous sample	HPLC	0.3–53071	0.981–0.999	0.03–1.2	–	[77]
SDME	Aqueous sample	HPLC	0.5-10	0.9169–0.9976	0.01–0.05	0.03–0.1	[171]
SDME	Seawater	GC-MS	0.01–10	0.9981–1	0.00033–0.0075	0.0011–0.025	[75]
HF-LPME	Aqueous sample	GC-MS	0.5–50	0.9984–0.9995	0.005–0.011	–	[98]
HF-LPME	Aqueous sample	HPLC-FLD	0.002 –1	0.9954–0.9986	0.0004 – 0.004	–	[100]
HF-LPME	Cigarette filter	HPLC-UV	0.2– 10	0.9984– 0.9996	0.04 –0.136	–	[96]
HF-LPME	Pine needles	GC-MS	10–2000 (ng g^{-1})	0.9915–0.9993	0.01–0.95 (ng g^{-1})	–	[97]
HS- HF-LPME	Soil and plant	GC-FID	1–10000 (ng g^{-1})	0.99–0.998	0.01–0.1 (ng g^{-1})	1–3(ng g^{-1})	[99]
DLLME	Aqueous sample	Molecular-FLD	2.5–500	0.9979 – 0.9981	17–2.3	2.3–4.8	[172]
DLLME	Aqueous sample	HPLC- Flu	0.02–200	0.9994– 0.9999	0.00003–0.002	0.0001–0.0067	[173]
DLLME	Aqueous sample	GC-MS	0.01–0.25	0.992– 0.998	0.0005–0.0087	0.0017–0.0287	[174]
DLLME	Aqueous sample	HPLC	0.1–500	0.9980–0.9996	0.045–1.1	–	[114]
DLLME	Aqueous sample	HPLC	0.02–200	0.9994–0.9999	0.00003–0.002	0.0001 – 0.0067	[173]
DLLME	Aqueous sample	GC-MS	0.01–10.00	0.995– 0.999	0.0003–0.0078	–	[115]
DLLME	Aqueous sample	GC-MS	0.05–50	0.9803 – 0.9965	0.0037–0.0391	0.01 – 0.15	[175]
DLLME	Aqueous sample	GC-MS	0.1–50	0.9915– 0.9964	0.023 – 0.058	0.077–0.193	[116]
DLLME	Aqueous sample	HPLC	0.2–600	0.9856 – 0.9999	0.02–0.6	0.02–0.61	[117]
DLLME	Aqueous sample	GC-MS	0.2–100	0.9966–0.9999	0.022–0.060	–	[176]
DLLME	Aqueous sample	GC-MS	0.5-50	0.9817–0.9991	0.0117–0.614	0.04–0.21	[177]
DLLME	Aqueous sample	HPLC-UV	0.5–150	0.9963–0.9994	0.0005–0.88	–	[44]
DLLME	Aqueous sample	GC-MS	0.01–100	0.9951	0.003–0.016	–	[178]
DLLME	Aqueous sample	GC-MS	0.4–10,000 (ng kg^{-1})	0.9989–0.9999	0.1–0.5 (ng kg^{-1})	0.4–0.8(ng kg^{-1})	[113]
DLLME	Aqueous sample	HPLC	0.01–800	0.9977 – 0.9988	0.002–0.8	–	[179]
DLLME	Aqueous sample	HPLC	0.3–800	0.995– 0.997	0.04–0.6	0.3–2	[180]
DLLME	Aqueous sample	UV–visible spectrum	11.9–395	0.993	0.5	–	[181]
DLLME	Seawater	GC-MS	0.005–2	0.976–0.998	0.001–0.01	–	[182]
DLLME	Smoked rice	HPLC	0.2 –100	0.996–0.998	0.05–0.12	0.14–0.38	[183]
DLLME	Smoked fish	GC-MS	1–200 (ng g^{-1})	0.981–0.993	0.36–1.6 (ng g^{-1})	0.11–0.48 (ng g^{-1})	[184]
DLLME	Food and beverages	GC-FID	0.0001–0.15	0.9944–0.9986	0.00002–0.00007	–	[185]
DLLME	Grilled Pork	HPLC	0.5–1000	0.9973–0.9997	0.1–0.3	0.3–0.5	[62]
DLLME	Honey	GC-MS	0.111–500	0.9971–0.9995	0.014–0.052 (ng g^{-1})	0.047–0.173 (ng g^{-1})	[186]
DLLME	Grilled meat	GC-MS	0.000097–1000 (ng g^{-1})	0.9789–0.9997	0.029–0.082 (ng g^{-1})	0.097–0.277 (ng g^{-1})	[187]
DLLME	Baby food	GC-MS	1–15 (µg kg^{-1})	0.9909–0.9993	0.1–0.3 (µg kg^{-1})	0.25–1 (µg kg^{-1})	[188]
DLLME	Tea beverages	HPLC-FLD	1–500	0.9952–0.9999	0.00202–0.00286	0.00673–0.0952	[61]
DLLME	Tea and coffee	HPLC-FD	0.005-50	0.9939–0.9999	0.001–0.3	–	[189]
DLLME	Sugar cane spirits	GC-MS	0.65–12.2	0.9939–0.9999	0.06–1.5	0.2–5	[190]

