

Extraction of Polycyclic Aromatic Hydrocarbons from Environmental Samples

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Polycyclic aromatic hydrocarbons (PAHs) comprise a group of chemical compounds consisting of two or more fused benzene rings. PAHs exhibit hydrophobicity and low water solubility, while some of their members are toxic substances resistant to degradation. Due to their low levels in environmental matrices, a preconcentration step is usually required for their determination. Nowadays, there is a wide variety of sample preparation techniques, including micro-extraction techniques (e.g., solid-phase microextraction and liquid phase microextraction) and miniaturized extraction techniques (e.g., dispersive solid-phase extraction, magnetic solid-phase extraction, stir bar sorptive extraction, fabric phase sorptive extraction etc.).

Keywords: PAHs ; sample preparation ; environmental samples ; extraction ; MSPE ; SPME ; FPSE ; SBSE ; DSPE ; PT-SPE

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a large group of chemical compounds composed of two or more fused benzene rings ^[1]. PAHs are hydrophobic compounds with low water solubility, and their solubility in water and volatility decrease with an increase in their molecular weight ^[2]. PAHs consisting of up to four rings are known as light PAHs, while PAHs that are made of more than four rings are known as heavy PAHs. Heavy PAHs are more stable and more toxic than the light PAHs. These chemical compounds are widespread environmental contaminants that are considered byproducts of the incomplete combustion of organic materials, such as coal, gas, garbage, meat, oil, tobacco and wood, during natural or anthropogenic processes ^{[1][3]}. PAHs are toxic substances, which are resistant to degradation and exposure to them may increase the risk of cancer ^[4]. As a result, PAHs are considered by US Environmental Protection Agency (EPA) and the European Environmental Agency to be priority pollutants ^[1]. Therefore, the determination of PAHs in environmental samples is of high importance. Since PAHs exist in traces in environmental matrices, a preconcentration technique is normally required. **Figure 1** shows the chemical structures of common PAHs.

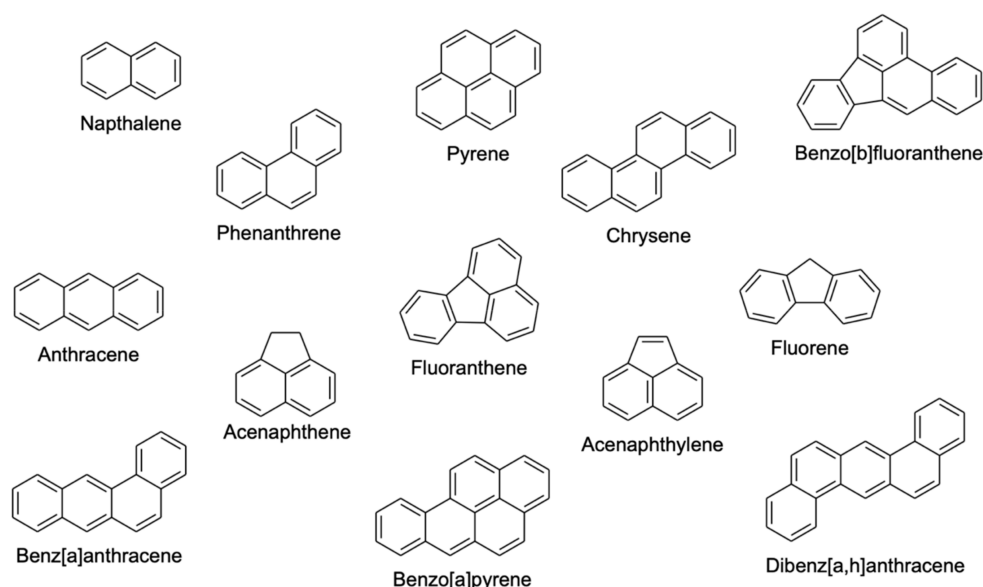


Figure 1. Chemical structures of common polycyclic aromatic hydrocarbons (PAHs).

Currently, the most widely used methods for analyzing these pollutants in environmental matrices are gas chromatography (GC), high performance liquid chromatography (HPLC) and ultra-high pressure liquid chromatography (UHPLC) ^{[3][5]}. Various detection systems, including ultraviolet detectors (UV) ^[6], diode array detectors (DAD) ^[3], fluorescence detectors (FLD) ^[1], mass detectors (MS) coupled with HPLC and UHPLC and flame ionization detectors

(FID) [7], MS detectors [5] and tandem MS detectors (MS/MS) [8] coupled with GC have been used. Due to the enhanced sensitivity in the determination of PAHs that results in lower LODs, mass detectors and tandem MS detectors are generally preferred.

Solid-phase extraction (SPE) and liquid–liquid extraction (LLE) are two major sample preparation techniques that have been widely used for the extraction and preconcentration of a wide variety of analytes from environmental samples. However, both conventional techniques tend to have many fundamental drawbacks, since they include complicated, time-consuming steps, while they require large amounts of sample and organic solvents. Moreover, in both techniques there are difficulties in automation [9][10].

In order to overcome these drawbacks, different microextraction techniques have been proposed as an efficient alternative to classical extraction techniques, since the introduction of solid-phase microextraction (SPME) by the research group of Pawliszyn [11]. Liquid-phase microextraction (LPME) was introduced a few years later by Liu and Dasgupta, by using organic droplets suspended from the tip of a microsyringe [12]. Those microextraction techniques are widely used today, and they offer certain benefits compared to the conventional sample preparation techniques. Microextraction techniques require a significantly lower sample amount, number of extraction steps, sample preparation time and organic solvent consumption, and they comply with Green Analytical Chemistry principles [10][13].

Typical examples of miniaturized sample preparation techniques include dispersive solid phase extraction (d-SPE) [14], magnetic solid-phase extraction (MSPE) [15], pipette tip solid-phase extraction (PT-SPE) [16], fabric phase sorptive extraction (FPSE) [17], stir bar sorptive extraction (SBSE) [18] etc. In recent years, a wide variety of novel sorbents, including molecular imprinted polymers (MIPs), graphene, graphene oxide (GO), carbon nanotubes (CNTs), metal organic frameworks (MOFs), covalent organic frameworks (COFs) and zeolitic imidazole frameworks (ZIFs) have been successfully coupled with miniaturized extraction techniques and microextraction techniques [14][19][20][21].

2. Extraction of PAHs from Environmental Matrices

A plethora of novel sample preparation techniques have been employed for the extraction of PAHs. **Figure 2** summarizes the recent advances in sorptive extraction techniques that have been employed for the determination of PAHs from environmental samples.

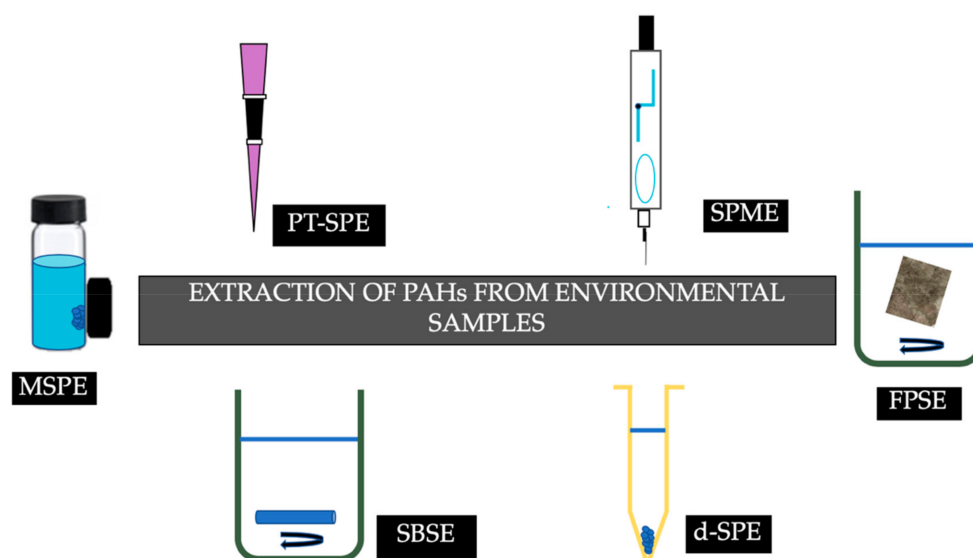


Figure 2. Recent advances in sorptive extraction techniques for the determination of PAHs from environmental samples.

2.1. Dispersive Solid-Phase Extraction of PAHs from Environmental Matrices

Dispersive solid-phase extraction (d-SPE), is a form of SPE in which the desired sorbent is added directly into the sample aqueous solution followed by dispersion. This technique is taking advantage of the contact between the adsorbent and the target analytes. Once the extraction process is completed, the sorbent with the adsorbed analytes is separated from the sample by a mechanical process, such as centrifugation or filtration. Compared to the conventional SPE process, the main benefit of d-SPE is the reduction of sample preparation time, as well as its simplicity, adaptability and easy handling. A wide variety of sorbents have been utilized for the d-SPE of PAHs from environmental samples [22][23].

This technique gained popularity when Anastassiades et al. [24] introduced the QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) approach for the determination of pesticide residue in food of plant origin. The initial method consists of acetonitrile extraction and addition of a mixture of salts, followed by a dispersive clean-up step with a primary–

secondary amine (PSA) as extraction sorbent. QuEChERS was quickly applied for the determination of other analytes in a variety of sample matrices. Cvetkovic et al. [25] developed a QuEChERS extraction procedure of PAHs in soil prior to their determination by GC-MS. The researchers evaluated different solvent systems (acetonitrile/water and hexane/water) and sorbents (PSA, C₁₈, Florisil, diatomaceous earth and clinoptilolite). Among the tested parameters, the best results were obtained with acetonitrile/water, as the extraction solvent and diatomaceous earth as the d-SPE extraction adsorbent.

Until today, a wide variety of novel extraction sorbents have been evaluated for the d-SPE of PAHs from environmental matrices. Among them, metal-organic frameworks and zeolitic imidazole frameworks are currently the most popular d-SPE adsorbents. MOFs became widely known in 1995, when Yaghi and Li [26] reported the hydrothermal synthesis of a MOF material with large rectangular channels. Metal-organic frameworks are a class of hybrid organic-inorganic supramolecular materials, which are based on the coordination of metal ions or clusters with bi- or multidentate organic linkers. What makes MOFs materials so attractive is their unique properties, such as high surface areas (up to 14,600 m²·g⁻¹) [27], pore size tunability, structure flexibility, luminosity, thermal stability, charge transfer ability from the ligand to the metal or from the metal to the ligands, etc [21][28][29][30][31]. As a result, MOFs have gained attention in a plethora of applications, such as gas storage and separation [32], catalysis [33], sensors [34], detoxification [35] and drug delivery [36]. In analytical chemistry, MOFs have been evaluated as stationary phases for GC [37][38] and HPLC [39][40] analysis. However, today, the most popular field of applications of MOFs in analytical chemistry is sample preparation [21][28].

