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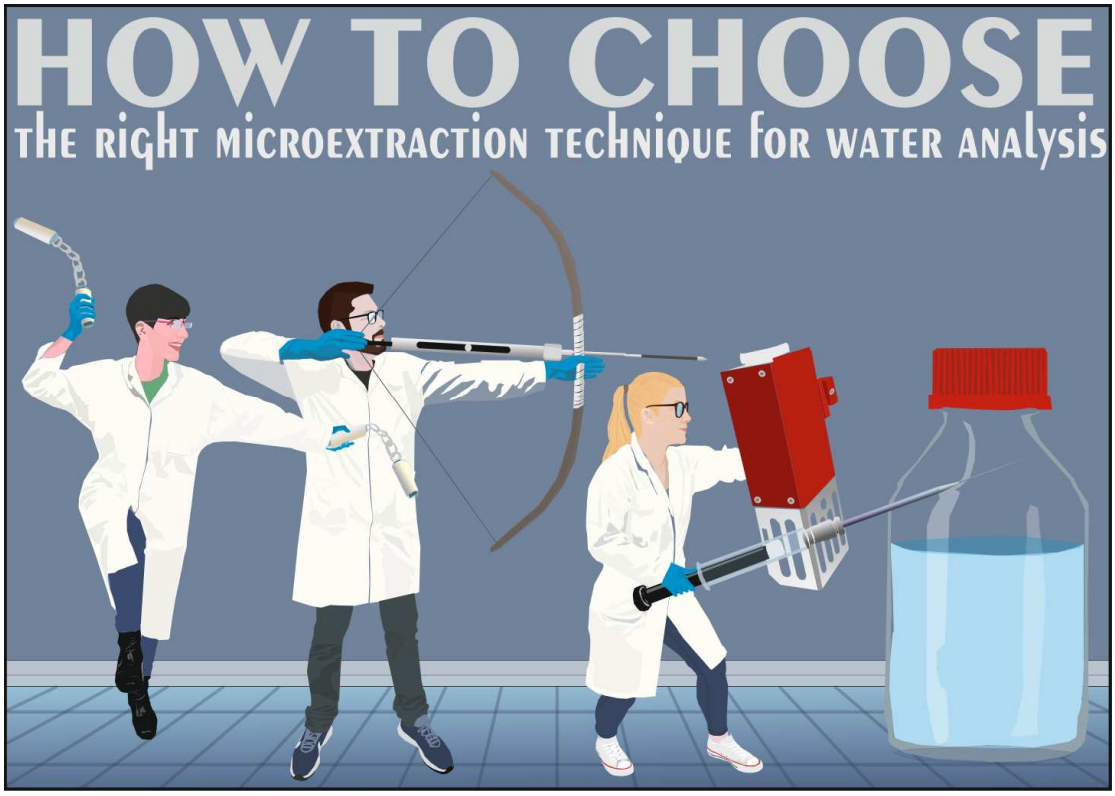
HOW TO CHOOSE
THE RIGHT MICROEXTRACTION TECHNIQUE FOR WATER ANALYSIS

Solventless microextraction techniques for water analysis

Nerea Lorenzo-Parodi[1], Wiebke Kaziur[1], Nenad Stojanović[1], Maik A. Jochmann[1], Torsten C. Schmidt[1, 2, 3].

[1] Instrumental Analytical Chemistry, University of Duisburg-Essen, Universitätsstrasse 5, 45141 Essen, Germany

[2] Centre for Water and Environmental Research, University of Duisburg-Essen, Universitätsstrasse 5, 45141 Essen, Germany

[3] IWW Water Centre, Moritzstrasse 26, 45476 Mülheim an der Ruhr, Germany

Keywords: SPME; SBSE; ITEX-DHS; SPDE; PAL SPME Arrow; GC-MS; Water analysis, Pollutants.

Abstract:

Microextraction techniques have been proven to provide similar or better results in terms of sensitivity and reproducibility in comparison to liquid-liquid extraction (LLE) and solid-phase extraction (SPE). Furthermore, the high time efficiency and decreased workload leads to a higher sample throughput. In this review the state of the art of some of these techniques, namely solid-phase microextraction (SPME), stir-bar sorptive extraction (SBSE), solid-phase dynamic extraction (SPDE), in-tube extraction-dynamic headspace (ITEX-DHS) and PAL SPME Arrow is shown. Furthermore, their benefits and drawbacks are discussed, together with their applicability to the analysis of water samples. To that end, the latest publications of microextraction techniques for a selection of regulated compound classes (chlorophenols (CPs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides, short-chained chlorinated paraffins (SCCPs) and volatile organic compounds (VOCs)) are compared. Finally, a guideline for choosing the best microextraction technique for different analytical needs is described.