3 Liquid-phase microextraction techniques

3.1 Single-drop microextraction

Single-drop microextraction (SDME) is the simplest mode of LPME, in which the extraction medium is a microdrop organic solvent at the tip of a microsyringe needle. The needle tip is placed in aqueous solution for extraction of the analyte, and the analyte is transmitted from the aqueous sample into a hanging drop. After the extraction process, the organic drop is aspirated into the syringe and transferred for further analysis [65, 66]. SDME has been applied as a sample preparation technique to obtain acceptable analytical data. Simplicity, ease of implementation, and low cost make SDME accessible to all laboratories. In addition, this technique has been shown to be applicable to real samples [67]. However, SDMS has also different limitations comprise the limited drop surface, instability of the microdrop, and consequently limitation of agitation slow kinetics [68, 69]. SDME can be done in the headspace (HS-SDME) or direct (DI-SDME) sampling modes. [70]. In DI-SDME, the extractant phase is directly immersed into a sample solution and both volatile and non-volatile compounds can be extracted. The HS-SDME mode uses a microdrop of an organic solvent in the headspace of the sample solution that is suitable for the extraction of volatile or semi-volatile analytes [71-73]. In this mode, unlike in DI-SDME, the extracting solvent doesn't need to be water-immiscible, since it is not in direct contact with the sample phase. In this mode, water can also be used as the extracting solvent for soluble analytes, which increases the range of extractable analytes and the variety of analytical techniques that can be coupled to SDME. On the other hand, HS-SDME provides excellent cleanup for samples of complex matrices [17].

Wu et al. [74] used HS-SDME followed by HPLC with fluorescence detection for the determination of trace PAHs in environmental samples. In this research, five PAHs were studied as target analytes and a solution of saturated β-cyclodextrin was used as the extraction solvent. In addition, performance parameters that affected extraction efficiency were investigated and the optimal extraction conditions were determined. The limit of detection (LOD) of this method ranged between 0.004–0.247 ng mL^{-1} with relative standard deviations (RSDs) ranging from 5.1–7.1%. It was also found that β-cyclodextrin improved the extraction efficiency of target analytes. The results demonstrated that the SDME technique generated satisfactory results for the analysis of trace PAHs in environmental samples [74].

Wang et al. [75] used SDME equipped with GC-MS for the determination of hydroxylated PAHs in seawater. In this study, the kinetics of mass transfer and derivatization were investigated. After optimization of the experimental parameters, the analytes in the upper and bottom layers of seawater from 25 sampling sites were analyzed. Under optimized conditions, the LOD and limit of quantification (LOQ) ranged between 0.33 to 7.50 ng L^{-1} and 1.11 to 25 ng L^{-1}, respectively. Recoveries ranged between 68% to 128% and RSDs were less than 15%. These results demonstrated that the SDME technique is capable of detecting hydroxylated PAHs in the surface and bottom layers of seawater [75].

Li et al. [76] identified 16 PAHs in environmental water samples using column clean-up along with continuous flow SDME, prior to PAH determination by GC-MS. In this method, purification, extraction, and enrichment steps were performed in a single step, which reduced the effect of interfering compounds on the determination of the analytes of interest. Additionally, this approach simplified the operation process and shortened the extraction time. The performance parameters that affected the extraction efficiency were optimized, including type and amount of column packing material, type and volume of extraction solvent, the flow rate of the sample solution, and extraction temperature. For allanalyte, the results showed linearity in the range of 0.02-10 μg L^{-1}, with correlation coefficients more than 0.99. The LOD and LOQ of the analytes were in the range of 0.0012–0.0101 μg L^{-1} and 0.0041–0.0336 μg L^{-1}, respectively. The recoveries of target analytes were in the range of 81.8–105.8%, with RSDs ranging from 0.5% to 6.4%. This method has several advantages including simplicity, fast processing time, satisfactory recoveries, and low consumption of organic solvent. The results showed that the proposed method has considerable potential for the analysis of trace PAHs in environmental water samples [76].