Other d-SPE sorbents that have been applied for the extraction of PAHs from environmental samples include graphene/sepiolite [41] and *N*-acetyl-L-cysteine modified CdS quantum dots [42].

2.2. Magnetic Solid-Phase Extraction of PAHs from Environmental Matrices

Magnetic solid-phase extraction (MSPE) is a form of d-SPE in which a magnetic nanomaterial is added into an aqueous sample solution to adsorb the target analytes. After the adsorption of the analyte, an external magnetic field is applied to collect the sorbent and the supernatant solution is discarded. Subsequently, elution of the adsorbed analytes is achieved with the addition of an appropriate solvent, and magnetic separation is performed once again to collect the eluent, which is further analyzed by a suitable analytical technique. Compared to the conventional SPE procedure, in MSPE there is no need for sorbent packing into cartridges, thus avoiding limitations of column blocking and high pressure. Meanwhile, sample and organic solvent consumption is significantly decreased compared to the classic SPE and LLE formats. Finally, the sorbent separation with a magnet is a simple and rapid process, compared to the time-consuming centrifugation and filtration steps that are required in conventional d-SPE [43][44][45].

Magnetic nanoparticles (MNPs) are characterized by the general formula MFe₂O₄ (M = Fe, Co, Cu, Mn, etc.), and they can be produced by a variety of methods, such as co-precipitation, solvothermal, hydrothermal etc. The most common magnetic nanoparticles that have been used in order to fabricate magnetic sorbents for MSPE are Fe₃O₄ nanoparticles. Iron oxides have been widely used in MSPE due to their super paramagnetism, their low toxicity, their high magnetic saturation, their simple preparation process and their low price [7]. The application of other magnetic nanoparticles, such as MnFe₂O₄, have been also reported [46]. However, the utilization of MNPs in sample preparation has some drawbacks, since their selectivity is low. Moreover, MNPs exhibit low stability in strong acidic aqueous media and low dispersion ability in many sample matrices. Therefore, surface modification of magnetic nanoparticles is usually required to enhance their stability and selectivity by the introduction of special functional groups [7]. As seen in **Table 1**, a wide variety of chemical compounds including carbon-based materials, polymeric materials, MOFs and other molecules have been employed for this purpose.

Table 1. Application of different sorbents for the magnetic solid-phase extraction (MSPE) of PAHs from environmental samples.

Sorbent	Matrix	Analytical Technique	Sorbent Mass (mg)	Time (min)	LODs (ng L ⁻¹)	Extraction Recovery (%)	Reusability	Ref.
HKUST-1	Water	UHPLC-FLD	5 Fe ₃ O ₄ /20 HKUST-1	10	0.8–12	39–59	NA	[47]
MIL-101(Cr)	Water	HPLC-PDA	1 Fe ₃ O ₄ @SiO ₂ /0.6 MIL-101	20	2.8–27.2	NA	NA	[48]

Sorbent	Matrix	Analytical Technique	Sorbent Mass (mg)	Time (min)	LODs (ng L ⁻¹)	Extraction Recovery (%)	Reusability	Ref.
Fe@MIL-101(Cr)	Water	HPLC-DAD	50	50	44–64	>80	At least 10 times	[49]
MIL-100(Fe)	Water	HPLC-FLD	10	10	32–2110	>80	NA	[50]
MIL-100(Fe)	Water	GC-FID	12.5	15	4.6–8.9	73–96	Up to 10 times	[51]
Fe ₃ O ₄ @polydopamine/ZIF-7	Water, particulate matter	GC-MS	3 Fe ₃ O ₄ @PDA 15 ZIF-7	40	0.71–5.79	>82	At least 10 times	[52]
TpPa-1 COF	Water	HPLC-FLD	5	21	0.24–1.01	73–110	NA	[53]
COF-LZU1@PEI@Fe ₃ O ₄	Water, soil	HPLC-FLD	5	33	0.2–20	NA	At least 6 times	[54]
G/CNF	Water	GC-FID	20	10	4–30	63.0–84.5	Up to 6 times	[55]
Fe ₃ O ₄ /C	Water	HPLC-FLD	50	30	0.2–0.6	76–110	At least 10 times	[56]
Hydrophilic Fe ₃ O ₄ /C	Water	GC-MS	10	30	15–335	NA	NA	[5]
CNF	Water	GC-FID	10	12	8–30	NA	At least 10 times	[7]
G/Fe ₃ O ₄ @PT	Water	GC-FID	20	10	9–20	83–107	At least 17 times	[57]
GO	Water	HPLC-UV	40	16	90–190	76.8–103.2	NA	[6]
GO-Fe ₃ O ₄ @PS	Water	GC-FID	15	10	3–10	69.5–88.7	NA	[58]
Poly(Py-co-Ani)@GO-Fe ₃ O ₄	Water	GC-FID	35		3–10	50.4–78.3	At least 20 times	[59]
CNTs	Water	UHPLC-FLD	5	10	25–73	76.4–106.5	Up to 3 times	[60]
mag-MIP	Water	HPLC-PDA	20	55	1.3–969	46–100	At least 3 times	[61]

Sorbent	Matrix	Analytical Technique	Sorbent Mass (mg)	Time (min)	LODs (ng L ⁻¹)	Extraction Recovery (%)	Reusability	Ref.
mag-MIP	Water	GC-MS	5–20	17	30–750	>76	NA	[62]
RAFT-MIP	Water	GC-MS	10	9	1–100	4.5–97	NA	[8]
PDA	Water	HPLC-FLD	20	5	0.5–1.9	76.4–107	NA	[63]
PPy	Water	GC-MS	20	3	0.38–5.01	27.4–115.7	NA	[64]
PANI/Alginate	Water	HPLC-FLD	400	20	10	86.0–97.8	Up to 6 times	[65]
PoT	Water	GC-FID	60	15	0.3–5.5	NA	Up to 15 times	[46]
IL-MNPs	Water	GC-MS	30	8	40–1111	75–102	Up to 10 times	[66]
MNP@CN/IL	Leachate, sludge	HPLC-DAD	30	35	400–590	89.50–110.2	NA	[67]
MNP-PANI-DICAT	Water, sludge, soil	GC-MS	15	40	0.8–208.6	80.2–111.9	Up to 5 times	[68]
Fe ₃ O ₄ @IL@MO	Water	HPLC-FLD	18	26	0.1–2	NA	NA	[69]
Fe ₃ O ₄ @SiO ₂ @Nap	Water	HPLC-FLD	40	12	0.04–0.12	>90	At least 10 times	[1]
PC	Water, milk	HPLC-FLD	100	10	0.2–0.6	>90	NA	[70]
Fe ₃ O ₄ -DVB-SO ₃ ⁻	Water	GC-MS	50	10	0.6–2.1	79.9–115.3	NA	[71]
MPNP	Water	UHPLC-DAD	200	15	10.83–18.53 nM	75.7–106.4	At least 5 times	[3]
Fe ₃ O ₄ /SiO ₂ /TPA	Water	HPLC-FLD	50	15	0.04–37.5	NA	NA	[72]
C ₁₈	Water	GC-MS	50	6	0.8–36 × 103	35–99	NA	[73]

Sorbent	Matrix	Analytical Technique	Sorbent Mass (mg)	Time (min)	LODs (ng L ⁻¹)	Extraction Recovery (%)	Reusability	Ref.
C ₁₀ –C ₁₈ carboxylates	Water	HPLC-FLD	200	18	0.1–0.25	>90	Up to 5 times	[74]
n-octadecylphosphonic acid	Water	GC-MS	50	1	14.1–70.0 × 103	61.9–119.1	NA	[75]
Nylon 6	Water	HPLC-PDA	40	30	0.05–0.58 × 103	36.2–87.0	NA	[76]
CTAB	Water	UHPLC-FLD	100 Fe ₃ O ₄ /50 CTAB	30	0.4–10.3	59.23–87.95	NA	[77]
Palm fatty acid	Leachate, sludge	HPLC-DAD	15	25	10–50	>81.1	Up to 5 times	[78]
TBCD	Water	HPLC-FLD	80	15	0.03–1.2	>80	NA	[79]
TCT	Water, urine	HPLC-FLD	40	13	0.09–0.15	89–93	At least 30 times	[80]
C ₁₆ -HO	Water	HPLC-UV	30	24	0.14–0.31	88–95	Up to 4 times	[81]

2.3. Solid-Phase Microextraction of PAHs from Environmental Matrices

Solid-phase microextraction is a sample preparation microextraction technique in which the analytes are directly extracted and preconcentrated at the outer coating of a fused-silica fiber [82]. There are two approaches of SPME that can be used to extract analytes, the headspace (HS-SPME), where the fiber is exposed to the gas phase above the sample, and direct immersion (DI-SPME), where the fiber is directly immersed into the sample solution [83]. After the extraction, desorption takes place either thermally in the injection port of a gas chromatograph or by the addition of an organic solvent [82][83].

Until now, there are many different commercial SPME coated fibers, such as polydimethylsiloxane (PDMS), polydimethylsiloxane/divinylbenzene (PDMS/DVB), polyacrylate (PA), carboxen/polydimethylsiloxane (CAR/PDMS) and divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) [83]. However, most of them more or less have some disadvantages, such as low selectivity, ease of fiber breakage, a short lifetime and swelling in organic solvents. In order to overcome them, various new coatings have been prepared and evaluated [84].

Ionic liquids and polymeric ionic liquids (PILs) have been successfully employed as SPME coatings, due to their simplicity of synthesis and their high tuneability, that enable the preparation of highly selective fibers [85]. PILs are polymers prepared from IL monomers. Compared with conventional ILs, PILs exhibit a number of advantages when used as coatings in SPME. Generally, PILs often have solid nature and good thermal and mechanical strength, while extraction selectivity is similar with ILs. As a result, they have proved to be more stable coatings [85][86]. Various PILs including poly(1-vinyl-3-hexadecylimidazolium) bis[(trifluoromethyl)sulfonyl]imide [87], poly(1-4-vinylbenzyl)-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide [88], poly (1-vinyl-3-octylimidazolium) 2-naphthalene-sulfonate [89] and poly(1-(4-vinylbenzyl)-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide [90] have been successfully used as coatings used for the SPME of PAHs. In most cases, the PIL was initially prepared and diluted in a volatile solvent (i.e., acetone or chloroform), and a bare fiber (usually made from stainless steel) was immersed in the solution, followed by slow removal and air drying to remove any excess of solvent that may contribute to high background signals in gas chromatography [87]

[88][90]. However, in situ polymerization of the IL and creation of the SPME coating on the surface of a stainless steel wire has also been reported [89].