Contents

Abbreviations: AC, Activated carbon; CAR, Carboxen; CPs, Chlorophenols; DBPs, Disinfection by-products; DI, Direct immersion; DVB, Divinylbenzene; EPA, Environmental Protection Agency; GC, Gas chromatography; GC/ECNI-MS, Gas chromatography/electron capture negative ionization-mass spectrometry; GC-HRMS, Gas chromatography-high resolution mass spectrometry; GC-MS, Gas chromatography-mass spectrometry; GC-MS/MS, Gas chromatography-tandem mass spectrometry; GC-QqQ-MS/MS, Gas chromatography-triple quadrupole-mass spectrometry; GCxGC-HRTOF, Comprehensive two-dimensional gas chromatography-time of flight high resolution mass spectrometry; GCxGC-TOF, Comprehensive two-dimensional gas chromatography-time of flight mass spectrometry; HS, Headspace; ITEX-DHS, In-tube extraction dynamic headspace; K_{AW}, Air-water partitioning constant; K_{OW},

Octanol-water partitioning constant; K_{PDMSW}, Polydimethylsiloxane-water partitioning constant; K_{PAW}, Polyacrylate-water partitioning constant; LD, Liquid desorption; LLE, Liquid-liquid extraction; LODs, Limits of detection; LOQs, Limits of quantification; MDLs, Method detection limits; NR, Not reported; PA, Polyacrylate; PAHs, Polycyclic aromatic hydrocarbons; PCBs, Polychlorinated biphenyls; PDMS, Polydimethylsiloxane; PP-LFERs, Polyparameter linear free energy relationship; SBSE, Stir-bar sorptive extraction; SCCPs, Short chain chlorinated paraffins; SI, Supplementary information; SIM, Single ion monitoring; SPDE, Solid-phase dynamic extraction; SPE, Solid-phase extraction; SPME, Solid-phase microextraction; TD, Thermal desorption; TOF, Time of flight; VOCs, Volatile organic compounds; WFD, Water Framework Directive; WHO, World Health Organization.

1 INTRODUCTION

As green analytical chemistry becomes more important, the reduction of reagents and organic solvents, and the miniaturization and automation of analytical operations, among others, gain relevance [1]. LLE and SPE are commonly used techniques in analytical laboratories for the analysis of water samples [2], however, they need large solvent volumes and are very laborious [1]. As a result, they are slowly being replaced by novel microextraction techniques, which enrich and enable the direct injection of the analytes into the separation unit, and which require less solvents, time and labor [1, 3]. These microextraction techniques are generally used in combination to gas chromatography-mass spectrometry; which will therefore be the focus of this review.

1.1 Solid-phase microextraction

SPME was first used for the analysis of water samples in 1992 [4]. With this technique, sample preparation was improved upon by combining sampling, extraction, enrichment and sample introduction in a two-step process (Fig. 1a). The analytes partition between the sample and the extraction phase, absorb/adsorb into/onto the extraction fiber, depending on the fiber material used, and are thermally desorbed into the gas chromatography (GC) injector [1, 3]. A detailed explanation of the relevant parameters for SPME and the following techniques can be seen in Section 2.

SPME is widely accepted, especially due to its advantages in comparison to SPE and LLE, such as an increased sensitivity and reduced carry-over and sample losses [2, 5]. However, one of the biggest drawbacks of SPME is the instability of the fibers: breaking and stripping of coatings, and bending of fibers can significantly reduce their overall lifetime [5]. Even though this can be improved by switching from direct immersion (DI) to headspace (HS) extraction, it is still an important drawback to consider.

