

Review

Applications of Hollow-Fiber and Related Microextraction Techniques for the Determination of Pesticides in Environmental and Food Samples—A Mini Review

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Abstract: Pesticides represent one of the most important groups of analytes in environmental analysis. Moreover, their levels are very frequently determined in food and beverages due to the concern over their possible adverse health effects. Their concentration in samples is usually very low; thus, they have to be preconcentrated. Conventional solvent and solid-phase extractions are mainly used for this purpose, but miniaturized approaches are also being applied more and more often. The present review covers solvent microextractions that use a semi-permeable membrane barrier between the sample and the solvent. The main representatives of this approach are hollow-fiber microextraction (HFME), solvent bar microextraction (SBME), electromembrane extraction (EME), and different variations of those, such as combinations with other sorbent or solvent microextractions, electromigration, etc. The relevant research from the last decade, dealing with the application of these microextractions to the isolation of pesticides from various environmental and food samples, is critically discussed with emphasis on their strengths and weak points.

Keywords: pesticides; hollow-fiber microextraction (HFME); solvent bar microextraction (SBME); supported liquid membrane extraction (SLME); electromembrane extraction (EME); semi-permeable membrane; environmental samples; food; beverages

1. Introduction

Pesticides are a mainstay of modern agriculture, and they will probably remain so for the next few decades. Their use brings undoubtful advantages in the control of unwanted organisms, especially insects, causing a positive impact on agricultural production. However, there are also less advantageous aspects of their use: their residues remain in the agricultural soil, they leach into surface and ground waters, and they can be transferred by air masses over long distance, unintentionally affecting non-target organisms. While most unintentional and adverse effects of pesticides are seen in non-target animal, plant, and microbial species, humans can be affected as well. Acute poisonings with pesticides are rare in humans and usually related to improper work conditions, which are easily avoided by strictly following the handling instructions. In spite of the improbability of acute poisoning, there is a great concern in the general public regarding the chronic exposure to pesticides through ingested food and drinking water. The possibility of chronic adverse effects is the main reason for the widespread monitoring and control of pesticides in drinking water, fruit, vegetables, and other foodstuffs of either animal or plant origin intended for human consumption [1].

The majority of monitoring is performed by routine multiresidue methods employing chromatographic methods based preferably on gas or liquid chromatography coupled to (tandem) mass spectrometry. Because the samples are often complex, different extraction techniques are employed for

the separation of analytes from the matrix and their preconcentration. The mainstay in the extraction of solid or semi-solid samples remains solvent extraction (SE), while, for liquid samples, solid-phase extraction (SPE) is more often used. While these approaches are efficient and time-tested, they are not environmentally friendly, because large quantities of organic solvents or SPE cartridges are discarded at the end of the procedure. Therefore, the trend in environmental sample preparation is to “go green” and miniaturize. Green analytical chemistry (GAC) is a concept that is currently widely recognized [2] and promotes the reduction or elimination of solvent consumption, among other goals. With the minimization of solvent consumption, waste material is reduced as well, and the operator is exposed to a diminished amount of harmful chemicals, which are also the principles of GAC.

The most successful miniaturized extraction technique to date is solid-phase microextraction (SPME), first described in 1990 [3]; however, miniaturization in solvent extraction also had a big sway in the last 24 years [4]. Several innovative techniques of liquid-phase microextraction (LPME) were invented: single-drop microextraction (SDME) [5,6], dispersive liquid–liquid microextraction (DLLME) [7], and its numerous variants. The focus of the present review, however, is on those solvent microextractions which employ a semi-permeable membrane between the sample and the solvent. There are several names and approaches: supported liquid membrane extraction (SLME), hollow-fiber microextraction (HFME), solvent bar microextraction (SBME), and electromembrane microextraction (EME). Hollow-fiber solid-phase microextraction (HF SPME), in spite of using a semi-permeable membrane, is not discussed in the review, because the principal extraction mechanism is the sorption to the SPME fiber and not the partitioning into the solvent. The same goes for thin-film microextraction (TFME) [8], which employs a thin membrane without solvent for the extraction. The membrane-based solvent microextraction techniques successfully apply the principles of GAC by minimizing the amount of sample and minimizing solvent consumption, thereby also minimizing the generated waste and exposure of the operator to the solvent fumes [9]. Moreover, they generally use simple equipment and, thus, consume very little energy. The great importance and the increased number of publications in the area of LPME are reflected in the fact that even “a review of reviews” was published [10].

The research of the last decade dealing with the application of membrane-based miniaturized solvent extraction techniques to the determination of pesticides in environmental, food, and beverage samples is reviewed. The search for papers was done in Web of Science, using the keywords of the current review.

2. Membrane-Based Solvent Microextraction Techniques

The emergence of hollow-fiber microextraction (HFME or HF-LPME) and related techniques is connected to the seminal publication by Pedersen-Bjergaard and Rasmussen [11]. In fact, the original paper used the name supported liquid membrane (SLM), which is still used as an umbrella term for membrane-based microextraction techniques. In HFME, a semi-permeable membrane in the form of a hollow fiber (HF) made from polymeric materials constitutes a barrier between the sample (donor solution) and the extraction solvent. The pores of the membrane are filled with an organic solvent in which analytes should have significant solubility. In the lumen of the HF, there could be the same organic solvent (acceptor solution): two-phase HFME or HF(2)ME. Another approach is to fill the fiber lumen with a different, usually aqueous acceptor solution with a pH that promotes the ionization of the analytes: three-phase HFME, HF-LLLME, or HF(3)ME [12,13]. Generally, the fibers are manually cut and placed into the organic solvent for the pores to fill. Next, they are mounted to a syringe needle and filled with the acceptor solution. Two syringes can be placed at each open end of a U-shaped fiber, or one end is sealed and the other attached to a syringe. After that, the fiber is exposed to the sample for a certain amount of time during which an equilibrium is established between the analyte in the donor and acceptor solutions (two-phase HFME), or in the donor solution, the solvent in the fiber wall, and the acceptor solution (three-phase HFME). At the end, the acceptor solution is removed from the fiber lumen via syringe, and the analyte concentration is determined by a suitable analytical method, usually HPLC or GC.

In 2004, a modification of HFME was proposed [14]; after filling the fiber with the acceptor solution, both fiber ends are sealed, and it is placed into a continuously stirred sample for a certain amount of time. Finally, the fiber is removed from the sample, and the acceptor solution is taken out by cutting it or pricking it with the syringe needle. The technique was named solvent bar microextraction (SBME); its main advantage over classical HFME is that there is no need to support the fiber during extraction and, thus, more samples can be processed concurrently [15].

Another modification that gained wide acceptance in the analytical community is electromembrane extraction (EME), introduced in 2006 [16]. In EME, a metal wire acting as an electrode is placed into a wide-bore fiber and another electrode in the sample solution. Fiber pores are filled with an organic solvent, while the acceptor solution is aqueous. Transport across the membrane is significantly accelerated because of electromigration, but the technique is suitable only for charged analytes [13].

Other modifications were proposed, e.g., hollow-fiber renewal liquid membrane extraction [17]. The difference to HFME is the direct addition of a small amount of the same solvent as present in the fiber wall into the sample to allow for the renewal of solvent in the fiber pores.