Graphene [91][92], graphene oxide [93][94][95], MWCNTs [96][97] and other carbon based materials [98] have also been successfully employed as SPME sorbent coatings, either neat or combined with other materials in order to generate more efficient composites. These materials exhibit high chemical, thermal and mechanical stability, as well as great affinity towards PAHs. Additionally, due to their unique structures and sufficient surface areas, rapid extraction and desorption of the target analytes can be achieved [85]. Various techniques for the preparation of the coated fibers including the chemical bonding [91][93][95], electrophoretic deposition [97] and sol-gel approaches [98] have been also evaluated.

Examples of other materials that have been employed to fabricate SPME coatings for the extraction of PAHs include polyaminithiophenol (PATP) with Au coating [99], poly(3,4-ethylenedioxythiophene)@gold nanoparticles[100], crosslinked methyl methacrylate–polyhedral oligomeric silsesquioxane hybrid polymeric coating [84], nanostructured octadecyl silica [101] and polythiophene/carboxylic acid modified multi-walled carbon nanotube composite [102]. In the latter approach, the researchers developed a novel SPME technology, in which the features of heating the sample, cooling the sorbent and extraction under vacuum condition were combined [102].

PAL (Prep And Load solution) SPME Arrow technique [103] has been also evaluated for the extraction of PAHs from environmental samples. This technique is based on the use of a robust stainless-steel backbone, carrying the connection to the PAL sampler, the coating and an arrow-shaped tip for septum penetration. SPME Arrow combines the benefits of conventional SPME with the larger sorption phase volumes that are used in stir bar sorptive extraction (SBSE). At the same time, the disadvantages of both techniques include the difficulty in automation for SBSE, and the small volume of sorption phase, as well as the low robustness of classical SPME fibers. The results indicated that extraction efficiency significantly benefited from the larger sorption phase volume.

2.4. Stir Bar Sorptive Extraction (SBSE) and Stir Rod Sorptive Extraction (SRSE) of PAHs from Environmental Matrices

Stir bar sorptive extraction was initially introduced by Baltussen et al. in 1999 [104]. In SBSE, a coated stir bar is placed into the vial together with the aqueous sample solution. Extraction of the target analytes takes place under rigorous stirring. When equilibrium is reached, the stir bar is removed and elution of the adsorbed analytes takes place either by the addition of an organic solvent or thermally [18]. SBSE by nature is an equilibrium technique, and for water samples the extraction of the target analytes into the extraction medium is controlled by the partitioning coefficient of the solutes between the coating phase and the aqueous phase [105]. Polydimethylsiloxane (PDMS) is the most used commercially available coating phase for stir bars, however, the synthesis and application of many novel coating materials has been reported.

PDMS coated SBSE bars have been successfully used for the extraction of PAHs resulting in good recoveries and low detection limits [106][107][108][109][110]. Apart from the conventional PDMS stir bars, various novel coating materials have been evaluated for the extraction of PAHs from environmental samples. Typical examples are polymeric materials that have been evaluated, as stir bar coatings are polypyrrole and polyaniline copolymer (PPy-PAN) [111] and (octyl methacrylate- ethylene dimethacrylate) copolymer [112]. Poly (ethylene glycol)-grafted multi-walled carbon nanotubes have been also evaluated for the extraction of PAHs from environmental samples [113]. In this case, the extraction efficiency was favored by the superior characteristics of MWCNTs and the ease in operation of the SBSE technique.

Automated stir plate sorptive extraction (SPSE) coupled with HPLC-FLD has been also evaluated for the extraction of PAHs. For this purpose, automatic extraction, desorption and sample loading, was controlled by a programmable flow injection system, and extraction of PAHs took place on the surface of a PDMS/ β -cyclodextrin/divinylbenzene (PDMS/ β -CD/DVB) coated plates. The researchers investigated three different operation modes, including static, circular flow and continuous flow SPSE. It was found that extraction efficiencies with continuous flow SPSE were slightly better than circular and manual SBSE, probably due to the continuous introduction of new sample solutions [114].

2.5. Liquid-Phase Microextraction of PAHs from Environmental Matrices

Liquid-phase microextraction (LPME) is a miniaturized version of classical LLE, which is characterized by minimum consumption of solvents. LPME can be divided into three main categories, the single-drop microextraction (SDME), the hollow fiber liquid-phase microextraction (HF-LPME) and the dispersive liquid-liquid microextraction (DLLME), with the latter being the most widely used LPME form [115].

HF-LPME is usually based on the use of disposable propylene porous hollow fibers that are filled with a small amount of extracting solvent (acceptor phase). In order to extract the target analytes, the fibers are immersed into the aqueous sample solution (donor phase) [115][116].

On the other hand, in single-drop microextraction (SDME), a drop acts as the acceptor phase for the extraction. SDME can be divided into two main categories i.e., the direct-immersion single-drop microextraction (DI-SDME), in which the drop is directly immersed into the sample, and the headspace single-drop microextraction (HS-SDME), in which the drop is suspending over the sample ^[117].

DLLME is based on the initial fast injection of a suitable mixture of two solvents, an extraction solvent and a dispersive solvent, into an aqueous sample solution with the assistance of a syringe, followed by the formation of a cloudy solution that contains droplets of the extraction solvent dispersed into the sample. After phase separation due to the difference in density of the two phases (e.g., by centrifugation), the extraction phase can be removed and analyzed. In the conventional form of DLLME, the extraction phase is accumulated at the bottom of the extraction container ^{[115][118]}. DLLME is considered to be simple, cheap and environmentally friendly, while it provides high enrichment. The proper selection of the extraction and dispersive solvents are two critical factors for the optimization of DLLME procedure. Therefore, the dispersive solvent has to be immiscible with the extraction solvent and the aqueous sample, in order to generate a cloudy solution that increases the interaction between the two phases, in order to increase the extraction efficiency ^[119].

Finally, Fernandez et al. ^[120] developed a lab on valve DLLME method for the extraction of PAHs, prior to their determination by HPLC-FLD. For this purpose, trichloroethylene was used as the extraction solvent, and acetonitrile was used as the dispersive solvent. The automated instrumentation simplified the extraction process and exhibited satisfactory enhancement factors (86–95). **Table 2** summarizes the applications of DLLME and USAEME in the extraction of PAHs from water samples. Even though DLLME is the predominant form of LPME that has been employed for the extraction of PAHs, the use of SDME ^{[121][122]} and HF-LPME ^{[123][124]} has been also evaluated.

Table 2. Applications of dispersive liquid-liquid microextraction (DLLME) and ultrasound-assisted emulsification microextraction (USAEME) in the extraction of PAHs from water samples.

Matrix	Analytical Technique	Extraction Solvent	Disperser Solvent	Phase Separation	LODs(ng·L ⁻¹)	EF	Extraction Recovery (%)	R _s
Surface water	GC-MS	Tetrachloroethylene	Acetone	Centrifugation	7–30	603–1113	-	^[1]
Rainwater	GC-MS	<i>n</i> -Hexane	Acetone	Addition of demulsification solvent	3.7–39.1	NA	-	^[1]
River water	GC-FID	Toluene	Methanol	Air flotation	14–41 × 10 ³	NA	-	^[1]
Sea water	GC-MS	Tetrachloroethylene	Diethyl Ether	Centrifugation	1–10	722–8133	59.2–90.5	^[1]
Sediment	HPLC-FLD	Dichloromethane	Acetonitrile	Centrifugation	2.3–6.8 ng g ⁻¹	NA	>94.0	^[1]
Tap, sea and spring water	GC-FID	Toluene	-	Centrifugation	20–50	1776–2714	99–103	^[1]
Tap, well, surface water etc.	GC-MS	Chloroform	-	Centrifugation	1–36	NA	-	^[1]
Tap, spring, surface water etc.	GC-MS	Iso-octane	-	Addition of NaCl	0.001–0.009	Up to 100000	-	^[1]

Matrix	Analytical Technique	Extraction Solvent	Disperser Solvent	Phase Separation	LODs($\text{ng}\cdot\text{L}^{-1}$)	EF	Extraction Recovery (%)	R _d
Tap, rain and wastewater	HPLC-FLD	Cyclohexane	-	Centrifugation	0.6–62.5	90–247	95–100	[137]
Well, river, lake water etc.	HPLC-FLD	TBAB/2-decanoic acid DES	-	Centrifugation/Solidification	0.7–6.6	163–198	>80.0	[138]
Tap, bottle, fountain water etc.	HPLC-FLD	[C ₈ MiM][PF ₆]	Acetone	Centrifugation	0.03–2	301–346	-	[139]
Tap, well, surface water etc.	HPLC-UV	[BBIM][Tf ₂ N]	Acetone	Centrifugation	2	2768–5409	-	[140]
Tap, rain and surface water	HPLC-FLD	Trichloroethylene	Acetonitrile	-	20–600	86–95	-	[141]

2.6. Fabric Phase Sorptive Extraction of PAHs from Environmental Matrices

Fabric phase sorptive extraction (FPSE) is a novel sample preparation technique proposed by Kabir and Furton in 2014. FPSE utilizes a natural or synthetic fabric substrate, which is chemically coated in the form of ultra-thin coating with sol-gel organic-inorganic hybrid sorbent as the extraction medium. For the FPSE procedure, the sol-gel sorbent coated FPSE media is immersed into a mixture of appropriate solvents, to remove any undesirable impurities from the material, and rinsed with deionized water to remove residual organic solvents. Subsequently, the FPSE media is submerged into the sample solution placed in a glass vial. A magnet is added into the sample solution, and the sample is magnetically stirred for certain time span for the adsorption of the target analytes. Finally, the FPSE media is removed, and elution of the analytes takes place into another vial containing appropriate elution solvent. Analysis of the eluent can take place after centrifugation and or/filtration [137][138][139][140].

FPSE provides high primary contact surface area, thus, rapid and efficient analyte extraction can be easily achieved. Moreover, FPSE is also characterized by low organic solvent consumption, ease in operation, reusability and good selectivity towards the target analytes, which is based directly on the different nature of the fabric substrates and the sol-gel coating. Until today, the use of various fabric substrates, including cellulose, fiber glass and polyester, as well as several sol-gel coatings, including polyethylene glycol, polytetrahydrofuran and polydimethyldiphenylsiloxane have been evaluated as adsorbents for a wide variety of analytes [17][138][141][142].