1.2 Stir-bar sorptive extraction

SBSE was first introduced in 1999 as a novel technique for the analysis of aqueous samples [6]. A stir bar coated with a polymer is used to extract the analytes from the aqueous sample typically by direct immersion, shown in Fig. 1b. The magnetic bar is stirred for a certain extraction time, during which the analytes are absorbed by the coating. Afterwards the bar is manually removed from the sample, rinsed, dried and then either desorbed thermally (thermal desorption, TD) into the injection port of the GC, or with the help of an organic solvent (liquid desorption, LD) and then injected. Therefore, SBSE-LD is not as green of a technique, moreover, the number of required steps is increased and prolongs the procedure. The extraction efficiency is affected by the same parameters as in SPME [1, 6, 7].

SBSE has high pre-concentration capabilities due to the higher volume of sorbent compared with SPME. However, it is not fully automated, and, for TD, it requires a special desorption unit and a cooled injector system. Although significantly longer extraction times are typically used, if several samples are extracted in parallel the average time needed per sample is similar to that of other techniques described here.

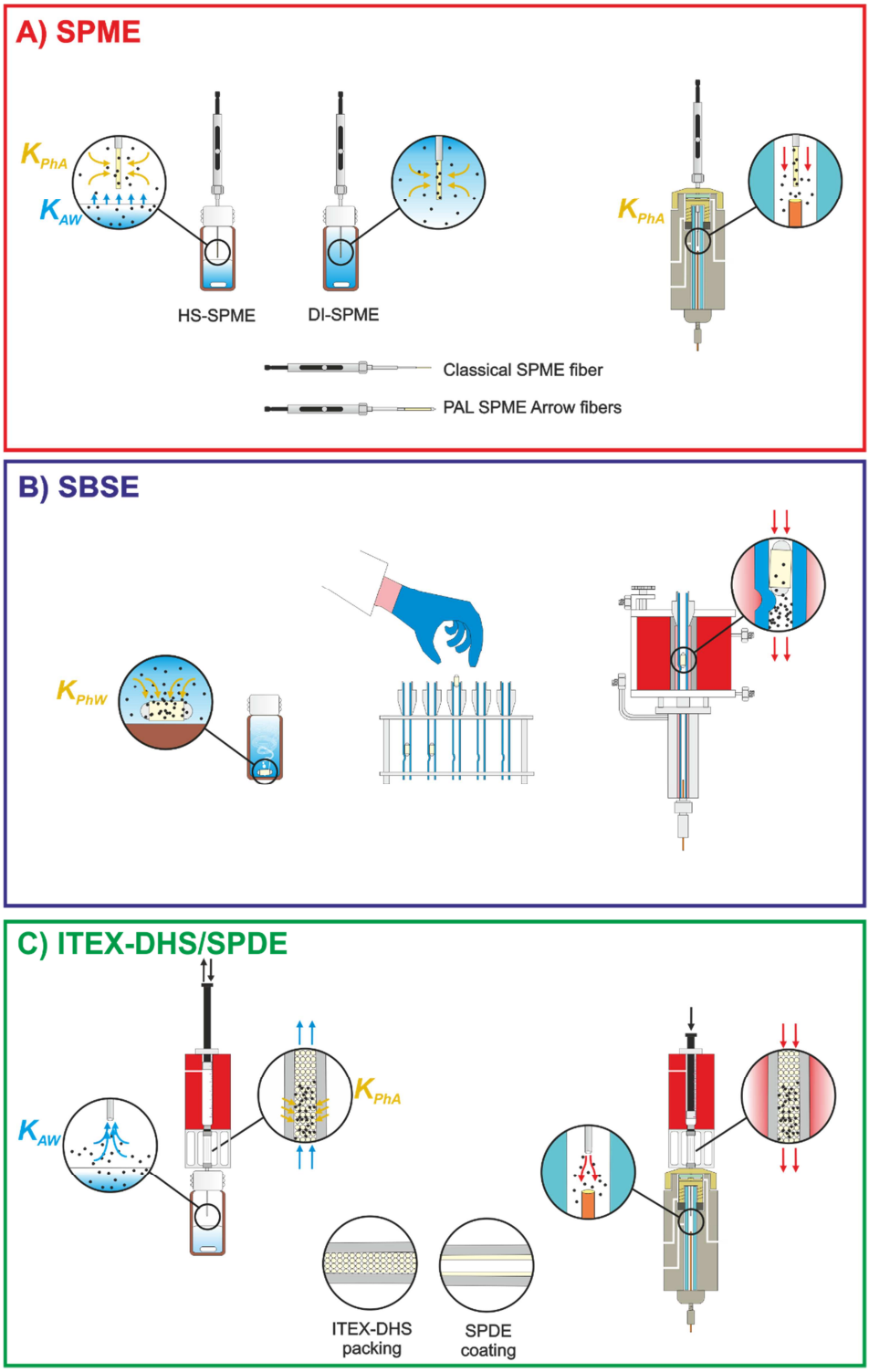

Fig. 1. Comparison of the different techniques discussed in this review: a) SPME/PAL SPME Arrow, b) SBSE and c) ITEX-DHS/SPDE. Sorption depends on the partitioning constants of the analytes between the sorbent phase and water, K_{PhW}, for direct immersion (DI), and between air and the water sample, K_{AW}, and the sorbent phase and air, K_{PhA}, for headspace (HS) sampling.

1.3 Solid-phase dynamic extraction

SPDE was introduced in 2001 with the determination of pesticides in water [8]. It was developed to overcome several SPME drawbacks, particularly the fiber fragility and low sorption capacities. In comparison to SPME, the sorbent material, similar to stationary phases used for GC columns, is placed in the internal surface of a needle, which increases the inter-phase contact and the mechanical stability (Fig. 1c) [1, 3]. Furthermore, in contrast to SBSE, no additional thermal desorption unit is needed, simplifying its integration into a xyz autosampler. Moreover, since it is a dynamic technique with 4-6 times more sorbent material than SPME, an increase in sensitivity and a reduction of the total analysis time can be achieved [3].