Recently, a novel modified membrane-based solvent microextraction was proposed for solid samples [18]. The proposed technique utilizes a porous polypropylene membrane to form a “bag” into which a small amount of solid sample is packed. The membrane bag with solid sample is then subjected to ultrasound extraction into a small amount (up to 1 mL) of organic solvent. No filtration or centrifugation is needed, and the membrane also prevents the extraction of high-molecular-weight substances. This is an interesting application of membrane-based solvent microextraction for solid samples, because the prevalent approach for solids until now was a previous extraction with a conventional extraction technique and further clean-up of the extract with the LPME technique [19,20].

There are several advantages and also some disadvantages of membrane-based solvent microextractions (Table 1).

Table 1. Advantages and disadvantages of membrane-based solvent microextractions.

Property	Advantage	Adheres to GAC
Low amount of organic solvent	√	yes
Aqueous acceptor phase (3-phase HFME)	√	yes
High preconcentration factors	√	NA
No solvent evaporation needed	√	yes
No clean-up of extract needed	√	yes
No filtration of extract needed	√	yes
No filtration of sample needed	√/X	yes
Compatibility of solvents with GC	√/X	NA
Compatibility of solvents with LC	√/X	NA
Disposable fiber	√/X	no
Manual preparation of HF, SB, etc.	X	NA
Long extraction time (HFME, SBME)	X	no
Only for liquid samples	X	NA

NA—not applicable; GAC—green analytical chemistry; HFME—hollow-fiber microextraction; SBME—solvent bar microextraction; GC—gas chromatography; LC—liquid chromatography.

A very small amount of organic solvent is used (few μL), which certainly makes them a prime representative of green chemistry. Furthermore, preconcentration factors are usually high, and there is no need for further reducing the volume of the solvent. Solvents can be compatible with HPLC or GC, avoiding the step of changing the solvent by drying and reconstituting. However, solvents used in two-phase SLME are mostly non-polar and, thus, compatible with GC, while solvents used as the acceptor phase in three-phase SLME are usually aqueous and, thus, compatible with LC. Otherwise, evaporation and change of solvent are still needed. Fiber is used only once, so there can be no carryover. While this property is advantageous from the point of repeatability and selectivity of the method, it generates additional waste plastic material. The techniques are applicable to liquid samples containing

moderate proportions of solid particles because the membrane acts as a filter as well, although pores may become clogged with small particles. Thus, filtration is still advisable for samples containing an increased amount of solids. Natural organic matter is not extracted, but it may interfere by binding the analytes.

However, there are also disadvantages, the main ones being the long equilibration times and the need to manually prepare disposable HFMs or solvent bars. In complex samples, interfering compounds may co-extract, but additional clean-up of the extract is difficult because of the small volume. To decrease the amount of manual work, promising steps toward automation were taken with parallel artificial liquid membrane extraction [21] and parallel electromembrane extraction [22], both of which use a commercially available 96-well plate. A purpose-made dynamic HFME apparatus using a peristaltic pump [23], or an assembly using a syringe-driven pump and online injection with a six-port injection valve [24] were also proposed for the purpose of automation. Another recently proposed approach, a bundled hollow-fiber liquid-phase microextraction [25], is also promising.

For more information on the different membrane-based microextractions and the recent developments in this field, the interested reader is referred to some excellent reviews published recently [12,15,26,27].

3. Factors Influencing Membrane-Based Solvent Microextraction Techniques

Several factors can be optimized in HFME and similar techniques: type of fiber membrane, type and volume of extraction solvent (related to fiber length), stirring rate, temperature, and ionic strength and pH of the sample (donor solution). Fiber length also determines the contact surface. In EME, the direct current potential between electrodes can be optimized as well.

In classical solvent and solid-phase extractions, extraction yield is a measure of extraction efficiency. In solvent microextractions, this criterion cannot be applied due to the small volume of extracting solvent that prevents an exhaustive extraction. Thus, enrichment factor (EF) is the usual criterion, defined as the ratio between analyte concentration in the extract and initial analyte concentration in the sample [12].

The fiber that was used in the majority of applications to date is a hollow microporous polypropylene (PP) fiber Acurel 3/2 Q with the following dimensions: inner diameter 600 μm , wall thickness 200 μm , pore size 0.2 μm , wall porosity of ca. 70% of volume [4]. Polypropylene fibers of different dimensions and porosity are also used, while other materials are seldom utilized: polysulfone [28], cellulose [29], polyvinylidene fluoride (PVDF), and polytetrafluoroethylene (PTFE) [30]. An interesting new development in fiber materials is the combination of polypropylene with various sorbents, e.g., multi-walled carbon nanotubes, graphene, ceramic metal oxides, and self-synthesized polymers. An organic solvent is present in the remaining pores, resulting in a mixed-mode extraction mechanism: solid-phase sorption and liquid-phase partitioning [31].

The solvent in the membrane pores or the “supported liquid” (in two-phase HFME, the same solvent is also in the lumen) should be immiscible with water and compatible with the fiber material; additional preferred features are low volatility and viscosity. For this, 1-octanol is used most commonly, but toluene, di-*n*-hexyl ether, *n*-hexane, 1-nonanol, *n*-nonane, 1-undecanol, *n*-tetradecane, cyclohexane, and ethyl acetate are used as well [15]. Different ionic liquids are also applied instead of organic solvents [15,32].

In three-phase HFME, the fiber lumen typically contains an aqueous acceptor phase, but an ionic liquid or a second immiscible organic solvent can also be used. In the aqueous acceptor phase, the pH is adjusted to promote the ionization of analytes and prevent their partitioning back to the organic phase in the fiber wall. Thus, an acidic pH is used for analytes with basic properties and vice versa [13].

The volume of extraction solvent is related to the fiber or solvent bar length and inner diameter. Typically, it is between 4 and 20 μL . In EME, wider fibers are used to accommodate the wire electrode.

In the donor solution (sample), conditions should be adjusted to promote the partitioning of analytes into organic solvent. Preferably, the pH should be at least three units below or above pK_a

for acidic or basic analytes, respectively [13]. Increasing the ionic strength of the sample is generally beneficial for the extraction efficiency of organic compounds; nevertheless, this factor should be carefully optimized for each application as it was also shown to have a detrimental effect, especially in EME [12].

During extraction, vigorous mechanical stirring, vibration, stirring with microwaves, or ultrasound is applied to promote the transport of analytes to the fiber. However, excessive stirring may result in the formation of air bubbles that attach to the fiber and diminish the contact surface.

Increased temperature of the sample increases the diffusion coefficient and shortens the extraction time, but it also affects the solubility of organic solvents in water and affects the fiber integrity. For PP fibers, a temperature below 40 °C should be used [12].

Extraction time is usually a compromise between extraction efficiency and feasibility. Typical extraction time in HFME is 20–90 min, while it is shorter in EME (5–10 min) [4].

For further detailed information on method optimization, readers should refer to previously published reviews [4,12,13,15,26,31,32].

4. Applications of HFME for Extraction of Pesticides

Among the membrane-based extraction techniques covered in the present review, HFME is the most frequently used. Table 2 shows the relevant applications of the “classical” HFME with either a U-shaped fiber suspended in the sample on two syringes, or HFME with one end of the HF sealed and the other suspended on the syringe. Entries in Table 2 are organized according to the type of sample. Where different types of samples were analyzed in the same paper, the paper was entered under the most complex sample. Overall, 26 publications from the last decade were found in Web of Science, dealing with the application of these types of HFME on pesticide extraction from various samples [30,33–57]. The majority of these publications discussed the optimization of HFME parameters for the particular analytes and particular samples, most often with simple aqueous matrices: fiber wall solvent, acceptor solvent in three-phase HFME, pH and ionic strength of sample, stirring rate, and time of extraction. The developed methods were usually at least partially validated, and limits of detection (LODs) or limits of quantitation (LOQs) or both were given. In cases where both were given, LOQs are shown preferably in Table 2. Although enrichment factor (EF) is the most widely accepted measure of HFME efficacy, it was not given in all publications. Instead, relative recovery for a certain type of sample was frequently given. This may cause some confusion for the readers, because “recovery” could be understood as extraction recovery, and, due to the non-exhaustive nature of HF microextraction and limited solvent volume, it is not expected to be high. “Recovery”, in most publications, was in fact meant as an accuracy measure of the method, given as the ratio of calculated concentration and spiked concentration.