A trace-level determination of selected PAHs in environmental water samples using FPSE prior to their determination by HPLC-FLD has been reported. For this purpose, a non-polar sol-gel C₁₈ coated FPSE media was prepared and conditioned in a mixture of methanol and acetonitrile for 5 min, and then rinsed with deionized water. The extraction of PAHs took place in a glass vial containing 10 mL of the aqueous sample solution, in which the sol-gel C₁₈ coated FPSE media was directly immersed. After 30 min under constant stirring at 1000 rpm, the FPSE media was removed and PAHs were eluted with acetonitrile under ultrasonic radiation for 5 min. The developed FPSE-HPLC-FLD protocol was proved to simple, efficient, fast, sensitive, green, economical and reliable for trace level determination of environmentally important PAHs [143].

Recently, fabric-phase sorptive extraction was coupled with ion mobility spectrometry (IMS) for on-site rapid detection of PAHs in aquatic environment [144]. Ion mobility spectrometry is a rapid and sensitive gas-phase analytical technique, which can be employed for the in the field testing of various chemical compounds, due to its fast analysis and compact size [145]. For the fabrication of the FPSE media, PDMS was coated on the glass fiber cloth through a sol-gel reaction. Glass wool was chosen based on the inlet temperature of IMS, since the thermal desorption of the PAHs was performed

after inserting the FPSE media the inlet port of the IMS instrument directly after analyte extraction. Under optimum conditions, low LODs and satisfactory recoveries were obtaining, thus enabling the on-site monitoring water quality.

2.7. Other Extraction Techniques for the Determination of PAHs in Environmental Matrices

Yang et al. [146] synthesized MOF-5 from terephthalic acid and zinc acetate, and evaluated it as a sorbent for the SPE of PAHs from environmental samples. Therefore, 300 mg of MOF-5 was packed into SPE cartridges. Although MOF-5 is known to be unstable when exposed to water, the researchers reported that the derived material of MOF-5 still demonstrated good extraction characteristics. This was attributed to the π - π conjugate effect between the terephthalic acid molecules of the framework and the PAHs and the π -complexation between PAHs and the central zinc ions. The analytes were further separated and detected in a HPLC-UV system. The method exhibited satisfactory extraction ability and low LODs (0.4–4.0 ng L⁻¹), however, no sorbent reusability was reported.

Hu et al. [147] evaluated two zeolitic imidazolate frameworks for the SPE disk extraction of PAHs in aid of filter membrane of PAHs from environmental water samples. The studied ZIFs were both composed of the same metal ion (zinc) and organic linker (benzimidazole), thus differing in spatial structures with one in cube (ZIF-7), while the other was in rhombic dodecahedron (ZIF-11). ZIF-11 with markedly better extraction efficiencies due to its unique spatial structure with large cages and its molecular composition that was composed of abundant benzyl groups and metal sites on the surface.

ZIF-8 [148] has been also evaluated for the porous membrane-protected micro-solid-phase extraction (μ -SPE) of PAHs. For this purpose, the sorbent was packed in a sealed porous polypropylene membrane envelope. The novel extraction devices exhibited good extraction characteristics and decreased consumption of the organic solvent.

A molecularly imprinted polymer has been also applied for the SPE of 16 PAHs from seawater, prior to their determination by GC-MS [149]. MIPs were prepared by using the 16 PAHs mixture through non-covalent polymerization as a template based on sol-gel surface imprinting. The developed sorbent exhibited good affinity towards the target analytes. Other examples of novel SPE sorbents that have been implemented for the extraction and preconcentration of PAHs from environmental samples include a cyclodextrin-silica microporous composite [150][151], aminopropyl imidazole-modified silica gel [152], tetraazacalix[2]arene[2]triazine [153], titanium oxide nanotubes [154] and a titanate nanotube array modified by cetyltrimethylammonium bromide [155].

Krupadam et al. [156] prepared MIP microspheres in a continuous segmented flow microfluidic reactor, and used them as packing material for microtraps for the selective extraction of benzo[a]pyrene from environmental water samples. For this purpose, the pumping of monodisperse droplets of acetonitrile containing methacrylic acid as the functional monomer took place, benzo[a]pyrene was used as a template, and ethylene glycol dimethacrylate as cross-linking monomer into the microchannels of the microfluidic reactor. The obtained microspheres exhibited high extraction efficiency and selectivity towards benzo[a]pyrene. In comparison with commercially available activated carbon, the novel microspheres showed 300% higher adsorption capacity.

A portable system for the in situ extraction of PAHs was proposed by Foan et al. [157]. The researchers designed a microfluidic device for the fast extraction of PAHs using low volume samples. The work was performed on a lab-on-a-chip, made of a silicon/glass microfluidic device functionalized with PDMS. Among the benefits of the novel technique was the low organic solvent consumption and the portability. A comparison of the novel device with SBSE showed approximately 50 times less sample preparation time for the high molecular weight PAHs. However, for the lightest PAHs, the performance of the microchip required improvement.

Flow injection solid-phase extraction (FI-SPE) of PAHs from environmental samples with novel extraction sorbents has been also proposed by the research groups of Wu [158] and Zhou [159]. The first group used a multi-walled carbon nanotubes (MWCNTs)-packed micro-column for the extraction of PAHs, prior to their determination by GC-MS, while the second group prepared a copper(II) isonicotinate coordination polymer packed in a pre-column for the extraction of PAHs, prior to their determination by HPLC-DAD. Both methods exhibited good extraction characteristics. In the case of GC-MS detection, after the FI-SPE process, the eluates were collected, and manual injection was performed, while for the HPLC-DAD analysis elution of the adsorbed analytes was also performed on-line in the backflush mode by the HPLC mobile phase directly into the chromatographic column, thus minimizing the required analysis steps.

In-syringe solid-phase extraction of PAHs has been also proposed for the on-site sampling of water samples. In-syringe SPE is characterized by portability, simplicity in use, low cost and short extraction time. Zhang et al. [160] evaluated the application of MIL-101 as a novel sorbent, due to its good thermal and mechanical stability, as well as its resistance towards organic solvent and waters. The proposed technique exhibited excellent adsorption performance, since the analytes could be completely adsorbed during one adsorption cycle, thus reducing the extraction time. Moreover, it was found that the adsorbed analytes remained stable on the in-syringe device for at least 7 days.

References

1. Cai, Y.; Yan, Z.H.; Wang, N.Y.; Cai, Q.Y.; Yao, S.Z. Preparation of naphthyl functionalized magnetic nanoparticles for extraction of polycyclic aromatic hydrocarbons from river waters. *RSC Adv.* 2015, 5, 56189–56197.
2. Pérez, R.A.; Alberro, B.; Tadeo, J.L.; Fraile, M.V.; Sánchez-Brunete, C. Determination of PAHs in soil leachates by magnetic solid-phase extraction using nanoparticles and gas chromatography-tandem mass spectrometry. *Anal. Methods* 2014, 6, 1941–1950.
3. Zhang, X.; Xie, S.; Paa, M.C.; Zheng, B.; Yuan, H.; Xiao, D.; Choi, M.M.F. Ultrahigh performance liquid chromatographic analysis and magnetic preconcentration of polycyclic aromatic hydrocarbons by Fe₃O₄-doped polymeric nanoparticles. *J. Chromatogr. A* 2012, 1247, 1–9.
4. Boffetta, P.; Jourenkova, N.; Gustavsson, P. Cancer risk from occupational and environmental exposure to polycyclic aromatic hydrocarbons. *Cancer Causes Control* 1997, 8, 444–472.
5. Bai, L.; Mei, B.; Guo, Q.Z.; Shi, Z.G.; Feng, Y.Q. Magnetic solid-phase extraction of hydrophobic analytes in environmental samples by a surface hydrophilic carbon-ferromagnetic nanocomposite. *J. Chromatogr. A* 2010, 1217, 7331–7336.
6. Han, Q.; Wang, Z.; Xia, J.; Chen, S.; Zhang, X.; Ding, M. Facile and tunable fabrication of Fe₃O₄/graphene oxide nanocomposites and their application in the magnetic solid-phase extraction of polycyclic aromatic hydrocarbons from environmental water samples. *Talanta* 2012, 101, 388–395.
7. Sarafraz-Yazdi, A.; Rokhian, T.; Amiri, A.; Ghaemi, F. Carbon nanofibers decorated with magnetic nanoparticles as a new sorbent for the magnetic solid phase extraction of selected polycyclic aromatic hydrocarbons from water samples. *New J. Chem.* 2015, 39, 5621–5627.
8. Azizi, A.; Shahhoseini, F.; Bottaro, C.S. Magnetic molecularly imprinted polymers prepared by reversible addition fragmentation chain transfer polymerization for dispersive solid phase extraction of polycyclic aromatic hydrocarbons in water. *J. Chromatogr. A* 2020, 1610, 460534.
9. Manousi, N.; Raber, G.; Papadoyannis, I. Recent Advances in Microextraction Techniques of Antipsychotics in Biological Fluids Prior to Liquid Chromatography Analysis. *Separations* 2017, 4, 18.
10. Filippou, O.; Bitas, D.; Samanidou, V. Green approaches in sample preparation of bioanalytical samples prior to chromatographic analysis. *J. Chromatogr. B Anal. Technol. Biomed. Life Sci.* 2017, 1043, 44–62.
11. Arthur, C.L.; Pawliszyn, J. Solid Phase Microextraction with Thermal Desorption Using Fused Silica Optical Fibers. *Anal. Chem.* 1990, 62, 2145–2148.
12. Liu, H.; Dasgupta, P.K. Analytical chemistry in a drop. solvent extraction in a microdrop. *Anal. Chem.* 1996, 68, 1817–1821.
13. Armenta, S.; Garrigues, S.; de la Guardia, M. The role of green extraction techniques in Green Analytical Chemistry. *TrAC - Trends Anal. Chem.* 2015, 71, 2–8.
14. Manousi, N.; Gomez-Gomez, B.; Madrid, Y.; Deliyanni, E.A.; Zachariadis, G.A. Determination of rare earth elements by inductively coupled plasma-mass spectrometry after dispersive solid phase extraction with novel oxidized graphene oxide and optimization with response surface methodology and central composite design. *Microchem. J.* 2020, 152.
15. Filippou, O.; Deliyanni, E.A.; Samanidou, V.F. Fabrication and evaluation of magnetic activated carbon as adsorbent for ultrasonic assisted magnetic solid phase dispersive extraction of bisphenol A from milk prior to high performance liquid chromatographic analysis with ultraviolet detection. *J. Chromatogr. A* 2017, 1479, 20–31.
16. Chen, Z.; Yu, C.; Xi, J.; Tang, S.; Bao, T.; Zhang, J. A hybrid material prepared by controlled growth of a covalent organic framework on amino-modified MIL-68 for pipette tip solid-phase extraction of sulfonamides prior to their determination by HPLC. *Microchim. Acta* 2019, 186, 393.
17. Karageorgou, E.; Manousi, N.; Samanidou, V.; Kabir, A.; Furton, K.G. Fabric phase sorptive extraction for the fast isolation of sulfonamides residues from raw milk followed by high performance liquid chromatography with ultraviolet detection. *Food Chem.* 2016, 196, 428–436.
18. Nazyropoulou, C.; Samanidou, V. Stir bar sorptive extraction applied to the analysis of biological fluids. *Bioanalysis* 2015, 7, 2241–2250.
19. Li, N.; Jiang, H.L.; Wang, X.; Wang, X.; Xu, G.; Zhang, B.; Wang, L.; Zhao, R.S.; Lin, J.M. Recent advances in graphene-based magnetic composites for magnetic solid-phase extraction. *TrAC - Trends Anal. Chem.* 2018, 102, 60–74.
20. Riahi-Zanjani, B.; Balali-Mood, M.; Asoodeh, A.; Es'haghi, Z.; Ghorani-Azam, A. Developing a new sensitive solid-phase microextraction fiber based on carbon nanotubes for preconcentration of morphine. *Appl. Nanosci.* 2018, 8, 2047–2056.
21. Manousi, N.; Zachariadis, G.A.; Deliyanni, E.A.; Samanidou, V.F. Applications of metal-organic frameworks in food sample preparation. *Molecules* 2018, 23, E2896.