In another study, SDME coupled to HPLC along with a new class of ionic liquids (containing the tris (pentafluoroethyl) trifluorophosphate anion paired with imidazolium, phosphonium, and pyrrolidinium cations) was used as extraction solvents for the extraction of PAHs from aqueous samples. The extraction parameters that were investigated included stirring rate, extraction time, salt content, microdroplet, and sample volume. The LOD was in the range of 0.03–1.2 μg L^{-1} and the correlation coefficients were between 0.981 and 0.999. This study demonstrated that the application of SDME for analysis of PAHs had high efficiency [77].

Comments: Since its introduction, the SDME sample preparation technique has been widely applied for the sampling and analysis of a variety of compounds, including PAHs. Despite its history of reliability, SDME still needs to be improved in several aspects comprising stabilization of the microdrop, using environmentally friendly solvents, and the realization of high extraction efficiency. Future studies should also assess the use of new materials to permit combined extractant, improvement of the SDME devices, and online and or automated coupling with chromatographic and spectroscopic instruments. Furthermore, new applications such as integrative artificial intelligence systems to predict appropriate extraction conditions are expected to ensure the future vitality of this technique.

3.2 Hollow-fiber liquid phase microextraction

In 1999, HF-LPME was introduced by Pedersen and Rasmussen as a way of avoiding the drop instability in SDME [66, 78]. In HF-LPME, extraction takes place inside a porous hollow-fiber typically made of propylene. Prior to the extraction, the hollow fiber is dipped into a water-immiscible organic solvent, which enters the pores of the fiber by capillary forces and becomes a supporting liquid membrane. During the extraction, the fiber helps to mechanically protect the sample and prevents losses of it [79-81]. In this technique, the target analytes are extracted from the aqueous sample into the organic phase in the pores of the fiber. The pores can increase selectivity by preventing the extraction of high molecular weight materials [82-84]. There are two main modes of HF-LPME: the two-phase and the three-phase mode. In two-phase HF-LPME, analyte is extracted from an aqueous sample placed in the membrane pores. The extractant uses the same organic solvent as that immobilized in the pores, and the analytes are extracted in an organic phase that is compatible with GC [85, 86]. In three-phase LPME, the analytes of interest are extracted from the aqueous sample, by the organic solvent in membrane pores, and then subsequently into another aqueous extractant, in a back-extraction-like process. In this mode, the extractant is another aqueous phase and the analytes are transported into it via the thin film of the organic solvent. This process makes this mode compatible with processes such as HPLC, capillary electrophoresis (CE), and atomic absorption spectrometry (AAS) [87-91]. Two-phase HF-LPME, is capable to extract uncharged hydrophobic analytes, which cannot be efficiently extracted by a three-phase mode. The important point is that the final extract can be directly injected into the GC. In this technique, only the partition coefficient determines the maximum enrichment [92]. Generally, this technique is more cost-effective and has a higher potential for automation and miniaturization than the SDME technique [93, 94]. HF-LPME is currently being used for passive sampling of different analytes. Recently Eduard et al. [95] applied HF-LPME as a new passive sampling device for effective monitoring of pesticides in water and their study showed good results by using this technique [95]. On the contrary to the attributed advantages, HF-LPME suffers from its low-speed passive diffusion, the need for pre-conditioning of the membrane, possibility of fiber pores getting blocked, and the possibility of carryover when membranes are reused [68, 69].

Demirci et al. [96] used HF-LPME-HPLC for the identification of different PAHs in cigarette filter tar. In this study, the performance parameters affecting the optimum conditions for HF-LPME, such as the sample solution condition, pH, extractant's type, mixing rate, and extraction time were investigated. The LOD of the six PAHs were in the range of 0.040 to 0.136 ng mL^{-1}, and the percentage of recoveries and enrichment factors for the model samples solutions ranged from 63% to 97% and 208 to 320, respectively. The recoveries from real samples were between 8% and 71%, and the enrichment factors ranged from 27 to 234. The total amounts of PAHs in the three brands of filter tar were 165.49, 50.49, and 51.04 ng, respectively. This study result showed that HF-LPME-HPLC can be a useful method for quantification of the PAHs in cigarette filter tar [96].