Table 2. Applications of HFME for extraction of pesticides.

HFME	Sample	Analytes	Preliminary Sample Preparation	Extraction Conditions	Analytical Technique	Method Performance	Additional Features	Reference
Water samples								
2-phase	Environmental waters	29 pesticides	None	PP (non-specified) 10 cm; WS + AS 40 µL ethyl decanoate; <i>T</i> 30 °C; stirring 300 rpm; extraction time 30 min; passive sampling: as above except room <i>T</i> , 600 rpm, 250 mL sample, extraction time 8–10 days	GC–MS	LOQs 0.012–0.802 µg/L	In situ passive sampling device in disposable plastic bottle for monitoring and estimating time-weighted average of pesticides	[33]
2-phase	Effluent wastewater, surface water	27 emerging contaminants including 14 pesticides	Filtered	PP1, 5.5 cm; WS + AS 60 µL 1-octanol; 1000 mL sample + 3% NaCl + pH 7; <i>T</i> 24 °C; 100 rpm; 30 min	LC–MS/MS	LOQs 2.13–126.50 ng/L; EFs 6–4177; RSD 3–15%	Parameters optimized by two fractional factorial designs	[34]
2-phase	Rain water, spring water, ground water	9 pyrethroid insecticides	Filtered 0.45 µm	PP1, 1 cm; WS 1-octanol; air in the lumen; sample 10 mL; 1500 rpm, 6 h; desorbed in 50 µL <i>i</i> -octane (US 15 min)	GC–MS	LOQs 0.003–0.026 µg/L; RSD 1.1–14.8%; EFs 35–255	Extractant solvent only in the pores and air in the lumen; fiber desorbed after extraction	[35]
2-phase	Environmental waters: river, tap, agricultural Canal	16 pesticides	None	PP2, 328 mm; WS + AS TOPO (10%) and TBP (10%) in DHE; sample 250 mL pH 8; 100 rpm, 4 h	LC–MS/MS	LOQs 0.087–0.269 µg/L; RSD 1.4–11.8%	Polar non-aqueous extracting solvents (not defined except by acronyms)	[36]
2-phase	Tap water, Farm water	Hexaconazole, quinalphos, methidathion	None	PP1, 1.8 cm; WS + AS toluene 4 µL; 4 mL sample + 1.5% NaCl (<i>w/v</i>); 850 rpm, 20 min	GC–ECD	LODs 3–7 ng/L; RSD 4.6–7.9%	Accuracy (as η) 98.2–101.5%	[37]
2-phase, continuous	Drinking water	Methidation, quinalphos, profenofos	None	PP1, 1.5 cm; WS + AS <i>i</i> -octane (3 µL) added continuously at 0.2 µL steps at 3-min intervals; sample 11 mL; 1260 rpm, 40 min	HPLC–UV	LODs 2.86–82.66 µg/L; RSD 0.10–0.29%; EFs 175.1–189.5	Continuous replenishment of acceptor phase in the fiber lumen; accuracy (as η) 79.80–86.14%	[38]
3-phase	Water	4 <i>N</i> -carbamate pesticides	None	PP1, 4 cm; WS <i>i</i> -octane + 5% TOPO; AS 0.1 M HCl + KCl pH 1; sample pH 11; 300 rpm, 30 min	HPLC–DAD, LC–MS	EFs 1–9; η 0–96.57%	Compared to SPE	[39]
3-phase	Environmental waters	6 sulfonylurea herbicides	None	PP1, 10 cm; WS dihexyl ether; AS 0.5 mM phosphate buffer pH 11; sample 12 mL + 5 mM HCl + 5% NaCl (<i>w/v</i>); 1200 rpm, 1 h	HPLC–DAD	LOQs 0.3–5.7 µg/L; RSD 2.2–8.4%	/	[40]

Table 2. Cont.

HFME	Sample	Analytes	Preliminary Sample Preparation	Extraction Conditions	Analytical Technique	Method Performance	Additional Features	Reference
Soil samples								
2-phase	Soil, water	6 pesticides + 2 metabolites	3 g s.s. + (2×) 20 mL MeOH + 2.5% (<i>w/v</i>) NaCl, US 10 min; centrifuged, filtered (0.45 µm); evaporated to dry, re-dissolved in 10 mL UPw	Soil: PP1, 2 cm; WS + AS 20 µL 1-octanol; 10 mL aqueous extract pH 9; 1440 rpm, 30 min; evap. to dry, re-dissolved in 50 µL mobile phase; water: as above, except 3 cm fiber, 20 mL sample pH 9 + 20% NaCl (<i>w/v</i>)	HPLC–FLD	Soil: LOQ 0.004–23.14 ng/g; accuracy (as η) 85–117%	/	[41]
Fruit and vegetables, whole or juice								
2-phase	Fruits (apple, peach, orange, kiwi), vegetable (parsley)	3 pyrethroid insecticides	Homogenized s.s., filtered	PP1, 8.8 cm; WS + AS 1-octanol 24 µL; sample 5 mL + 5 mL buffer (acetic acid/acetate, 0.1 M, pH 5.5) + 3% (<i>w/v</i>) NaCl + 1 mL UPw; 480 rpm, 41 min	GC–MS	LOQs 0.08–0.10 ng/mL; RSD 3.4–5.9%; EFs 519–528	Parameters optimized with rotatable-centered cube central composite design	[42]
2-phase	Different environmental waters, grape juice	4 triazole fungicides	Filtered; grape juice diluted with UPw (10×)	PP1, 1.5 cm; WS + AS 4 µL toluene; sample 5 mL; 720 rpm, 20 min	GC–MS	LOQs 1–2 µg/L; RSD 6.0–9.0%; EFs 134–239	No matrix effect observed; relative recovery 83–119% in different samples	[43]
2-phase	Fresh and commercial orange juice	18 pesticides	Centrifuged	PP1, 1.5 cm; WS + AS none (dry); 9 mL sample pH 7 + 4 g (NH ₄) ₂ SO ₄ + 400 µL toluene/EtAc (85:15, <i>v/v</i>); 35 min; desorbed in 50 µL MeOH/AC (50:50, <i>v/v</i>) by US, 2 min	LC–MS/MS	LOQs 0.01–1.11 mg/L; RSD 4.7–7.6%; relative recoveries given for different samples	Proposed hollow-fiber microporous membrane liquid–liquid extraction (HF–MMLLE); triangular surface mixture design for method optimization	[44]
2-phase	Vegetables: tomato, cabbage, water convolvulus	Chlorpyrifos, profenofos	Homogenized s.s., 12 g + 20 mL AC, US 30 min, filtered	PP1, 1.5 cm; WS + AS 3 µL <i>n</i> -dodecane; 11 mL sample; 1360 rpm, 30 min	GC–ECD	LOQs 0.331–0.427 µg/mL; RSD 0.54–8.00%	Accuracy (as η) 60.8–88.0%	[45]
3-phase	Environmental water, honey, tomato	7 triazine herbicides	Water: filtered; honey: dissolved in UPw 1:10; tomato: juiced, juice centrifuged, supernatant diluted to 100 mL with UPw, filtered	PP1, 3 cm; WS decane, AS 10 µL 1 mol/L H ₃ PO ₄ ; sample 6 mL with 15% NaCl (<i>m/v</i>); stirring 1200 rpm for 40 min; AS neutralized (NaOH) before analysis	Sweeping MEKC	LODs 0.07–0.69 µg/L; EFs 3100–10,000; RSD < 12%	Method validated by analyzing a CRM	[46]

Table 2. Cont.