22. Islas, G.; Ibarra, I.S.; Hernandez, P.; Miranda, J.M.; Cepeda, A. Dispersive Solid Phase Extraction for the Analysis of Veterinary Drugs Applied to Food Samples: A Review. *Int. J. Anal. Chem.* 2017, 2017, 8215271.
23. Han, L.; Sapozhnikova, Y.; Lehotay, S.J. Streamlined sample cleanup using combined dispersive solid-phase extraction and in-vial filtration for analysis of pesticides and environmental pollutants in shrimp. *Anal. Chim. Acta* 2014, 827, 40–46.
24. Anastassiades, M.; Lehotay, S.J.; Stajnbaher, D.; Schenck, F. Fast and Easy Multiresidue Method Employing Acetonitrile. *J. AOAC Int.* 2003, 86, 412–431.
25. Cvetkovic, J.S.; Mitic, V.D.; Stankov Jovanovic, V.P.; Dimitrijevic, M.V.; Petrovic, G.M.; Nikolic-Mandic, S.D.; Stojanovic, G.S. Optimization of the QuEChERS extraction procedure for the determination of polycyclic aromatic hydrocarbons in soil by gas chromatography-mass spectrometry. *Anal. Methods* 2016, 8, 1711–1720.
26. Yaghi, O.M.; Li, H. Hydrothermal Synthesis of a Metal-Organic Framework Containing Large Rectangular Channels. *J. Am. Chem. Soc.* 1995, 117, 10401–10402.
27. Farha, O.K.; Eryazici, I.; Jeong, N.C.; Hauser, B.G.; Wilmer, C.E.; Sarjeant, A.A.; Snurr, R.Q.; Nguyen, S.T.; Yazaydin, A.Ö.; Hupp, J.T. Metal-organic framework materials with ultrahigh surface areas: Is the sky the limit? *J. Am. Chem. Soc.* 2012, 134, 15016–15021.
28. Manousi, N.; Giannakoudakis, D.A.; Rosenberg, E.; Zachariadis, G.A. Extraction of metal ions with metal-organic frameworks. *Molecules* 2019, 24, E4605.
29. Vardali, S.C.; Manousi, N.; Barczak, M.; Giannakoudakis, D.A. Novel approaches utilizing metal-organic framework composites for the extraction of organic compounds and metal traces from fish and seafood. *Molecules* 2020, 25, E513.
30. Giliopoulos, D.; Zamboulis, A.; Giannakoudakis, D.; Bikiaris, D.; Triantafyllidis, K. Polymer/metal organic framework (MOF) nanocomposites for biomedical applications. *Molecules* 2020, 25, 185.
31. Giannakoudakis, D.A.; Hu, Y.; Florent, M.; Badosz, T.J. Smart textiles of MOF/g-C₃N₄ nanospheres for the rapid detection/detoxification of chemical warfare agents. *Nanoscale Horizons* 2017, 2, 356–364.
32. Li, H.; Li, L.; Lin, R.-B.; Zhou, W.; Zhang, Z.; Xiang, S.; Chen, B. Porous metal-organic frameworks for gas storage and separation: Status and challenges. *EnergyChem* 2019, 1, 100006.
33. Yang, D.; Gates, B.C. Catalysis by Metal Organic Frameworks: Perspective and Suggestions for Future Research. *ACS Catal.* 2019, 9, 1779–1798.
34. Achmann, S.; Hagen, G.; Kita, J.; Malkowsky, I.M.; Kiener, C.; Moos, R. Metal-Organic frameworks for sensing applications in the gas phase. *Sensors* 2009, 9, 1574–1589.
35. Rojas, S.; Baati, T.; Njim, L.; Manchego, L.; Neffati, F.; Abdeljelil, N.; Saguem, S.; Serre, C.; Najjar, M.F.; Zakhama, A.; et al. Metal-Organic Frameworks as Efficient Oral Detoxifying Agents. *J. Am. Chem. Soc.* 2018, 140, 9581–9586.
36. Wang, L.; Zheng, M.; Xie, Z. Nanoscale metal-organic frameworks for drug delivery: A conventional platform with new promise. *J. Mater. Chem. B* 2018, 6, 707–717.
37. Chen, B.; Liang, C.; Yang, J.; Contreras, D.S.; Clancy, Y.L.; Lobkovsky, E.B.; Yaghi, O.M.; Dai, S. A microporous metal-organic framework for gas-chromatographic separation of alkanes. *Angew. Chemie - Int. Ed.* 2006, 9, 1418–1421.
38. Gu, Z.Y.; Jiang, J.Q.; Yan, X.P. Fabrication of isorecticular metal-organic framework coated capillary columns for high-resolution gas chromatographic separation of persistent organic pollutants. *Anal. Chem.* 2011, 83, 5093–5100.
39. Yang, C.X.; Yan, X.P. Metal-organic framework MIL-101(Cr) for high-performance liquid chromatographic separation of substituted aromatics. *Anal. Chem.* 2011, 83, 7144–7150.
40. Yang, C.X.; Chen, Y.J.; Wang, H.F.; Yan, X.P. High-performance separation of fullerenes on metal-organic framework MIL-101(Cr). *Chem. - A Eur. J.* 2011, 42, 11734–11737.
41. Mateos, R.; Vera-López, S.; Saz, M.; Díez-Pascual, A.M.; San Andrés, M.P. Graphene/sepiolite mixtures as dispersive solid-phase extraction sorbents for the analysis of polycyclic aromatic hydrocarbons in wastewater using surfactant aqueous solutions for desorption. *J. Chromatogr. A* 2019, 1596, 30–40.
42. Yang, X.P.; Luo, N.; Zong, Y.Y.; Jia, Z.H.; Liao, X.J. Quantum dots extraction coupled with high-performance liquid chromatography for the determination of polycyclic aromatic hydrocarbons in water. *Appl. Ecol. Environ. Res.* 2017, 15, 171–186.
43. Hemmati, M.; Rajabi, M.; Asghari, A. Magnetic nanoparticle based solid-phase extraction of heavy metal ions: A review on recent advances. *Microchim. Acta* 2018, 185, 160.
44. Giakissikli, G.; Anthemidis, A.N. Magnetic materials as sorbents for metal/metalloid preconcentration and/or separation. A review. *Anal. Chim. Acta* 2013, 789, 1–16.
45. Manousi, N.; Rosenberg, E.; Deliyanni, E.; Zachariadis, G.A.; Samanidou, V. Magnetic Solid-Phase Extraction of Organic Compounds Based on Graphene Oxide Nanocomposites. *Molecules* 2020, 25, 1148.