The sample is typically pre-incubated at a defined temperature before the extraction step, in which it is repeatedly drawn into the syringe and dispensed out into the vial at a controlled speed. SPDE is usually performed in HS mode since residual water can remain in the needle when doing DI and is then difficult to get rid of. After extraction, desorption gas is aspirated and dispensed into the heated injection port, thermally desorbing the analytes. Afterwards, the syringe is purged with inert gas [3]. The extraction efficiency is affected by an extra set of parameters inherent to this technique, such as volume and flow of the gas used for extraction and desorption or the number of extraction strokes [3, 8].

1.4 In-tube extraction dynamic headspace

ITEX-DHS is a relatively new technique, first described in 2008 for the analysis of VOCs in aqueous samples [9]. A schematic representation of an ITEX-DHS tool can be seen in Fig. 1c. The headspace of the sample is cycled with a 1.3 mL headspace syringe through the sorbent material packed in a stainless steel needle, also called an ITEX-DHS trap. Thermal desorption is performed by heating the trap with a heater unit that surrounds the packed material, and injecting a defined volume of helium into the GC. The same factors as in SPDE influence the extraction efficiency [9].

ITEX-DHS presents several advantages when compared with the previously described techniques, especially the fact that desorption can be performed independently of the injector temperature due to the external heater unit [9]. Even though there is a significant number of

commercially available sorbent materials, so far mostly VOCs from different matrices have been analyzed. This could be due to the fact that ITEX-DHS is only suited for HS extraction.

1.5 PAL SPME Arrow

A different approach to overcome the drawbacks of SPME and SBSE was developed a few years later: the PAL SPME Arrow (Fig. 1a). The fragility of the SPME fiber was improved upon by coating a stainless steel rod with the sorbent material and protecting it, both from contaminations and from mechanical damage, with a sheath that encloses the fiber upon contact with the arrow-like tip [10, 11]. Another advantage derived from the use of such a tip is a gentler penetration of the septa, both in the vial and in the injector [11]. Furthermore, PAL SPME Arrow has a larger sorbent volume, providing a higher extraction capacity and less competition for adsorption sites than SPME. In contrast to SBSE, it can be fully automated, however, only with PAL RTC and RSI autosamplers [10]. Another disadvantage is that the injection port needs to be widened before use due to the bigger dimensions of the fiber [11], unless a modified injector is provided by GC manufacturers, which is becoming the norm with new instruments.

In the first two publications, amines and PAHs were studied in waste and groundwater, respectively, and the same parameters as for SPME were considered for the method optimization [10, 11].