Ratola et al. [97] used HF-LPME for the quantification of PAHs in complex pine needle samples. Important parameters including type of extractant, salt addition, sample agitation, and sampling time, were investigated and optimized, based on the response of the GC-MS instrument. The LOD for a signal-to-noise ratio (S/N) of 3, ranged between 0.01 and 0.95 ng g^{-1}, and the linear range concentration was between 10 and 2000 ng g^{-1} for most of the target analytes. In this study, the repeatability and reproducibility of HF-LPME results were also good for the analysis of PAHs. Results showed that HF-LPME is an effective and reliable technique in the determination of PAH residues in sonicated extracts of plant materials such as pine needles [97].

HF-LPME coupled with GC-MS was used for the analysis of PAHs in wastewater treatment plant effluents. In this study, the performance parameters and experimental conditions were controlled. Under optimal conditions, the calibration graphs were linear in the range of 0.5-50 μg L^{-1} for all of the target analytes, with determination coefficients bigger than 0.991. The LODs ranged between 0.005 and 0.011 μg L^{-1}. The method repeatability (intra-day) and reproducibility (inter-day) were found to be 2.7-11.3% and 7.9-14.4%, respectively. Additionally, it was shown that the performance of HF-LPME was comparable with solid-phase microextraction (SPME) for separation and preconcentration of organic analytes. This study demonstrated that HF-LPME has the ability to concentrate many organic analytes such as PAHs in aqueous samples [98].

Ghiasvand et al. [99] used cooling-assisted headspace HF-LPME, coupled with the GC-FID, for the determination of PAHs in soil samples for the first time, they used volatile solvents as the extraction phase for HF-LPME. Different performance parameters including type and volume of extraction solvent, extraction time and temperature, and temperature of the cooled organic solvent, were studied. The results showed that the linear concentration range was 1-10,000 ng g^{-1}, with good linearity of the calibration curves (> 0.99). The LODs and LOQs were obtained over the ranges of 0.01-0.1 ng g^{-1}, and 1-3 ng g^{-1}, respectively. The RSDs were found to be 4.7% to 10.1%. This study demonstrated that HS-HF-LPME coupled with GC-FID could be successfully used for the determination of PAHs in soil and plant samples [99].

In another study, ordered mesoporous carbon (OMC)–reinforced HF-LPME coupled with HPLC and fluorescence detection was used for the determination of PAHs in water samples. The influential experimental parameters including extraction time, fiber length, stirring rate, type of extraction solvent, pH, concentration of OMC, and salt effect were evaluated. Results showed good linearity in the range of 2 ng L^{-1} to 1,000 ng L^{-1}, with correlation coefficients of 0.9954 to 0.9986. The recoveries for the spiked samples were in the range of 88.96-100.17%. The LODs were 0.4 to 4 ng L^{-1}, and the RSDs were 4.2% to 5.9%. This study proved that the OMC-HF-LPME method has excellent enrichment factors and efficiency parameters and can be a good alternative approach for the determination of PAHs in environmental water samples [100].

Comments: As mentioned in the reviewed reports, HF-LPME possesses enormous potential for trace analysis of different compounds in a variety of matrices. To date, it has been used successfully to determine PAHs in a variety of liquid and solid samples. Nevertheless, HF-LPME could be improved in terms of automation, simplicity of workflow, and higher throughput to provide a robust and suitable alternative to the conventional extraction methods. Automation would help facilitate tasks, reduce operator-associated error, and increase reproducibility and accuracy of the analytical process. The development of commercial equipment to reduce manual labor can lead to broader applications of this technique in the routine analyses. Finally, future HF-LPME studies most likely will be focused on its automation, compatibility with different sample matrices, and online coupling with chromatographic systems.