46. Hesampour, M.; Ali Taher, M.; Behzadi, M. Synthesis, characterization and application of a (:O-toluidine) nanocomposite for magnetic solid-phase extraction of polycyclic aromatic hydrocarbons. *New J. Chem.* 2017, 41, 12910–12919.
47. Rocío-Bautista, P.; Pino, V.; Ayala, J.H.; Pasán, J.; Ruiz-Pérez, C.; Afonso, A.M. A magnetic-based dispersive micro-solid-phase extraction method using the metal-organic framework HKUST-1 and ultra-high-performance liquid chromatography with fluorescence detection for determining polycyclic aromatic hydrocarbons in waters and fruit tea. *J. Chromatogr. A* 2016, 1426, 42–50.
48. Huo, S.H.; Yan, X.P. Facile magnetization of metal-organic framework MIL-101 for magnetic solid-phase extraction of polycyclic aromatic hydrocarbons in environmental water samples. *Analyst* 2012, 137, 3445–3451.
49. Zhou, Q.; Lei, M.; Wu, Y.; Yuan, Y. Magnetic solid phase extraction of typical polycyclic aromatic hydrocarbons from environmental water samples with metal organic framework MIL-101 (Cr) modified zero valent iron nano-particles. *J. Chromatogr. A* 2017, 1487, 22–29.
50. Du, F.; Qin, Q.; Deng, J.; Ruan, G.; Yang, X.; Li, L.; Li, J. Magnetic metal-organic framework MIL-100(Fe) microspheres for the magnetic solid-phase extraction of trace polycyclic aromatic hydrocarbons from water samples. *J. Sep. Sci.* 2016, 12, 2356–2364.
51. Huo, S.H.; An, H.Y.; Yu, J.; Mao, X.F.; Zhang, Z.; Bai, L.; Huang, Y.F.; Zhou, P.X. Pyrolytic in situ magnetization of metal-organic framework MIL-100 for magnetic solid-phase extraction. *J. Chromatogr. A* 2017, 1517, 18–25.
52. Zhang, S.; Yao, W.; Ying, J.; Zhao, H. Polydopamine-reinforced magnetization of zeolitic imidazolate framework ZIF-7 for magnetic solid-phase extraction of polycyclic aromatic hydrocarbons from the air-water environment. *J. Chromatogr. A* 2016, 1452, 18–26.
53. He, S.; Zeng, T.; Wang, S.; Niu, H.; Cai, Y. Facile synthesis of magnetic covalent organic framework with three-dimensional bouquet-like structure for enhanced extraction of organic targets. *ACS Appl. Mater. Interfaces* 2017, 9, 2959–2965.
54. Wang, R.; Chen, Z. A covalent organic framework-based magnetic sorbent for solid phase extraction of polycyclic aromatic hydrocarbons, and its hyphenation to HPLC for quantitation. *Microchim. Acta* 2017, 184, 3867–3874.
55. Rezvani-Eivari, M.; Amiri, A.; Baghayeri, M.; Ghaemi, F. Magnetized graphene layers synthesized on the carbon nanofibers as novel adsorbent for the extraction of polycyclic aromatic hydrocarbons from environmental water samples. *J. Chromatogr. A* 2016, 1465, 1–8.
56. Zhang, S.; Niu, H.; Hu, Z.; Cai, Y.; Shi, Y. Preparation of carbon coated Fe₃O₄ nanoparticles and their application for solid-phase extraction of polycyclic aromatic hydrocarbons from environmental water samples. *J. Chromatogr. A* 2010, 1217, 4757–4764.
57. Mehdinia, A.; Khodaei, N.; Jabbari, A. Fabrication of graphene/Fe₃O₄@polythiophene nanocomposite and its application in the magnetic solid-phase extraction of polycyclic aromatic hydrocarbons from environmental water samples. *Anal. Chim. Acta* 2015, 868, 1–9.
58. Amiri, A.; Baghayeri, M.; Sedighi, M. Magnetic solid-phase extraction of polycyclic aromatic hydrocarbons using a graphene oxide/Fe₃O₄@polystyrene nanocomposite. *Microchim. Acta* 2018, 185, 393.
59. Amiri, A.; Baghayeri, M.; Hamidi, E. Poly(pyrrole-*co*-aniline)@graphene oxide/Fe₃O₄ sorbent for the extraction and preconcentration of polycyclic aromatic hydrocarbons from water samples. *New J. Chem.* 2018, 42, 16744–16751.
60. Corps Ricardo, A.I.; Guzmán Bernardo, F.J.; Zougagh, M.; Rodríguez Martín-Doimeadios, R.C.; Ríos, Á. Magnetic nanoparticles—carbon nanotubes hybrid composites for selective solid-phase extraction of polycyclic aromatic hydrocarbons and determination by ultra-high performance liquid chromatography. *Anal. Bioanal. Chem.* 2017, 409, 5125–5132.
61. Villar-Navarro, M.; Martín-Valero, M.J.; Fernández-Torres, R.M.; Callejón-Mochón, M.; Bello-López, M.Á. Easy, fast and environmental friendly method for the simultaneous extraction of the 16 EPA PAHs using magnetic molecular imprinted polymers (mag-MIPs). *J. Chromatogr. B Anal. Technol. Biomed. Life Sci.* 2017, 1044–1045, 63–69.
62. Benedetti, B.; Di Carro, M.; Magi, E. Multivariate optimization of an extraction procedure based on magnetic molecular imprinted polymer for the determination of polycyclic aromatic hydrocarbons in sea water. *Microchem. J.* 2019, 145, 119–1206.
63. Wang, Y.; Wang, S.; Niu, H.; Ma, Y.; Zeng, T.; Cai, Y.; Meng, Z. Preparation of polydopamine coated Fe₃O₄ nanoparticles and their application for enrichment of polycyclic aromatic hydrocarbons from environmental water samples. *J. Chromatogr. A* 2013, 1283, 20–26.
64. Xu, S.N.; Zhao, Q.; He, H.B.; Yuan, B.F.; Feng, Y.Q.; Yu, Q.W. Rapid determination of polycyclic aromatic hydrocarbons in environmental water based on magnetite nanoparticles/polypyrrole magnetic solid-phase extraction. *Anal. Methods* 2014, 6, 7046–7053.
65. Nurker, P.; Kanatharana, P.; Bunkoed, O. Polyaniline-coated magnetite nanoparticles incorporated in alginate beads for the extraction and enrichment of polycyclic aromatic hydrocarbons in water samples. *Int. J. Environ. Anal. Chem.* 2017, 2, 145–158.

66. Galán-Cano, F.; Del Carmen Alcudía-León, M.; Lucena, R.; Cárdenas, S.; Valcárcel, M. Ionic liquid coated magnetic nanoparticles for the gas chromatography/mass spectrometric determination of polycyclic aromatic hydrocarbons in water samples. *J. Chromatogr. A* 2013, 1300, 134–140.
67. Bakhshaei, S.; Kamboh, M.A.; Nodeh, H.R.; Md Zain, S.; Mahmud Rozi, S.K.; Mohamad, S.; Mohammed Mohialdeen, I.A. Magnetic solid phase extraction of polycyclic aromatic hydrocarbons and chlorophenols based on cyano-ionic liquid functionalized magnetic nanoparticles and their determination by HPLC-DAD. *RSC Adv.* 2016, 6, 77047–77058.
68. Shahrman, M.S.; Ramachandran, M.R.; Zain, N.N.M.; Mohamad, S.; Manan, N.S.A.; Yaman, S.M. Polyaniline-dicationic ionic liquid coated with magnetic nanoparticles composite for magnetic solid phase extraction of polycyclic aromatic hydrocarbons in environmental samples. *Talanta* 2018, 178, 211–221.
69. Liu, X.; Lu, X.; Huang, Y.; Liu, C.; Zhao, S. Fe₃O₄@ionic orange nanoparticles as a novel nano-adsorbent for magnetic solid-phase extraction of polycyclic aromatic hydrocarbons in environmental water samples. *Talanta* 2014, 119, 341–347.
70. Zhang, S.; Niu, H.; Zhang, Y.; Liu, J.; Shi, Y.; Zhang, X.; Cai, Y. Biocompatible phosphatidylcholine bilayer coated on magnetic nanoparticles and their application in the extraction of several polycyclic aromatic hydrocarbons from environmental water and milk samples. *J. Chromatogr. A* 2012, 1238, 38–45.
71. Xue, S.W.; Tang, M.Q.; Xu, L.; Shi, Z. Magnetic nanoparticles with hydrophobicity and hydrophilicity for solid-phase extraction of polycyclic aromatic hydrocarbons from environmental water samples. *J. Chromatogr. A* 2015, 1411, 9–16.
72. Long, Y.; Chen, Y.; Yang, F.; Chen, C.; Pan, D.; Cai, Q.; Yao, S. Triphenylamine-functionalized magnetic microparticles as a new adsorbent coupled with high performance liquid chromatography for the analysis of trace polycyclic aromatic hydrocarbons in aqueous samples. *Analyst* 2012, 137, 2716–2722.
73. Liu, Y.; Li, H.; Lin, J.M. Magnetic solid-phase extraction based on octadecyl functionalization of monodisperse magnetic ferrite microspheres for the determination of polycyclic aromatic hydrocarbons in aqueous samples coupled with gas chromatography-mass spectrometry. *Talanta* 2009, 77, 1037–1042.
74. Ballesteros-Gómez, A.; Rubio, S. Hemimicelles of alkyl carboxylates chemisorbed onto magnetic nanoparticles: Study and application to the extraction of carcinogenic polycyclic aromatic hydrocarbons in environmental water samples. *Anal. Chem.* 2009, 81, 9012–9020.
75. Ding, J.; Gao, Q.; Luo, D.; Shi, Z.G.; Feng, Y.Q. n-Octadecylphosphonic acid grafted mesoporous magnetic nanoparticles: Preparation, characterization, and application in magnetic solid-phase extraction. *J. Chromatogr. A* 2010, 1217, 7351–7358.
76. Reyes-Gallardo, E.M.; Lucena, R.; Cárdenas, S.; Valcárcel, M. Magnetic nanoparticles-nylon 6 composite for the dispersive micro solid phase extraction of selected polycyclic aromatic hydrocarbons from water samples. *J. Chromatogr. A* 2014, 1345, 43–49.
77. Wang, H.; Zhao, X.; Meng, W.; Wang, P.; Wu, F.; Tang, Z.; Han, X.; Giesy, J.P. Cetyltrimethylammonium Bromide-Coated Fe₃O₄ Magnetic Nanoparticles for Analysis of 15 Trace Polycyclic Aromatic Hydrocarbons in Aquatic Environments by Ultraperformance, Liquid Chromatography With Fluorescence Detection. *Anal. Chem.* 2015, 87, 7667–7675.
78. Rozi, S.K.M.; Nodeh, H.R.; Kamboh, M.A.; Manan, N.S.A.; Mohamad, S. Novel palm fatty acid functionalized magnetite nanoparticles for magnetic solid-phase extraction of trace polycyclic aromatic hydrocarbons from environmental samples. *J. Oleo Sci.* 2017, 66, 771–784.
79. Zou, Y.; Chen, Y.; Yan, Z.; Chen, C.; Wang, J.; Yao, S. Magnetic solid-phase extraction based on tetrabenzyl modified Fe₃O₄ nanoparticles for the analysis of trace polycyclic aromatic hydrocarbons in environmental water samples. *Analyst* 2013, 138, 5904–5912.
80. Zhang, W.; Zhang, Y.; Jiang, Q.; Zhao, W.; Yu, A.; Chang, H.; Lu, X.; Xie, F.; Ye, B.; Zhang, S. Tetraazacalixarene-coated Fe₃O₄/SiO₂ Magnetic Nanoparticles for Simultaneous Dispersive Solid Phase Extraction and Determination of Trace Multitarget Analytes. *Anal. Chem.* 2016, 88, 10523–10532.
81. Al-rashdi, A.A. Double-functionalized magnetic nanoparticles for preconcentration and determination of polycyclic aromatic hydrocarbons in water samples. *Anal. Chem. Res.* 2016, 10, 9–17.
82. Kataoka, H.; Lord, H.L.; Pawliszyn, J. Applications of solid-phase microextraction in food analysis. *J. Chromatogr. A* 2000, 880, 35–62.
83. Aulakh, J.S.; Malik, A.K.; Kaur, V.; Schmitt-Kopplin, P. A review on solid phase micro extraction - High performance liquid chromatography (SPME-HPLC) analysis of pesticides. *Crit. Rev. Anal. Chem.* 2005, 35, 71–85.
84. Chen, C.; Liang, X.; Wang, J.; Yang, S.; Yan, Z.; Cai, Q.; Yao, S. Development of a highly robust solid phase microextraction fiber based on crosslinked methyl methacrylate-polyhedral oligomeric silsesquioxane hybrid polymeric coating. *Anal. Chim. Acta* 2013, 792, 45–51.
85. Rocío-Bautista, P.; Pacheco-Fernández, I.; Pasán, J.; Pino, V. Are metal-organic frameworks able to provide a new generation of solid-phase microextraction coatings? – A review. *Anal. Chim. Acta* 2016, 939, 26–41.