HFME	Sample	Analytes	Preliminary Sample Preparation	Extraction Conditions	Analytical Technique	Method Performance	Additional Features	Reference
3-phase comb. with DLLME	Grape juice	Parathion-methyl, chlorpyrifos, difenoconazole	None	PP1, 2 cm on SS-wire; WS dodecanol; sample 9 mL + 0.5 mL buffer (pH 6) + 250 µL HX/AC (1:7.5 v/v); agitated 60 min; fiber desorbed with 100 µL ACN, 10 min (US)	HPLC–DAD	LOQs 58–107 µg/L; RSD 3.5–16.3%	2-level factorial design for optimization; calibrated for each sample by SAD	[47]
3-phase	Apple juice	Carbendazim, thiabendazole	None	PP1, 7.5 cm; WS 1-octanol; AS 20 µL 5 mM HCl pH 2.5; sample 4 mL pH 7.5; 800 rpm, 40 min	HPLC–FLD	LODs 0.8–1.5 µg/L; RSD 3.3–8.5%; EFs 106–114	Accuracy (as η) 86.3–106.0%	[48]
3-phase	Roots of <i>Panax ginseng</i>	5 pesticides	Roots crushed; powder sieved (0.25 mm mesh)	PP1, 4 cm; WS 1-octanol; AS aqueous sol. pH 3; sample 500 mg + 5 mL 10% NaCl solution, US nebulized; 20 min; eluted (2×) with 200 µL MeOH 5 min; evaporated, re-dissolved in 10 µL MeOH	HPLC–UV	LODs 12.4–22.2 µg/kg; RSD 3.3–13.1%	Analytes extracted to 10% NaCl solution, nebulized and extracted by 3-phase HFME from headspace; accuracy (as η) 78.2–116.2%	[49]
3-phase	Orange juice	Fungicides thiabendazole, carbendazim, imazalil	None	PP3, 2.2 cm; WS 2-octanone; AS 20 µL 10 mM HCl; sample 3 mL + 0.5 mL 0.84 M NaOH; 1000 rpm, 30 min	CE, LC–MS	LOQs 0.17–0.33 µg/L; RSDs 3.4–10.6%; η 17.0–33.7%	Fiber attached to pipette tip	[50]
3-phase, online	Vegetables	8 carbamate pesticides	12.50 g s.s. + 25 mL buffer sol. (83.8 mM Na ₂ HPO ₄ + 23.4 mM KH ₂ PO ₄ , pH 7.5), vortex 2 min, kept 3 min, filtered 0.22 µm	PP4, 10 cm; WS dodecanol; AS 10 µL 0.3 M NaOH sol.; sample 5 × 1 mL, F = 2 mL/min; 25–30 °C, 22 min	EFA–UV	LOD carbaryl 2 µg/kg; RSD 1.0–4.3%; EFs 300	Wash cycle with 2 mL MeOH between extractions	[51]
3-phase, online	Vegetables, fruit	4 carbamate pesticides	10 g s.s. + 10 mL buffer 83.8 mM Na ₂ HPO ₄ + 23.4 mM KH ₂ PO ₄ (pH 7.5) homogenized (2×), filtered	PP5, 7 mm; WS dodecanol; AS 0.20 µL buffer 30 mM methylamine hydrochloride (pH 11.6) + 0.5 mM tetradecyltrimethylammonium bromide; sample 15 mL; 25–30 °C; 800 rpm, 15 min	CZE	LODs 6–10 ng/g; RSD 4.5–5.5%; EFs 1100–1410; accuracy (as η) 90.3–92.7%	HFME followed by base-stacking prior to CZE	[52]

Table 2. Cont.

HFME	Sample	Analytes	Preliminary Sample Preparation	Extraction Conditions	Analytical Technique	Method Performance	Additional Features	Reference
Animal plasma and tissues								
2-phase	Fish tissue (grass carp, tilapia, turbot)	8 organophosphorous pesticides	8 g frozen tissue + 5 g activated anhydrous Na ₂ SO ₄ + 2× 15 mL AC, US 25 min, centrifuge 5000 rpm 10 min; extracts evaporated under vacuum to near dry, re-dissolved in 8 mL of 5% (v/v) MeOH/UPw	PVDF1, 2 cm sealed at one end; WS + AS 30 µL <i>o</i> -xylene; 8 mL sample extract; 500 rpm, 30 min	GC–MS	LOQs 7.0–15.2 ng/g; RSD 4.8–18.1%	Compared to SE + gel permeation chromatography clean-up	[30]
2-phase	Orange juice, tomato pulp, porcine plasma	40 persistent organic pollutants incl. 20 organochlorine pesticides	None	PP1, 2.6 cm; WS + AS toluene; sample 4 mL; 1100 rpm, 37 min, 46 °C	GC–MS/MS	Orange juice: LODs 12–39 ng/L; EFs 38–60; tomato pulp: LODs 38–182 ng/L; EFs 53–170; porcine plasma: LODs 12–160 ng/L; EFs 1–146; only for some analytes: RSD 1–18% and accuracy (as η) 65–120%	Full second-order central composite design for parameter optimization; HF attached to micropipette tip	[53]
Other types of food								
2-phase	Cereal-based baby food, wheat flour	13 organophosphorous pesticides including metabolites	1.5 g s.s. + 20 mL ACN + 1.25% (v/v) HCOOH shaken (2 min), US (5 min), centrifuged; supernatant filtered 0.45 µm (2× repeated); extracts combined, evaporated to dry under vacuum, re-dissolved in 10 mL UPw	PP1, 2 cm; WS + AS 1-octanol 20 µL; sample 10 mL pH 7 + 5% (w/v) NaCl; 960 rpm, 45 min; fiber desorbed in 350 µL ACN 10 min (US), evaporated, re-dissolved in 50 µL of CyHX	GC–NPD	LOQs 0.96–10.7 µg/kg	Fiber additionally desorbed in ACN after extraction	[54]

Table 2. Cont.