3.3 Dispersive liquid-liquid microextraction technique

Dispersive liquid-liquid microextraction (DLLME) is another sample preparation technique derived from LPME, in which small volumes (μL) of an extraction solvent is used. DLLME is a powerful preparation technique based on the use of a ternary solvent system [101]. The solvent system includes an aqueous sample, a disperser organic solvent, and an organic extracting solvent. The extraction solvent is dispersed in the aqueous sample by getting help from the disperser and consequently forms microdroplets of the extractant, inside the aqueous sample, which enables a very fast extraction process [102, 103]. After the extraction, the extractant is settled by centrifugation or solidification and the quantification of the enriched analytes performed by an analytical instrument. The enriched analytes can be analyzed by GC, due to the use of water-immiscible solvents in DLLME. Nevertheless, DLLME can also be used in combination with other analytical tools such as LC [104, 105]. The choice of an appropriate extraction solvent that ensures high extraction efficiency requires the consideration of many physicochemical properties such as the capability to extract the analytes of interest, low solubility in water, the formation of tiny droplets in the disperser solvent, and the compatibility of the solvent with the analytical instrumentation [106, 107]. The main advantages of the DLLME technique are low consumption of organic solvents, short extraction time, and high enrichment factors. Accordingly, the DLLME technique is a simple, fast, high-performance, and low-cost operation that also meets the requirement for the development of green analytical chemistry. However, it suffers from a few drawbacks like using two different organic solvents in the extraction process, need for high density extracting solvents (which limited the choice of suitable solvent), and need for centrifugation or solidification, as an extra step [69]. Since the invention of DLLME in 2006, the number of studies concerning its application in the determination of PAHs has been continually growing [68, 108-112].

A magnetic SPE sorbent coupled with DLLME (MSPE–DLLME) followed by GC–MS was used in the determination of 16 PAHs from real environmental samples, including tap water, seawater, wastewater, sewage, and soil samples. The parameters of influence, such as the amount of extraction adsorbent, type of stripping, extraction solvents, salt effect, and the pH and volume of the sample solution were studied. Under optimal conditions, the LOD values were in the range of 0.1–0.5 ng kg^{-1} at S/N = 3 and the method precision values were satisfactory (RSD% ≤ 8.66). The results showed good linearity in the range of 0.4–10,000 ng kg^{-1}, with the correlation determinations between 0.9989 and 0.9999. Overall, the study results indicated that the combined MSPE–DLLME method shows excellent performance for the trace analysis of PAHs in environmental samples [113].

A DLLME procedure based on the solidification of floating organic droplets was investigated for the determination of PAHs in water samples. In this method, an organic solvent with a low density and an appropriate melting point is used. Thus, the needle tip of a microsyringe and a hollow fiber are not required and the extractant droplet (extraction phase) can be obtained by solidifying it at a lower temperature. In this study, the performance parameters were also investigated. Under optimal conditions, the LOD values were in the range of 0.045–1.1 ng ml^{-1} and the linear range concentrations ranged between 0.10–500 ng ml^{-1}. The recoveries were also in the range of 92–110% and RSDs values ranged from 3.4–5.8%. In addition, the results showed correlation coefficients between 0.99600 and 0.9986. The results of this study confirmed that this method is a simple and low-cost method that can be successfully applied to determine PAHs in environmental water samples and provides an alternative method for the analysis of non-polar compounds in complex environmental water [114].

Leong et al. [115] used DLLME-GC–MS for the extraction and determination of 16 PAHs in water samples. In their study, they proposed the use of a low-toxic bromo-solvent as the extractant, whereas in the conventional DLLME, chloro-solvents are mostly used. The extraction efficiencies of five chloro-solvents and 13 bromo/iodo- solvents were investigated. The results indicated that some of the bromo/iodo- solvents have high extraction capability and lower toxicity than chloro-solvents. The range of enrichment factors and extraction recoveries were 372–1308 and 87–105%, respectively. The linear concentrations ranges were found to be 0.01–10.00 µg L^{-1}, and the LOD values were between 0. 3 and 7.8 ng L^{-1}. The RSDs values for 10 ng L^{-1} of PAHs in tap water were also in the range of 5.1–10.0%. These results showed that the low-toxic DLLME method can be successfully used in the separation and preconcentration of trace PAHs in water samples [115].

An automated low-density-solvent-based DLLME method, coupled with GC-MS, was carried out for the determination of PAHs in environmental water samples. In that study, different types of extraction parameters were investigated, including the type and volume of extraction solvent, the dispersive solvent extraction and demulsification times, and the speed of solvent injection. In the study, the LOD and LOQ values ranged from 0.023–0.058 µg L^{-1} and 0.077–0.193 µg L^{-1}, respectively. The calibration graphs were linear in the concentration range of 0.1–50 µg L^{-1} with correlation coefficients were between 0.9915 and 0.9964. The RSDs values (n = 6) were determined to range between 4.9% and 7.3%. These study results showed that an automated method that integrates low-density-solvent-based DLLME and GC–MS was successfully used to determine PAHs in environmental aqueous samples [116].