86. Yu, H.; Ho, T.D.; Anderson, J.L. Ionic liquid and polymeric ionic liquid coatings in solid-phase microextraction. *TrAC - Trends Anal. Chem.* 2013, 45, 219–232.
87. López-Darias, J.; Pino, V.; Anderson, J.L.; Graham, C.M.; Afonso, A.M. Determination of water pollutants by direct-immersion solid-phase microextraction using polymeric ionic liquid coatings. *J. Chromatogr. A* 2010, 1217, 1236–1243.
88. Meng, Y.; Anderson, J.L. Tuning the selectivity of polymeric ionic liquid sorbent coatings for the extraction of polycyclic aromatic hydrocarbons using solid-phase microextraction. *J. Chromatogr. A* 2010, 1217, 6143–6152.
89. Feng, J.; Sun, M.; Li, J.; Liu, X.; Jiang, S. A novel aromatically functional polymeric ionic liquid as sorbent material for solid-phase microextraction. *J. Chromatogr. A* 2012, 1227, 54–59.
90. López-Darias, J.; Pino, V.; Meng, Y.; Anderson, J.L.; Afonso, A.M. Utilization of a benzyl functionalized polymeric ionic liquid for the sensitive determination of polycyclic aromatic hydrocarbons; parabens and alkylphenols in waters using solid-phase microextraction coupled to gas chromatography-flame ionization detection. *J. Chromatogr. A* 2010, 1217, 7189–7197.
91. Zhang, S.; Du, Z.; Li, G. Layer-by-layer fabrication of chemical-bonded graphene coating for solid-phase microextraction. *Anal. Chem.* 2011, 83, 7531–7541.
92. Wang, F.; Zheng, Y.; Qiu, J.; Liu, S.; Tong, Y.; Zhu, F.; Ouyang, G. Graphene-based metal and nitrogen-doped carbon composites as adsorbents for highly sensitive solid phase microextraction of polycyclic aromatic hydrocarbons. *Nanoscale* 2018, 10, 10073–10078.
93. Xu, L.; Feng, J.; Liang, X.; Li, J.; Jiang, S. C18 functionalized graphene oxide as a novel coating for solid-phase microextraction. *J. Sep. Sci.* 2012, 35, 1531–1537.
94. Sun, M.; Feng, J.; Bu, Y.; Duan, H.; Wang, X.; Luo, C. Development of a solid-phase microextraction fiber by the chemical binding of graphene oxide on a silver-coated stainless-steel wire with an ionic liquid as the crosslinking agent. *J. Sep. Sci.* 2014, 37, 3691–3698.
95. Xu, L.; Feng, J.; Li, J.; Liu, X.; Jiang, S. Graphene oxide bonded fused-silica fiber for solid-phase microextraction-gas chromatography of polycyclic aromatic hydrocarbons in water. *J. Sep. Sci.* 2012, 35, 93–100.
96. Behzadi, M.; Noroozian, E.; Mirzaei, M. A novel coating based on carbon nanotubes/poly-ortho-phenylenediamine composite for headspace solid-phase microextraction of polycyclic aromatic hydrocarbons. *Talanta* 2013, 108, 66–73.
97. Maghsoudi, S.; Noroozian, E. HP-SPME of volatile polycyclic aromatic hydrocarbons from water using multiwalled carbon nanotubes coated on a steel fiber through electrophoretic deposition. *Chromatographia* 2012, 75, 913–921.
98. Zhang, X.; Zang, X.H.; Wang, J.T.; Wang, C.; Wu, Q.H.; Wang, Z. Porous carbon derived from aluminum-based metal organic framework as a fiber coating for the solid-phase microextraction of polycyclic aromatic hydrocarbons from water and soil. *Microchim. Acta* 2015, 182, 2353–2359.
99. Mehdinia, A.; Mohammadi, A.A.; Davarani, S.S.H.; Banitaba, M.H. Application of self-assembled monolayers in the preparation of solid-phase microextraction coatings. *Chromatographia* 2011, 5–6, 421–427.
100. Yang, L.; Zhang, J.; Zhao, F.; Zeng, B. Electrodeposition of self-assembled poly(3,4-ethylenedioxythiophene) @gold nanoparticles on stainless steel wires for the headspace solid-phase microextraction and gas chromatographic determination of several polycyclic aromatic hydrocarbons. *J. Chromatogr. A* 2016, 1471, 80–86.
101. Harati, F.; Ghiasvand, A.; Dalvand, K.; Haddad, P.R. Fused-silica capillary internally modified with nanostructured octadecyl silica for dynamic in-tube solid-phase microextraction of polycyclic aromatic hydrocarbons from aqueous media. *Microchem. J.* 2020, 155, 104672.
102. Ghiasvand, A.; Yazdankhah, F.; Paull, B. Heating-, Cooling- and Vacuum-Assisted Solid-Phase Microextraction (HCV-SPME) for Efficient Sampling of Environmental Pollutants in Complex Matrices. *Chromatographia* 2020, 83, 531–540.
103. Kremser, A.; Jochmann, M.A.; Schmidt, T.C. PAL SPME Arrow - Evaluation of a novel solid-phase microextraction device for freely dissolved PAHs in water. *Anal. Bioanal. Chem.* 2016, 408, 943–952.
104. Baltussen, E.; Sandra, P.; David, F.; Cramers, C. Stir bar sorptive extraction (SBSE), a novel extraction technique for aqueous samples: Theory and principles. *J. Microcolumn Sep.* 1999, 10, 737–747.
105. David, F.; Sandra, P. Stir bar sorptive extraction for trace analysis. *J. Chromatogr. A* 2007, 1152, 54–69.
106. García-Falcón, M.S.; Cancho-Grande, B.; Simal-Gándara, J. Stirring bar sorptive extraction in the determination of PAHs in drinking waters. *Water Res.* 2004, 38, 1679–1684.
107. Popp, P.; Bauer, C.; Wennrich, L. Application of stir bar sorptive extraction in combination with column liquid chromatography for the determination of polycyclic aromatic hydrocarbons in water samples. *Anal. Chim. Acta* 2001, 436, 1–9.
108. Popp, P.; Bauer, C.; Hauser, B.; Keil, P.; Wennrich, L. Extraction of polycyclic aromatic hydrocarbons and organochloride compounds from water: A comparison between solid-phase microextraction and stir bar sorptive extraction. *J. Sep. Sci.* 2003, 9–10, 961–967.

109. Bourdat-Deschamps, M.; Daudin, J.J.; Barriuso, E. An experimental design approach to optimise the determination of polycyclic aromatic hydrocarbons from rainfall water using stir bar sorptive extraction and high performance liquid chromatography-fluorescence detection. *J. Chromatogr. A* 2007, 1167, 143–153.
110. Mao, X.; Hu, B.; He, M.; Fan, W. Stir bar sorptive extraction approaches with a home-made portable electric stirrer for the analysis of polycyclic aromatic hydrocarbon compounds in environmental water. *J. Chromatogr. A* 2012, 1260, 16–24.
111. Mollahosseini, A.; Rokue, M.; Mojtahedi, M.M.; Togholi, M.; Kamankesh, M.; Motaharian, A. Mechanical stir bar sorptive extraction followed by gas chromatography as a new method for determining polycyclic aromatic hydrocarbons in water samples. *Microchem. J.* 2016, 126, 431–437.
112. Huang, X.; Yuan, D. Preparation of stir bars for sorptive extraction based on monolithic material. *J. Chromatogr. A* 2007, 1154, 152–157.
113. Ekbatani Amlashi, N.; Hadjmohammadi, M.R. Sol–gel coating of poly(ethylene glycol)-grafted multiwalled carbon nanotubes for stir bar sorptive extraction and its application to the analysis of polycyclic aromatic hydrocarbons in water. *J. Sep. Sci.* 2016, 39, 3445–3456.
114. Yu, C.; Hu, B. Automated stir plate (bar) sorptive extraction coupled to high-performance liquid chromatography for the determination of polycyclic aromatic hydrocarbons. *J. Sep. Sci.* 2010, 33, 2176–2183.
115. Rutkowska, M.; Plotka-Wasyłka, J.; Sajid, M.; Andruch, V. Liquid–phase microextraction: A review of reviews. *Microchem. J.* 2019, 149, 103989.
116. Bello-López, M.Á.; Ramos-Payán, M.; Ocaña-González, J.A.; Fernández-Torres, R.; Callejón-Mochón, M. Analytical Applications of Hollow Fiber Liquid Phase Microextraction (HF-LPME): A Review. *Anal. Lett.* 2012, 45, 804–830.
117. Kokosa, J.M. Recent trends in using single-drop microextraction and related techniques in green analytical methods. *TrAC - Trends Anal. Chem.* 2015, 71, 194–204.
118. Kocúrová, L.; Balogh, I.S.; Šandrejová, J.; Andruch, V. Recent advances in dispersive liquid-liquid microextraction using organic solvents lighter than water. A review. *Microchem. J.* 2012, 102, 11–17.
119. Rykowska, I.; Ziemblińska, J.; Nowak, I. Modern approaches in dispersive liquid-liquid microextraction (DLLME) based on ionic liquids: A review. *J. Mol. Liq.* 2018, 259, 319–339.
120. Fernández, M.; Clavijo, S.; Forteza, R.; Cerdà, V. Determination of polycyclic aromatic hydrocarbons using lab on valve dispersive liquid-liquid microextraction coupled to high performance chromatography. *Talanta* 2015, 138, 190–195.
121. Pena-Pereira, F.; Costas-Mora, I.; Lavilla, I.; Bendicho, C. Rapid screening of polycyclic aromatic hydrocarbons (PAHs) in waters by directly suspended droplet microextraction-microvolume fluorospectrometry. *Talanta* 2012, 89, 217–222.
122. Santos, L.O.; dos Anjos, J.P.; Ferreira, S.L.C.; de Andrade, J.B. Simultaneous determination of PAHs, nitro-PAHs and quinones in surface and groundwater samples using SDME/GC-MS. *Microchem. J.* 2017, 133, 431–440.
123. Sibiya, P.; Cukrowska, E.; Jönsson, J.Å.; Chimuka, L. Hollow-fibre liquid-phase microextraction for the determination of polycyclic aromatic hydrocarbons in Johannesburg Jukskei River, South Africa. *Chromatographia* 2013, 76, 427–436.
124. Ratola, N.; Alves, A.; Kalogerakis, N.; Psillakis, E. Hollow-fibre liquid-phase microextraction: A simple and fast cleanup step used for PAHs determination in pine needles. *Anal. Chim. Acta* 2008, 618, 70–78.
125. Rezaee, M.; Assadi, Y.; Milani Hosseini, M.R.; Aghaee, E.; Ahmadi, F.; Berijani, S. Determination of organic compounds in water using dispersive liquid-liquid microextraction. *J. Chromatogr. A* 2006, 1116, 1–9.
126. Guo, L.; Lee, H.K. Low-density solvent-based solvent demulsification dispersive liquid-liquid microextraction for the fast determination of trace levels of sixteen priority polycyclic aromatic hydrocarbons in environmental water samples. *J. Chromatogr. A* 2011, 1218, 5040–5046.
127. Hosseini, M.H.; Rezaee, M.; Akbarian, S.; Mizani, F.; Pourjavadi, M.R.; Arabieh, M. Homogeneous liquid-liquid microextraction via flotation assistance for rapid and efficient determination of polycyclic aromatic hydrocarbons in water samples. *Anal. Chim. Acta* 2013, 762, 54–60.
128. Song, X.; Li, J.; Liao, C.; Chen, L. Ultrasound-assisted dispersive liquid-liquid microextraction combined with low solvent consumption for determination of polycyclic aromatic hydrocarbons in seawater by GC-MS. *Chromatographia* 2011, 74, 89–98.
129. Leng, G.; Lui, G.; Chen, Y.; Yin, H.; Dan, D. Vortex-assisted extraction combined with dispersive liquid-liquid microextraction for the determination of polycyclic aromatic hydrocarbons in sediment by high performance liquid chromatography. *J. Sep. Sci.* 2012, 35, 2796–2804.
130. Saleh, A.; Yamini, Y.; Faraji, M.; Rezaee, M.; Ghambarian, M. Ultrasound-assisted emulsification microextraction method based on applying low density organic solvents followed by gas chromatography analysis for the determination of polycyclic aromatic hydrocarbons in water samples. *J. Chromatogr. A* 2009, 1216, 6673–6679.
131. Ozcan, S.; Tor, A.; Aydin, M.E. Determination of polycyclic aromatic hydrocarbons in waters by ultrasound-assisted emulsification-microextraction and gas chromatography-mass spectrometry. *Anal. Chim. Acta* 2010, 665, 193–199.