1.6 Selection criteria and general considerations

Many more microextraction techniques were developed in parallel, however, we selected those that are commercially available and can be automated to a degree that allows their use in routine laboratory analysis. Unfortunately, due to a lack of standardization these techniques are not yet widespread for routine analysis (see Table S3). In general, recent publications focus on the development and application of new fiber materials, however, hardly any found its way into commercial success. More detailed accounts of alternative techniques and novel sorption materials can be found in several reviews [1, 5, 7, 12-14].

In recent years concerns have been raised about the use and production of certain substances as a result of a better understanding of their toxicological properties and environmental risks. Several of these substances have been either banned or strictly regulated on a worldwide scale.

For example, the US Environmental Protection Agency (EPA), the European Parliament and Council, and the World Health Organization (WHO) established, under the Clean Water Act, the Water Framework Directive (WFD) and the Guidelines for drinking-water quality, respectively, a list of priority pollutants to be reduced and/or controlled in aquatic environments and drinking water. Furthermore, the Basel, Rotterdam and Stockholm conventions aim to reduce or control the production or transportation of hazardous waste, hazardous chemicals and pesticides, and persistent organic pollutants, respectively.

The aim of this review is to provide an overview of the capabilities of different solventless microextraction techniques for the analysis of such toxicologically and environmentally relevant compounds from water samples and to help with the selection of the best suited microextraction technique for different research questions and its optimization.

2 CHOICE AND OPTIMIZATION OF AN APPROPRIATE MICROEXTRACTION TECHNIQUE

The selection of the optimal microextraction technique for a specific analytical problem can be an overwhelming task, where each technique's advantages and disadvantages (Table 1), as well as the characteristics of the analytes (i.e. the air-water and octanol-water partitioning constants, K_{AW} and K_{OW}) and the question at hand (e.g. need to measure particle-bound analytes) needs to be considered. To help the reader choose the best technique, a decision flowchart can be seen in Fig. 2.

Table 1. Comparison of the microextraction techniques discussed in the review. PAL SPME Arrow is a relatively new technique which could potentially be used for on-site sampling in the future.

	SPME	**SBSE**	**SPDE**	**ITEX-DHS**	**PAL SPME Arrow**
Sampling mode	static	static	dynamic	dynamic	static
Extraction mode	HS / DI	(HS)[1] / DI	HS / (DI)[1]	HS	HS / DI
Phase volume / µL	0.026-0.612	24-126	~4.5	~160	3.8-11.8
Average number of measurement	~50-100	~50-100	~500	~500	~500
Commercial sorbent materials	7	2	6	9	5
Fully automated	✓	✗	✓	✓	✓
Manual extraction possible	✓	✓	✗	✗	✓
Instrument modification needed	✗	✓[2]	✗	✗	✓[2]
On-site sampling	✓	(✓)	✗	✗	(✓)

✓ = Yes, ✗ = No

( ) Extraction modes and on-site sampling techniques that are not commonly used are presented in parenthesis.

[1]For HS-SBSE a special magnet is required to hold the stir-bar(s) in the headspace and a second stir-bar stirs the sample, DI-SPDE is not recommended due to water droplets being retained in the needle.

[2]For SBSE a thermal desorption unit is needed, for PAL SPME Arrow the injection port has to be widened, so that the thicker diameter of the PAL SPME Arrow can fit through the needle guide, septum and liner nut.