Fernández et al. [117] used the DLLME technique coupled with an HPLC fluorescence detector for the determination of 15 PAHs in water samples, including tap water, rainwater, and river water. The authors investigated the parameters affecting the extraction efficiency including type and volume of extractant solvent, type and volume of dispersive solvent, and extraction time. The intra-day and inter-day relative standard deviations ranged from 1.6–4.7% and 2.1–5.3%, respectively. The DLLME technique exhibited good linearity in the range of 0.2–600 µg L^{-1} with correlation coefficients higher than 0.999. The LOD and LOQ values were 0.02–0.61 µg L^{-1} and 0.02–0.61 µg L^{-1}, respectively. The enrichment factors of PAHs were in the range of 86–95, and the extraction time had no effect on the recovery of the PAHs. Their results indicated the successful application of DLLME in the separation and pre-concentration of low concentration PAHs compounds in water samples [117].

Vera et al. [61] used an ionic liquid based DLLME method, coupled to a HPLC with fluorescence detector, in the determination of carcinogenic PAHs in tea beverages. The performance parameters associated with the extraction efficiency and tea infusion preparation were optimized. This method exhibited good precision, with RSDs values between 2 and 5%. The LOD and LOQ values ranged from 2.0 to 30.8 ng L^{-1} and 6.73 to 95.2 ng L^{-1}, respectively. The calibration plots for chlorobenzenes were linear in the range of 1-500 µg L^{-1}, and the recoveries ranged from 56% to 94%. Given the results obtained, this method can be considered as a good alternative for the analysis of PAHs in tea beverages [61].

In another study, Tan et al. [118] coupled microwave-assisted extraction with DLLME (MAE-DLLME) for the extraction of PAHs from vegetables. They investigated the influential parameters in the efficiency of DLLME including extraction solvent, dispersive solvent, and extraction time, as well as MAE parameters such as solvent type, microwave power, and irradiation time. A GC-FID was used for the determination of PAHs. In addition, they studied the impacts of the physiochemical properties of the extraction solvents on the extraction efficiency. The results showed that extraction solvents with low viscosity and low polarity have higher extraction efficiency. The results indicated that the selected dispersive solvents and extraction time had no significant effect on the extraction efficiency. The results demonstrated that the MAE–DLLME–GC-FID method can be successfully used for the sampling and analysis of PAHs in vegetable samples [118].

Comments: DLLME has been successfully applied for the extraction and separation of a wide range of analytes from a variety of samples, including environmental, biological, water, and food. However, still, there is a need for the application of new extraction media for better viscosity hydrophobicity, and other properties that improve the selectivity and efficiency of this technique. Furthermore, more additional research must be conducted to develop automatic DLLME systems. One of the significant challenges in the utilization of microextraction techniques such as DLLME is in-line coupling of them to different chromatographic and spectroscopic systems, to reduce time and cost of analysis, as well as to improve sensitivity and enrichment factor.

4 Extraction media used in LPME techniques

The choice of an appropriate extractant is the most important factor in the ultimate results of LPME experiments. To develop new LPME extracting solvents different physicochemical properties like polarity, boiling points, density, viscosity, cost, and toxicity must be considered. In recent years, the use of new solvents in LPME techniques has increased remarkably to improve extraction efficiency and selectivity [119, 120].

4.1 Ionic liquids

The term ILs describes liquids that made up of cations and anions (salts) which melt at or below 100 °C. Indeed, ILs are organic salts that are liquid at mild temperature conditions. These compounds were first introduced by Walden, in the nineteenth century. ILs are composed of large asymmetric organic cations and inorganic or organic anions and their characters are determined by the structure and interaction of the ions in the melt [121, 122]. ILs are mostly non-flammable, non-volatile, and low vapor pressure (meaning the risk of atmospheric contamination) solvents. For this reason, they are usually considered as “green solvents” for green technologies. The high solubility of organic species in ILs makes them appropriate solvents for the extraction of various analytes from a variety of sample matrices [123-125]. In addition, ILs offers high thermal and chemical stability, significant recoverability, electrical conductivity, and efficient dissolution ability for biopolymers. [126]. The first use of ILs in microextraction techniques reported in 2003 and since then, the potential of ILs as alternative solvents for LPME techniques is increasingly being pursued [127]. ILs have shown higher selectivity than the other conventional extracting solvents. It has been proved that IL-based LPME techniques are potential sample pretreatment methods for the analysis of target analytes in complex matrices like biological, pharmaceutical, food, and environmental samples [128]. However, the flammability, toxicity, and causticity of some ILs have not yet been thoroughly investigated and much care should be taken to choose them as the extraction solvent. On the other hand, the cost of ILs used in LPME is high and the synthesis of cheaper and more functional IL must be a targeted aim in the IL-based microextraction techniques [129].