HFME	Sample	Analytes	Preliminary Sample Preparation	Extraction Conditions	Analytical Technique	Method Performance	Additional Features	Reference
Other samples								
2-phase, dynamic	Human plasma	5 nitrophenolic herbicides	1 mL plasma + 0.5 mL UPw mixed 30 min, then added 0.9 mL UPw, 0.1 mL <i>i</i> -propanol, 2 drops H ₂ SO ₄ , US 1 min	PP2; WS dihexyl ether; AS aqueous pH 10, <i>F</i> = 7.5 µL/min; sample pH 2/6 + 10–400 mM NaCl, <i>F</i> = 30 µL/min	LC–MS	LOQs 0.05–0.1 µg/mL; RSD 1–4%; EFs 40–205	Experimental design for parameter optimization; dynamic system with donor and acceptor phase flow by syringe pumps; wash cycle 30 min between extractions to prevent carry-over	[55]
2-phase	Textiles (cotton, terylene, fur)	10 organochlorine pesticides	Textile piece 5 mm × 5 mm extracted with 100 mL NaCl solution (0.5%) in US (40 min), 8 mL to HFME	PVDF1, 1.5 cm sealed at one end; WS + AS 30 µL <i>n</i> -octanol; 8 mL sample extract in 0.5% NaCl; 800 rpm, 50 min	GC–MS	LODs 0.07–2.30 ng/g; RSD 0.6–10.8%	Compared to SPME method (PDMS fiber) and to SE (AC, HX)	[56]
2-phase microdialysis	Microbial cell culture	Alachlor and its metabolite	Dilution	Regenerated cellulose HF 20 cm; WS + AS hexane at <i>F</i> = 4 µL/min; 50 mL sample pH 7	HPLC–UV	LODs 14–72 ng/mL; RSD < 5%; EFs 386–403 (for 40 cm HF and <i>F</i> 0.1 µL/min)	Microdialysis method using an HF as dialysis membrane	[57]

Abbreviations: WS—fiber wall solvent; AS—acceptor solvent in the fiber lumen; PP1—polypropylene fiber Accurel (Q3/2 PP, 600 µm inner diameter (i.d.), 200 µm wall thickness, pores 0.2 µm, 66% porosity); PP2—polypropylene fiber 50/280 (280 µm i.d., 50 µm wall thickness, 0.1 µm pores, 40–60% porosity); PP3—polypropylene fiber (1200 µm i.d., 200 µm wall thickness, 0.2 µm pores); PP4—polypropylene fiber (450 µm i.d., pores 0.45 µm); PP5—polypropylene fiber (400 µm i.d., 70 µm wall thickness, 0.2 µm pores); PVDF1—polyvinylidene fluoride fiber (1.2 mm i.d., 200 µm wall thickness, pores 0.2 µm); SAD—standard addition; SPE—solid-phase extraction; SS—stainless steel; US—ultrasonication; η—recovery, LOD—limit of detection; LOQ—limit of quantification; EF—enrichment factor; RSD—relative standard deviation in %; *F*—flow rate; s.s.—solid sample. Solvents: AC—acetone; ACN—acetonitrile; CyHX—cyclohexane; EtAc—ethyl acetate; HX—*n*-hexane; IL—ionic liquid; MeOH—methanol; TOPO—tri-*n*-octyl phosphine oxide; UPw—ultrapure water (or MilliQ). Techniques: CZE—capillary zone electrophoresis; DAD—diode array detection; ECD—electron capture detection; EFA—electrokinetic flow analysis; FLD—fluorescence detection; GC—gas chromatography; (HP/UP)LC—(high-performance/ultrahigh-performance) liquid chromatography; IM—ion mobility spectroscopy; MEKC—micellar electrokinetic chromatography; MS—mass spectrometry; MS/MS—tandem mass spectrometry; UV—ultraviolet spectrometry.

Perhaps a notable omission of most publications is the lack of comparison of the performance of the developed HFME method with some more established extraction approaches. Results are rather frequently compared to results from other publications from different authors, using a different extraction. However, such a comparison is seldom accurate or meaningful, because, in the compared publications, different analytical techniques were used (or, at least, a different instrument and method conditions), and, more than once, there was even difference in the type of analyzed samples. There are exceptions to this oversight, however. Cai et al. [56] compared the developed two-phase HFME method for determination of organochlorine pesticides in textiles with SPME and with classical solvent extraction. The HFME method yielded comparable precision and accuracy, with somewhat lower LOQs, but longer extraction time. Nevertheless, HFME performed best in terms of cost and low environmental impact. Sun et al. [30] developed a method for determination of organophosphorus pesticides in fish tissue. Frozen tissue was submitted to ultrasound-assisted solvent extraction and the clean-up of the extracts was done by two-phase HFME. The method was partially validated, and the results were compared with the standard method using solvent extraction with clean-up by gel permeation chromatography. Results were comparable, but HFME was less labor-intensive, less time-consuming, and more cost-efficient. Msagati and Mamba [39] compared the extraction efficiency of three-phase HFME and SPE for *N*-carbamate pesticides in water. Results were confusing, however, because, for both extraction approaches, the recoveries were in a very wide range from 0% to almost 100%. Calculated EFs in HFME also ranged from 1–9.

In the reviewed publications, some interesting new methodologies were found. For two-phase HFME, additional desorption from the fiber was sometimes applied, minimizing the possible losses of analyte remaining in the residual solvent in fiber wall [35,54]. Desorption was in fact obligatory in the work by San Román et al. [35], because air was present in the fiber lumen and solvent was only in the fiber wall. An interesting approach was proposed by Bedendo et al. [44], named hollow-fiber microporous membrane liquid–liquid extraction (HF-MMLLE). A dry (i.e., solventless) HF was immersed into the sample to which a small amount (ca. 4–5%) of non-polar organic solvent and a soluble inorganic salt were added. After extraction, the fiber was desorbed in a polar solvent. Li et al. [49] described an ultrasonic nebulization extraction coupled to headspace HFME for extraction of pesticides from a plant root sample. A suspension of powdered sample in NaCl solution was nebulized by ultrasound. An HF with wall solvent and acceptor solution was suspended in the headspace, and pesticides were extracted from the nebulized microdrops by three-phase HFME.

Dynamic HFME methods are described as well. Hansson et al. [55] applied a dynamic system consisting of two syringe pumps (for donor/sample and acceptor solutions) for HF microextraction of nitrophenolic herbicides from human plasma. Raharjo et al. [38] used a continuous replenishment of acceptor phase in the fiber lumen in small steps up to the final volume. Although not strictly a dynamic system, it was adopted with a rationale of preventing solvent loss during extraction and provided better EFs. A two-phase HFME method was also applied as a microdialysis method for extraction of alachlor and its metabolite from a microbial cell culture [57]. The sample was static, while the acceptor phase (same as the wall solvent) was perfused at an optimal flow rate through the HF. Finally, two publications from the same research group showed the applicability of three-phase HFME for online coupling to electrokinetic flow analysis [51] or to capillary zone electrophoresis (CZE) [52]. In the latter case, analytes were further preconcentrated by base-stacking before CZE [52].

The work by Huang et al. [58] is not included in Table 2 because it is not considered a “true” HFME. Instead, it is a combination of dynamic two-phase HFME combined with the single-drop microextraction (SDME) approach. The solvent was cooled during extraction to diminish evaporation. Because of increased solvent volume, higher EFs were obtained. The main drawbacks, however, were longer equilibration times and higher relative standard deviation (RSD).

Another approach that does not fit exactly into the HFME definition is described in publications by Wu et al. [59] and Wang et al. [60] from the same research group. Polypropylene hollow fiber was reinforced by oxidized multi-walled carbon nanotubes (MWCNTs) by dispersing them in the fiber

pores with the help of 1-octanol. A metal wire was subsequently inserted into the HF so that no lumen was available. Extraction of triazine [59] or organophosphorus pesticides [60] from the sample was performed by adding a small volume of non-polar organic solvent to the sample and inserting the MWNCT-reinforced HF. Analytes were extracted to the dispersed organic solvent and subsequently transferred to the fiber wall and sorbed to MWCNT. After extraction, they were desorbed in a suitable polar solvent. Although applying an HF membrane, this approach is more a combination of solvent microextraction with sorbent microextraction; the membrane serves only as a holder for the sorbent.