132. Avino, P.; Notardonato, I.; Perugini, L.; Russo, M.V. New protocol based on high-volume sampling followed by DLLME-GC-IT/MS for determining PAHs at ultra-trace levels in surface water samples. *Microchem. J.* 2017, 133, 251–257.
133. Cheng, J.; Matsadiq, G.; Liu, L.; Zhou, Y.W.; Chen, G. Development of a novel ultrasound-assisted surfactant-enhanced emulsification microextraction method and its application to the analysis of eleven polycyclic aromatic hydrocarbons at trace levels in water. *J. Chromatogr. A* 2011, 1218, 2476–2482.
134. Yousefi, S.M.; Shemirani, F.; Ghorbanian, S.A. Hydrophobic Deep Eutectic Solvents in Developing Microextraction Methods Based on Solidification of Floating Drop: Application to the Trace HPLC/FLD Determination of PAHs. *Chromatographia* 2018 81, 1201–1211.
135. Pena, M.T.; Casais, M.C.; Mejuto, M.C.; Cela, R. Development of an ionic liquid based dispersive liquid-liquid microextraction method for the analysis of polycyclic aromatic hydrocarbons in water samples. *J. Chromatogr. A* 2009, 1216, 6356–6364.
136. Liu, L.; He, L.; Jiang, X.; Zhao, W.; Xiang, G.; Anderson, J.L. Macrocyclic polyamine-functionalized silica as a solid-phase extraction material coupled with ionic liquid dispersive liquid-liquid extraction for the enrichment of polycyclic aromatic hydrocarbons. *J. Sep. Sci.* 2014, 37, 1004–1011.
137. Aznar, M.; Alfaro, P.; Nerin, C.; Kabir, A.; Furton, K.G. Fabric phase sorptive extraction: An innovative sample preparation approach applied to the analysis of specific migration from food packaging. *Anal. Chim. Acta* 2016, 936, 97–107.
138. Zilfidou, E.; Kabir, A.; Furton, K.G.; Samanidou, V. Fabric phase sorptive extraction: Current state of the art and future perspectives. *Separations* 2018, 5, 40.
139. Kabir, A.; Furton, K.G. Sample preparation in food analysis: Practices, problems and future outlook. In *Analytical Chemistry: Developments, Applications and Challenges in Food Analysis*; Nova Science Publishers, Inc.: Hauppauge, NY, USA, 2017; ISBN 9781536122824.
140. Locatelli, M.; Kabir, A.; Innosa, D.; Lopatriello, T.; Furton, K.G. A fabric phase sorptive extraction-High performance liquid chromatography-Photo diode array detection method for the determination of twelve azole antimicrobial drug residues in human plasma and urine. *J. Chromatogr. B Anal. Technol. Biomed. Life Sci.* 2017, 1040, 192–198.
141. Samanidou, V.; Galanopoulos, L.D.; Kabir, A.; Furton, K.G. Fast extraction of amphenicols residues from raw milk using novel fabric phase sorptive extraction followed by high-performance liquid chromatography-diode array detection. *Anal. Chim. Acta* 2015, 855, 41–50.
142. Samanidou, V.; Michaelidou, K.; Kabir, A.; Furton, K.G. Fabric phase sorptive extraction of selected penicillin antibiotic residues from intact milk followed by high performance liquid chromatography with diode array detection. *Food Chem.* 2017, 224, 131–138.
143. Saini, S.S.; Kabir, A.; Rao, A.L.J.; Malik, A.K.; Furton, K.G. A novel protocol to monitor trace levels of selected polycyclic aromatic hydrocarbons in environmental water using fabric phase sorptive extraction followed by high performance liquid chromatography-fluorescence detection. *Separations* 2017, 4, 22.
144. Sun, T.; Wang, D.; Tang, Y.; Xing, X.; Zhuang, J.; Cheng, J.; Du, Z. Fabric-phase sorptive extraction coupled with ion mobility spectrometry for on-site rapid detection of PAHs in aquatic environment. *Talanta* 2019, 195, 109–116.
145. Armenta, S.; Alcalá, M.; Blanco, M. A review of recent, unconventional applications of ion mobility spectrometry (IMS). *Anal. Chim. Acta* 2011, 703, 114–123.
146. Yang, S.; Chen, C.; Yan, Z.; Cai, Q.; Yao, S. Evaluation of metal-organic framework 5 as a new SPE material for the determination of polycyclic aromatic hydrocarbons in environmental waters. *J. Sep. Sci.* 2013, 36, 1283–1290.
147. Hu, H.; Liu, S.; Chen, C.; Wang, J.; Zou, Y.; Lin, L.; Yao, S. Two novel zeolitic imidazolate frameworks (ZIFs) as sorbents for solid-phase extraction (SPE) of polycyclic aromatic hydrocarbons (PAHs) in environmental water samples. *Analyst* 2014, 139, 5818–5826.
148. Ge, D.; Lee, H.K. Water stability of zeolite imidazolate framework 8 and application to porous membrane-protected micro-solid-phase extraction of polycyclic aromatic hydrocarbons from environmental water samples. *J. Chromatogr. A* 2011, 1218, 8490–8495.
149. Song, X.; Li, J.; Xu, S.; Ying, R.; Ma, J.; Liao, C.; Liu, D.; Yu, J.; Chen, L. Determination of 16 polycyclic aromatic hydrocarbons in seawater using molecularly imprinted solid-phase extraction coupled with gas chromatography-mass spectrometry. *Talanta* 2012, 99, 75–82.
150. Mauri-Aucejo, A.; Amorós, P.; Moragues, A.; Guillem, C.; Belenguer-Sapiña, C. Comparison of the solid-phase extraction efficiency of a bounded and an included cyclodextrin-silica microporous composite for polycyclic aromatic hydrocarbons determination in water samples. *Talanta* 2016, 32, 659–665.
151. Soler-Seguí, S.; Belenguer-Sapiña, C.; Amorós, P.; Mauri-Aucejo, A. Evaluation of a cyclodextrin-silica hybrid microporous composite for the solid-phase extraction of polycyclic aromatic hydrocarbons. *Anal. Sci.* 2016, 32, 659–665.
152. Wang, N.; Guo, Y.; Wang, L.; Liang, X.; Liu, S.; Jiang, S. Preparation of an aminopropyl imidazole-modified silica gel as a sorbent for solid-phase extraction of carboxylic acid compounds and polycyclic aromatic hydrocarbons. *Analyst* 2014, 139, 2531–2537.

153. Zhao, W.; Yang, L.; He, L.; Zhang, S. Simultaneous Enrichment of Polycyclic Aromatic Hydrocarbons and Cu²⁺ in Water Using Tetraazacalixarenetriazine as a Solid-Phase Extraction Selector. *J. Agric. Food Chem.* 2016, 64, 6233–6239.
154. Kefi, B.B.; El Atrache, L.L.; Kochkar, H.; Ghorbel, A. TiO₂ nanotubes as solid-phase extraction adsorbent for the determination of polycyclic aromatic hydrocarbons in environmental water samples. *J. Environ. Sci.* 2011, 23, 860–867.
155. Huang, Y.; Zhou, Q.; Xie, G. Development of micro-solid phase extraction with titanate nanotube array modified by cetyl trimethylammonium bromide for sensitive determination of polycyclic aromatic hydrocarbons from environmental water samples. *J. Hazard. Mater.* 2011, 183, 82–89.
156. Krupadam, R.J.; Korde, B.A.; Ashokkumar, M.; Kolev, S.D. Novel molecularly imprinted polymeric microspheres for pre concentration and preservation of polycyclic aromatic hydrocarbons from environmental samples. *Anal. Bioanal. Chem.* 2014, 406, 5313–5321.
157. Foan, L.; Ricoul, F.; Vignoud, S. A novel microfluidic device for fast extraction of polycyclic aromatic hydrocarbons (PAHs) from environmental waters – comparison with stir-bar sorptive extraction (SBSE). *Int. J. Environ. Anal. Chem.* 2015, 95, 1171–1185.
158. Wu, H.; Wang, X.; Liu, B.; Lu, J.; Du, B.; Zhang, L.; Ji, J.; Yue, Q.; Han, B. Flow injection solid-phase extraction using multi-walled carbon nanotubes packed micro-column for the determination of polycyclic aromatic hydrocarbons in water by gas chromatography-mass spectrometry. *J. Chromatogr. A* 2010, 1217, 2911–2917.
159. Zhou, Y.Y.; Yan, X.P.; Kim, K.N.; Wang, S.W.; Liu, M.G. Exploration of coordination polymer as sorbent for flow injection solid-phase extraction on-line coupled with high-performance liquid chromatography for determination of polycyclic aromatic hydrocarbons in environmental materials. *J. Chromatogr. A* 2006, 1116, 172–178.
160. Zhang, X.; Wang, P.; Han, Q.; Li, H.; Wang, T.; Ding, M. Metal–organic framework based in-syringe solid-phase extraction for the on-site sampling of polycyclic aromatic hydrocarbons from environmental water samples. *J. Sep. Sci.* 2018, 41, 1856–1863.

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