4.2 Magnetic ionic liquids

Magnetic ionic liquids (MILs) have been introduced as a new subclass of ILs for numerous analytical applications. MILs are produced by the incorporation of a paramagnetic part into the cation or anion in the IL structure [130, 131]. MIL solvents are used in solvent-based extractions and microextractions, membrane applications, gas absorption, chromatographic separations, electrochemical and sensing applications, magnet-based sensors, etc. [132-134]. In addition to the general characters of ILS, MILs have more tunable solvation properties, which make them suitable extraction solvents for the LPME applications [135]. The use of MIL solvents can be magnetically manipulated and their physicochemical properties are possible to be tailored to perform specific applications. as a result, the use of MILs in analytical chemistry is significantly increasing due to their unique advantages and tunable properties, in the presence of an external magnetic field [136].

4.3 Deep eutectic solvents

DESs are a new class of solvents that can address the main limitations of common ILs like costly and laborious synthesis process, high toxicity, and non-biodegradability. DESs were introduced in 2003 by Abbot and co-workers. These solvents are produced by mixing of choline chloride with a metal salt, at temperatures below 100 °C, followed by freeze drying [137, 138]. Compared to other solvents, DESs offer outstanding advantages such as biodegradability, low-toxicity, good solvating ability, sustainability, low-cost, and easy preparation method. For this reason, they have been applied in a large range of applications like drug development, catalysis, synthesis of new compounds, and analytical chemistry [120, 139]. In this regard, the applications of DESs in analytical chemistry can be divided into several areas including extraction of target analytes from complex matrixes, sorbent modifiers, dissolution or digestion of solid samples, elution solvent for dispersive solid-phase extraction, and application in chromatography as mobile phase additive or modifier [116, 140-142]. DESs have potential applications in chemical analysis for both liquid samples and solid samples, especially for the extracting of polar analytes. These solvents have the ability to extract both dissociated and undissociated forms of acidic compounds [143]. In this sense, it can be anticipated that these type of solvent need to be more studied because applications of DESs in analytical chemistry and separation sciences is still in its infancy stage [144]. More recently, significant attention has been given to the application of DESs in LPME techniques in order to reduce toxic waste and to improve selectivity and extraction efficiency [145-147].

4.4 Supramolecular solvents

Supramolecular solvents (SUPRASs) is a term that describes nano-structured liquids produced by spontaneous, sequential phenomena of self-assembly, and coacervation. SUPRASs are well-known in analytical chemistry and have been employed for different extraction processes [148]. SUPRASs have a unique array of physicochemical properties including use of self-assembly based synthetic routs, ubiquity of amphiphiles in nature and synthetic chemistry, tunability of solvent properties by varying the hydrophobic or polar group of the amphiphile, presence of different polarity regions in the supramolecular, non-volatility, and non-flammability (permits the implementation of safer processes). SUPRASs are eco-friendly solvents produced from inexpensive bio-surfactants [149-151]. These solvents have been widely used in extraction methods due to their high ability to extract various compounds including organic and inorganic specie [152]. They can form different ionic, hydrogen bonding, π-cation, and hydrophobic interactions with target analytes to enhance the extraction efficiency [153, 154]. They can efficiently extract compounds covering a wide polarity range by a selection of proper functional groups of the amphiphiles [155]. SUPRASs are appropriate green alternatives for the conventional solvents in microextraction methods and can be widely used for the extraction of organic and inorganic traces from different samples [156-159]. These solvents are properly compatible with different LPME formats, as well as various detection instruments. According to literature, SUPRASs-LPME has been described as a fast, cost effective, and highly efficient extraction technique [160, 161].