Finally, the paper by Valenzuela et al. [33] was very interesting, not because of any new extraction combination, but because of its potential wide usability. In the paper, authors described an in situ passive sampling device for monitoring and estimating the time-weighted average of pesticides in natural waters. The device was made of a disposable plastic bottle with custom-made holes with a long hollow fiber inside. Since this is a very recent publication, this innovative approach is expected to be encountered more often in upcoming years.

5. Applications of SBME for Extraction of Pesticides

Solvent bar microextraction is a more recent technique compared to “classical” HFME [14]. A recent review on this technique [15] extensively covered the extraction of organic compounds, but only some of them were pesticides. Likewise, in our review of the literature for the last 10 years, a total of 17 publications [61–77] were found in Web of Science in which SBME was applied to pesticide extraction, which is less than for HFME. These applications are presented in Table 3. Entries in Table 3 are organized according to the type of sample. Where different types of samples were analyzed in the same paper, the paper was entered under the most complex sample. It is of interest to note here that several papers preferred to use the name HFME in spite of applying the SBME approach [66–69,72–75,77].

Most of the discussion in the previous chapter, related to publications dealing with HFME methods, can be applied to SBME publications as well. The majority of papers presented the optimization of SBME variables and the validation of the optimized method for a certain type of samples. EFs were given in some papers, but recoveries (i.e., accuracy) of the method were more frequently calculated.

Comparison with results of different extraction approaches were given only in a few publications. Piao et al. [75] developed a method for extraction of triazines from solid food samples (e.g., peanuts) with matrix solid-phase dispersion (MSPD) and clean-up with SBSE. Results were compared with extraction with MSPD only and extraction with SBME only. Guo and Lee [65] compared the optimized three-phase SBME method with hydrophobic ionic liquid as wall sorbent and alkaline aqueous acceptor solution with three-phase SBME with 1-octanol as acceptor solution and with three-phase “classical” HFME with the same ionic liquid as wall solvent. Xu et al. [62] extracted acidic herbicides from river water via two-phase SBME (1-octanol as solvent) and compared the results with two-phase HFME and single-drop microextraction using the same solvent. In all three papers [62,65,75], the results of the developed SBME method were superior to results of the compared methods.

Two developments of the SBME approach were noted in the reviewed publications. The first was the addition of sorbents, usually in the form of nanoparticles, to the acceptor solution (most often 1-octanol) [66,67,72–74]. The added sorbents were graphene [67,74], octadecylsilica-graphene [72], mesoporous carbon [66], and MWCNT [73]. The addition of a sorbent improved the extraction efficiency, but the disadvantage was the need to desorb the analytes after extraction, using a suitable solvent.

The second modification was the inclusion of a small piece of stainless-steel wire into the solvent bar, thereby creating a magnetic solvent bar [63,70,71]. The only real advantage of the proposed approach seems to be the ease of collection of the solvent bars from the sample after extraction.

Table 3. Applications of SBME for extraction of pesticides.

SBME	Sample	Analytes	Preliminary Sample Preparation	Extraction Conditions	Analytical Technique	Method Performance	Additional Features	Reference
Water samples								
2-phase	Environmental waters	4 organophosphorous pesticides	None	PVDF3, 4 cm; WS + AS IL [C ₈ mim] PF ₆ ; sample 25 mL; 30 °C; 600 rpm, 60 min; washed with 100 µL ACN	HPLC–UV	LOQs 0.050–0.087 µg/L; RSD 0.91–3.26%;	Accuracy (as η) 86.71–103.7%	[61]
2-phase	River water	6 acidic herbicides	None	PP1, 2 cm; WS + AS 1-octanol 10 µL; sample pH 1; 700 rpm, 30 min; diluted with MeOH (2×)	NACE–UV	LODs 0.08–0.14 ng/mL; RSD 6.09–10.8%	Comparison: single-drop microextraction and HFME, both with 1-octanol	[62]
2-phase magnetic	Bottled, tap, ground, river water	6 triazine pesticides	None	PP1, 2.2 cm + SS wire; WS IL [C ₄ MIM] [PF ₆]; sample 10 mL pH 4 + 2.5 g NaCl + 10 µL [C ₈ MIM] [BF ₄] + 0.1 g NH ₄ PF ₆ ; 9 bars added to collect extract, 750 rpm, 15 min; eluted with 0.8 mL MeOH, 5 min, evaporated	HPLC–DAD	LOQs 0.46–1.59 µg/L; RSD 0.1–9.2%	Accuracy (as η) 73.4–118.5%	[63]
2-phase	Environmental water including seawater	Lindane, aldrin, terbutylazine atrazine	Filtered: 0.7 µm pore size glass filter	PP6, 2 cm; WS + AS toluene; sample pH 6 + 35 g/L NaCl; 40 rpm, 60 min	GC–µECD	LODs 0.001–0.086 µg/L; RSD 2.8–9.6%, EFs 40–107; accuracy (as η) 79–113%	Sample salinity up to 35 g/L (real seawater) no effect	[64]
3-phase	Seawater	6 phenols including pentachlorophenol	None	PP1, 2.2 cm; WS IL [BMIM] [PF ₆]; AS 4.8 µL 0.1 M NaOH solution; 10 mL sample + HCl to 0.1 M + 15% NaCl; 60 °C; 700 rpm, 20 min	HPLC–UV	PCP: LOD 0.05 µg/L; RSD 7.2%; EF 99	comparison: conventional 3-phase SBME (AS 1-octanol) and 3-phase HFME with same IL as AS	[65]

Table 3. Cont.

SBME	Sample	Analytes	Preliminary Sample Preparation	Extraction Conditions	Analytical Technique	Method Performance	Additional Features	Reference
Soil and sediment samples								
3-phase with MC	Water, soil, sediment	4 phenylurea pesticides	Water: filtered 0.45 µm; soil and sediment: air-dried and sieved, washed with 19 mL UPw + 2× 1 mL ACN; liquids combined and diluted to 20 mL with UPw	PP1, 6 cm; WS 1-octanol; AS 15 µL 1-octanol + 1.5 mg/mL MC; 20 mL sample solution + 3 g NaCl; 800 rpm, 30 min; desorbed with 50 µL ACN 2 min (vortex)	HPLC–DAD	Water: LODs 0.05–0.1 ng/mL, RSD 4.6–6.2%; soil: LODs 0.5–1.0 ng/g, RSD 5.7–6.8%	MC particles dispersed in AS, but desorption with ACN needed to change solvent	[66]
Fruit and vegetables, whole or juice								
2-phase with graphene	Fruit (apple, pear)	4 carbamate pesticides	Homogenized s.s., centrifuged (4000 rpm, 5 min), washed 2× 1 mL ACN; liquids combined and diluted to 15 mL with UPw	PP1, 6 cm; WS 1-octanol; AS 15 µL 1-octanol + 2 mg/mL graphene; 15 mL sample solution + 10 µL 1-octanol + 2.25 g NaCl; 800 rpm 30 min; desorbed with 50 µL MeOH 2 min (vortex)	HPLC–DAD	LODs 0.2–1.0 ng/g, RSD 6.2–7.8%, EFs 60–70	/	[67]
2-phase	Cucumbers	7 pesticides: propoxur, carbofuran, atrazine, cyanatryn, metolachlor, prometryn, tebuconazole	2 g of homogenized s.s. + 5 mL UPw; shaken + US; centrifugated	PVDF2, 8 cm; WS + AS: 32 µL CHCl ₃ ; 5 mL sample supernatant; 300 rpm, 20 min; desorbed 1 min; solvent exchange to MeOH/UPw (1:1)	UPLC–MS/MS	Method parameters for UPw only: LOQs 0.05–1.0 µg/kg; EFs 100–147	Matrix effect as ratio of calibration slopes matrix/UPw 76.25–121.62%	[68]
2-phase	Cucumbers	7 pesticides: propoxur, carbofuran, atrazine, cyanatryn, metolachlor, prometryn, tebuconazole	2 g of homogenized s.s. + 5 mL UPw; shaken + US; centrifugated	PVDF2, 8 cm; WS + AS: 32 µL CHCl ₃ ; 5 mL sample supernatant; 300 rpm, 20 min; desorbed 1 min; concentrated to 32 µL	IMS	LODs 0.02–0.1 mg/kg, RSDs 0.7–14.5%, matrix effect 79.87–98.77%	Accuracy as η from spiked samples: 60.92–88.48%	[69]

Table 3. Cont.

SBME	Sample	Analytes	Preliminary Sample Preparation	Extraction Conditions	Analytical Technique	Method Performance	Additional Features	Reference
2-phase magnetic	Fruit juice (lemon, orange, apple, peach)	8 organophosphorous pesticides	None	PP1 + SS wire 1.2 cm; WS + AS 1-octanol; 6 bars; sample 10 mL + 10% NaCl; 30 °C; 600 rpm, 25 min; elution 400 µL MeOH (US 3 min); evaporated to dry, re-dissolved in 100 µL HX, filtered	GC–MS	LOQs 0.06–0.32 µg/L; RSD 1.0–6.1%	Parameters optimized by three-factor, three-level Box–Behnken design; accuracy (as η) 81.3–104.6%	[70]
2-phase magnetic	Pears	4 sulfonylurea pesticides	Homogenized	PP1 + SS wire 1.2 cm; WS + AS CHCl ₃ ; 8 bars; sample 1 g + 5 mL UPw pH 3 + 10% NaCl; 30 °C; 700 rpm, 20 min; desorbed with 500 µL ACN (US 5 min); evap. to dry, re-dissolved in 100 µL ACN, filtered	HPLC–UV	LOQs 24.99–27.52 ng/g; RSD 1.3–6.8%	Accuracy (as η) 80.08–105.56%	[71]
3-phase with NP	Vegetables (radish, rape)	4 carbamate pesticides	Homogenized s.s.; centrifuged (4000 rpm, 5 min) and 2× washed with 1 mL AC; combined liquid phase diluted to 15 mL with UPw	PP1, 6 cm; WS 1-octanol; AS 15 µL 1-octanol + 2 mg/mL ODS-graphene; 15 mL sample solution + 10 µL 1-octanol + 2.25 g NaCl; 800 rpm 30 min; desorbed with 50 µL MeOH 2 min (vortex)	HPLC–UV	LOQs 0.6–1.8 ng/g; RSD 6.4–7.3%	ODS-graphene NPs dispersed in AS, but desorption to solvent (MeOH) needed	[72]
3-phase with MW CNT	Tap and lake water, fruit	5 carbamate pesticides	Water: filtered; fruit: homogenized, centrifuged	PP1, 9 cm; WS 1-octanol; AS 20 µL MWCNT (1 mg/mL) in 1-octanol; sample 15 mL + 10 µL 1-octanol + 3.75 g NaCl; 800 rpm, 30 min; desorbed with 50 µL MeOH 5 min (US)	HPLC–DAD	LODs 0.1–2 ng/g; RSD 3.1–9.2%; accuracy (as η) 77.5–103.7%	MWCNT particles dispersed in AS, but desorption with MeOH needed	[73]

Table 3. Cont.

SBME	Sample	Analytes	Preliminary Sample Preparation	Extraction Conditions	Analytical Technique	Method Performance	Additional Features	Reference
Other types of food								
2-phase with graphene	Milk	5 phenylurea pesticides	None	PP1, 7 cm; WS 1-octanol; AS 20 µL 1-octanol + 2 mg/mL graphene; 15 mL sample solution + 10 µL 1-octanol + 2.25 g NaCl; 800 rpm, 30 min; desorbed with 75 µL ACN 1 min (vortex)	HPLC–UV	LOQs 4.6–6.0 µg/L; RSD 5.2–7.3%	Graphene particles dispersed in AS, but desorption with ACN needed to exchange solvent	[74]
2-phase	Peanuts, soybeans	5 triazine herbicides	Crushing of s.s.; MSPD 1 g sample + 1.75 g diatomite; eluted with 7 mL ACN, evaporated & reconstructed in 0.1 mL ACN + 4 mL UPw	PP1, 2 cm; 15 µL of IL [C ₄ mim] [PF ₆]; extract (4.1 mL) + 1.2 g NaCl + pH 8; stirred with 4 SBME bars, 800 rpm, 40 min; cut and IL dissolved in 100 µL ACN	HPLC–UV	LOQs 1.68–5.71 µg/kg; RSD <8.5%; extraction η 89.3–112.8%	Method compared to HFME only and to MSPD only with superior performance	[75]
Other types of samples								
2-phase	Hemolymph lipoproteins in hemipteran <i>Triatoma infestans</i>	Insecticide deltamethrin (DLM)	Insect hemolymph obtained by centrifugation; added phenylmethylsulfonyl fluoride to concentration 2 mM; added DLM in AC; 1 h at 30 °C vortex at 10-min intervals; centrifuged; lipoproteins fractionated by ultra-centrifugation	PP1, 1.2 cm; WS + AS 1-octanol; sample 90 µL lipoprotein fraction + 150 µL AC + UPw to 3 mL; 65 °C; 800 rpm, 20 min	GC–µECD	LOD 0.05 ng	Purpose: to determine DLM binding in vitro to hemolymph lipoproteins in <i>Triatoma infestans</i>	[76]

Table 3. Cont.

SBME	Sample	Analytes	Preliminary Sample Preparation	Extraction Conditions	Analytical Technique	Method Performance	Additional Features	Reference
3-phase	Environmental waters, human urine	Atrazine and 4 metabolites	Water: filtered; urine: left to sediment and filtered	PP2, 20 cm; WS di- <i>n</i> -hexylether; AS 1 M HCl 10–12 µL; 200 mL sample pH 7 (5 mM phosphate buffer) + 20% NaCl; 150 rpm, 5 h; AS neutralized with 7 M NaOH	HPLC–DAD	Water: LOQs 0.1–2.8 µg/L, RSD 5.2–11.1%, EFs 10–2351; urine: LOQs 0.17–3.73 µg/L, RSD 6.1–13.5%, EFs 103–2351	Humic acid addition to water at 0–50% (<i>w/v</i>) no impact on EFs	[77]

Abbreviations: WS—fiber wall solvent; AS—acceptor solvent in the fiber lumen; MC—mesoporous carbon; MWCNT—multi-walled carbon nanotube; NP—nanoparticles; ODS—octadecylsilica; MSPD—matrix solid-phase dispersion; PP1—polypropylene fiber Accurel (Q3/2 PP, 600 µm i.d., 200 µm wall thickness, pores 0.2 µm, 66% porosity), PP2—polypropylene fiber Accurel 50/280 (280 µm i.d., 50 µm wall thickness, pores 0.1 µm), PP6—polypropylene fiber S6/2 (1800 µm i.d., 450 µm wall thickness, 72% porosity), PVDF2—polyvinylidene fluoride fiber (0.80 mm i.d., 0.16 µm pores, 82% porosity); PVDF3—polyvinylidene fluoride (300 µm wall thickness, pores 0.1 µm); s.s.—solid sample; recovery; LOD—limit of detection; LOQ—limit of quantification; EF—enrichment factor; RSD—relative standard deviation in %. Solvents: AC—acetone; ACN—acetonitrile; IL—ionic liquid; HX—*n*-hexane; MeOH—methanol; UPw—ultrapure water (or MilliQ). Techniques: DAD—diode array detection; ECD—electron capture detection; GC—gas chromatography; (HP/UP)LC—(high-performance/ultrahigh-performance) liquid chromatography; IMS—ion mobility spectroscopy; MS—mass spectrometry; MS/MS—tandem mass spectrometry; NACE—non-aqueous capillary electrophoresis; UV—ultraviolet spectrometry.