5 Influential parameters on extraction efficiency of LPME techniques

Different parameters can affect the extraction efficiency of LPME techniques. These parameters include the organic solvent, sample volume, extractant volume, extraction time, pH, agitation, and salting-out effect, which may differ according to the extraction strategy and sample/solvent specifications [162]. The choice of a suitable organic solvent is one of the most important factors in the ultimate success of the analysis in LPME techniques. Several parameters must be considered when choosing an organic solvent, including boiling points, density, viscosity, economic factors, and compatibility of the solvent with the proposed analytical instrumentation [106, 107]. The viscosity of the solvent of choice must be enough to form a stable microdrop in SDME, or a properly settled drop in DLLME. Further, a high boiling point and low vapor pressure should be consideredto reducing evaporation during the extraction process [67, 163]. The volume of sample and extractant solutions are the most important factors that affect the enrichment factor. However, it should be noted that when the volume ratio of sample/extractant increases the enrichment factor can increase. [84, 164]. The extraction process in LPME techniques is time dependent because the extraction efficiency is attained at the equilibrium between the extraction phase and the sample. Generally, longer extraction times in the non-equilibrium-based extraction systems lead to higher extraction efficiencies but such conditions are not sometimes feasible, in terms of time, cost, and required sensitivity of the analysis. Due to the large surface area between the extractant and sample solution, in the dispersed system, extraction time in DLLME is almost shorter than SDME and HF-LPME. Some novel methods accelerate the process through carrier-mediated extraction or electrokinetic migration [103, 165, 166]. Another affecting factor in extraction efficiency is the pH adjustment, since the pH of sample and extractant affects the solubility, distribution ratio, enrichment factor, and recoveries of target analytes, especially for the analytes with acid-base characters. In the LPME sampling of ionic analytes, pH of the sample solution should be precisely adjusted to allow ionization of the target analytes and obtain an efficient extraction [82, 164]. For this purpose, using of suitable buffers can lead to increase in the reproducibility, selectivity, and sensitivity of the sampling process [167]. The agitation of the sample is important to enhance extraction efficiency. This creates continuous exposure of the extraction phase to the aqueous sample and thus equilibrium can be achieved in a shorter time [84]. Based on the convective-diffusive mass transfer theory, increasing of stirring rate decreases the thickness of the stagnant film around the extracting phase, improve the mass transfer, and results in a reduction in extraction time. Various methods like agitation, stirring, vibration, shaking, and irradiation with ultrasonic waves have been applied to improve the extraction efficiency of LPME methods via increasing the mass transfer rate [83, 168]. The addition of salt or increasing of ionic strength in an aqueous solution almost improves the partitioning of lipophilic analytes into the extraction phase. However, the high concentrations of salt may change the physical characteristics of the Nernst diffusion layer and decrease the transmission of the analytes into the extraction phase. The enhancing effect of salt addition was clearly demonstrated by Wand et al. for the analysis of hydroxylated PAHs in water samples [75]. However, the nature of the target analytes and sample solution play an important role in salting-out effect [164, 169].

6 Conclusions and prospects

The screening of trace and ultra-trace levels of PAHs is important to avoid health complications caused by exposure. To date, the conventional sample preparation methods have been widely applied for the sampling of PAHs. However, these methods usually are tedious, costly, and time-consuming, and use large amounts of toxic organic solvents. Notwithstanding significant advances in the analytical instrumentation, sample preparation steps are still inevitable prior to instrumental analysis of complex samples. Sample preparation is an essential step in most of the analytical process, and generally involves a combination of extraction, preconcentration, and presenting the analytes into a form that is compatible with the analytical system, depending on the case. Thus, many efforts have been directed toward the development of green sample preparation methods that minimize dangerous solvent consumption and result in the determination of target analytes in a highly efficient manner. In this way, the use of different types of LPME techniques has increased remarkably for determining of PAHs. Here, we reviewed the studies that utilize LPME techniques for the sampling and analysis of PAHs. LPME techniques are advantageous due to their high performance, simplicity, automation, short analysis time, ease of coupling with chromatographic systems, lower cost, higher sensitivity and selectivity, and environmental friendliness. Considering the studies discussed in this review, LPME techniques show considerable opportunity for the determination of trace amounts of PAHs in different samples. These techniques have been successfully used for the sampling and analysis of PAHs at different concentrations in various matrices. Altogether, the combined use of LPME techniques with a sensitive analysis instrument provides a powerful method for the sampling and analysis of PAHs. Therefore, LPME techniques are recommended as an alternative for the conventional methods for the analysis of PAHs. These considerations clearly suggest that in the future, these techniques will be applied more frequently in multiple fields, including PAHs analysis. It is still desirable to widen the applications of LPME to more analytes and complex matrices in various forms. In the coming years, new efforts are expected to be more focused on automation of different configurations of LPME system, as well as to develop more efficient green extracting solvents. Especially, more research needs to be initiated to implement safer and lower toxicity extraction solvents, which will lead to an increase in the green aspects of the LPME techniques. In-line coupling of LPME to the sensitive analytical instrument by using flow-based hyphenation systems and application of chemometric models for the optimization of the methods are other aspects that are expected to be more investigated.

Declaration of conflict of interest

The authors have declared no conflict of interest.

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