Practically in all publications reviewed, the developed SBME method for a certain group of pesticides in a certain type of sample was more or less the “proof of concept”. However, Dulbecco et al. [76] developed a two-phase SBME method for a focused purpose: to monitor the in vitro binding of pesticide deltamethrin to hemolymph lipoproteins in a hemipteran *Triatoma infestans*, which is a major disease vector in South America. This insect is controlled by pyrethroid insecticides, among them deltamethrin, but it is developing a resistance. Therefore, the study researched the possible reasons for the resistance development. SBME was chosen because of low solvent consumption and clean extracts with no need for further purification.

6. Applications of EME for Extraction of Pesticides

EME, as compared to HFME and SBME, requires more equipment: a source of electrical current, two electrodes, and some more preliminary preparation, as one of the electrodes has to be inside the HF. There are also additional parameters to optimize. All of the above and the fact that this type of extraction can be applied only to charged compounds probably contribute to a small number of papers dealing with the application of EME for pesticide extraction. Only four publications were found in Web of Science for the last decade [78–81], as can be seen in Table 4. Strictly speaking, two of these publications [79,80] were on the edge of the “microextraction” definition because researchers used a bag made of a polypropylene sheet which contained an increased volume of acceptor solution compared to HF. Both papers were published by the same research group and dealt with the extraction of chlorophenols, including the pesticide pentachlorophenol (PCP) from seawater [80] or from drain water [79]. In the method by Guo and Lee [79], additional clean-up of extracts was performed by ultrasound-assisted emulsification microextraction with low-density solvent and concurrent derivatization.

Another interesting publication is the work by Nilash et al. [81], who extracted fungicide thiabendazole from fruit juice by using an HF impregnated with silica mesoporous material SBA-15 suspended in 2-nitrophenyl-octylether. The acceptor solution in the fiber lumen was 0.1 M HCl. The results were compared to standard EME without the SBA-15 material and were found to be superior.

Table 4. Applications of electromembrane extraction (EME) for extraction of pesticides.

EME	Sample	Analytes	Preliminary Sample Preparation	Extraction Conditions	Analytical Technique	Method Performance	Additional Features	Reference
Water samples								
3-phase	Tap and river water	Fungicides thiabendazole, carbendazim	Filtered; tap water: ascorbic acid added (10 mg/L) to remove chlorine	PP7, 2.8 cm; WS ENB; AS 20 µL 10 mM HCl solution + Pt wire $d = 0.2$ mm; sample + HCl to 1 mM, counter-electrode Pt wire $d = 0.3$ mm; 300 V, 1300 rpm, 15 min	CE–UV	LODs 1.1–2.3 µg/L; RSD 2.5–2.8%; EFs 26–50	Face-centered central composition design for parameter optimization	[78]
3-phase	Drain water	6 chlorophenols incl. pentachlorophenol	None	PP8, bag 3.0 cm × 1.5 cm; WS 1-octanol; AS 1 mL pH 12 + electrode; sample 100 mL pH 12 + electrode; 50 V, 1000 rpm, 10 min	GC–MS	LOQs 0.030–0.070 µg/L; RSD 5.1–9.7%; EFs 1450–2198; accuracy (as η) 78–105%	Followed by low-density solvent-based US-assisted emulsification microextraction + derivatization	[79]
3-phase	Seawater	Chlorophenols including pentachlorophenol (PCP)	None	PP8, bag 2.2 cm × 0.6 cm; WS 1-octanol; AS 20 µL pH 12; sample 1 mL, pH 12; 10 V, 1250 rpm, 10 min	HPLC–UV	PCP: LOQ 0.4 ng/mL; RSD 6.8%; EF 23; Accuracy (as η) 74%	Compared to HFME at same conditions except electric current	[80]
Fruit juice samples								
3-phase	Fruit juice (lemon)	Thiabendazole	Centrifuged	PP1, 6 cm; WS silica nanoporous material SBA-15 (3 mg/mL) in NPOE; AS 20 µL 0.1 M HCl solution + Pt wire; sample pH 2 + Pt wire; 175 V, 100 rpm, 30 min	CD–IMS	LOD 0.9 ng/mL; EF 167; η 83%	Compared to conventional EME	[81]

Abbreviations: WS—fiber wall solvent; AS—acceptor solvent in the fiber lumen; PP1—polypropylene fiber Accurel (Q3/2 PP, 600 µm i.d., 200 µm wall thickness, pores 0.2 µm, 66% porosity); PP7—polypropylene fiber (1.2 mm i.d., 300 µm wall thickness, pores 0.2 µm); PP8—polypropylene membrane sheet (157 µm thickness, 0.2 µm pores); d —diameter; η —recovery; LOD—limit of detection; LOQ—limit of quantification; EF—enrichment factor; RSD—relative standard deviation in %. Solvents: ENB—1-ethyl-2-nitrobenzene; NPOE—2-nitrophenyl-octylether. Techniques: CD—corona discharge; CE—capillary electrophoresis; GC—gas chromatography; HPLC—high-performance liquid chromatography; IMS—ion mobility spectroscopy; MS—mass spectrometry; UV—ultraviolet spectrometry.

7. Conclusions

Comparison of the performance of the developed methods based on HFME, SBME, and EME (Tables 2–4) shows that they are very comparable in terms of EFs, LODs or LOQs, consumption of sample, and consumption of solvents. The latter is an especially important aspect for assessing the method from the point of GAC. There are several tools to measure the “green-ness” of the analytical method; the most known are the Analytical Eco-Scale [82] and Green Analytical Procedure Index [83]. Although a direct comparison of the papers using these tools would not be valid, because they were not applied for the same analytes and on the same samples, a quick evaluation using the Analytical Eco-Scale tool shows that they would mostly fall in the category of excellent green analysis due to the small amount of solvent per sample (<1 mL), low consumption of energy (<0.1 kWh per sample), hermetic extraction with no emission of solvent vapors, and small amount of generated waste (<1 g, i.e., the fiber) [82]. Therefore, these techniques are prime representatives of green analytical chemistry.

Membrane-based solvent extractions continue to thrive and develop 20 years after the first publication [11]. Although it is not likely that they will ever gain the popularity of sorbent-based microextractions, they offer some interesting possibilities that are not feasible with the latter, such as passive sampling devices or online coupling to capillary electrophoresis. In addition, the hybrid sorbent–solvent membrane-based microextractions appear quite often in the reviewed publications. These are all new trends that are expected to find wider acceptance and applications in the future. Another area of their application that is very much under-developed at present is the direct extraction of solid samples, but there are promising steps in this direction as well [18].

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