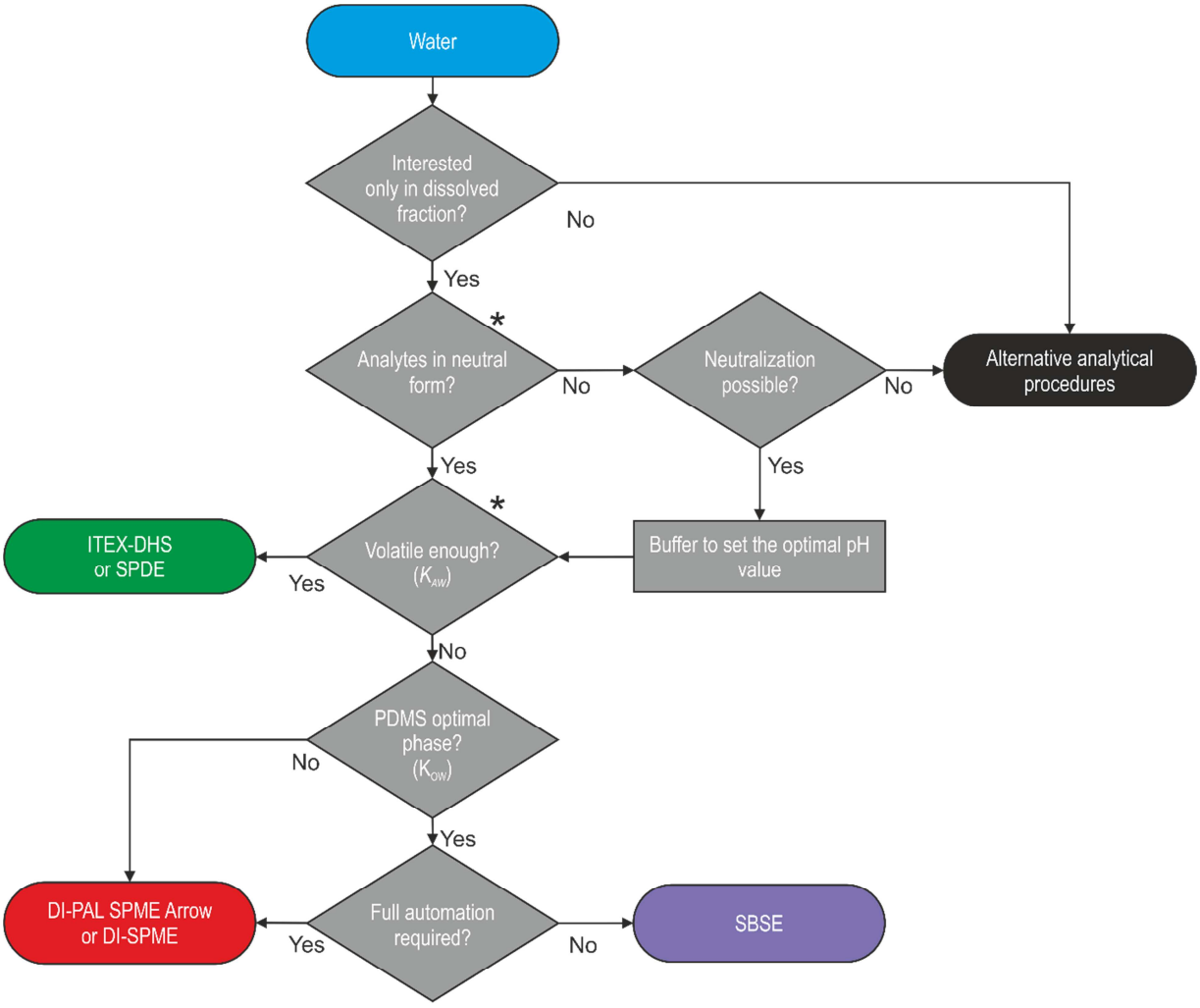

Fig. 2. Flowchart of the selection of the recommended microextraction technique for the analysis of aqueous samples. SPME and PAL SPME Arrow can also be used for HS analysis.

The first and most important step to achieve a successful analysis of an aqueous sample is to understand the behavior of the analytes of interest. If the fraction sorbed into suspended particulate matter (when present) needs to be quantified, alternative analytical techniques should be used. Furthermore, microextraction techniques can be used only if the analytes, or a fraction of them, are present in their neutral form (according to their pKa). It should be mentioned that derivatization can be used to change the chemical properties of the analytes and favor extraction, however, it should be considered with care for each specific situation. Further information regarding the most common derivatization procedures can be found in literature [5, 7, 13].

The analytes´ partitioning constants can help predict whether the extraction should be performed in DI or HS mode, as shown in Fig. 3. The partitioning constants between the sample, the air and the sorbent material can be calculated using polyparameter linear free energy relationships (PP-LFERs) with the help of the UFZ database, although only for polydimethylsiloxane (PDMS) and polyacrylate (PA) (see Supplementary information (SI), A1) [15]. If the partitioning constant between PDMS and water (K_{PDMSW}) is not available, K_{OW} is often used as a substitute, however this only works for apolar compounds showing no relevant specific molecular interactions (see SI, A1).

If the analytes are sufficiently volatile, HS is always preferred over DI extraction. By using HS, more interferences are excluded, equilibrium is reached faster due to the diffusion boundary layer being thinner, and the sorbent material's lifetime is prolonged, discussed for SPME in the following references [1, 16, 17].

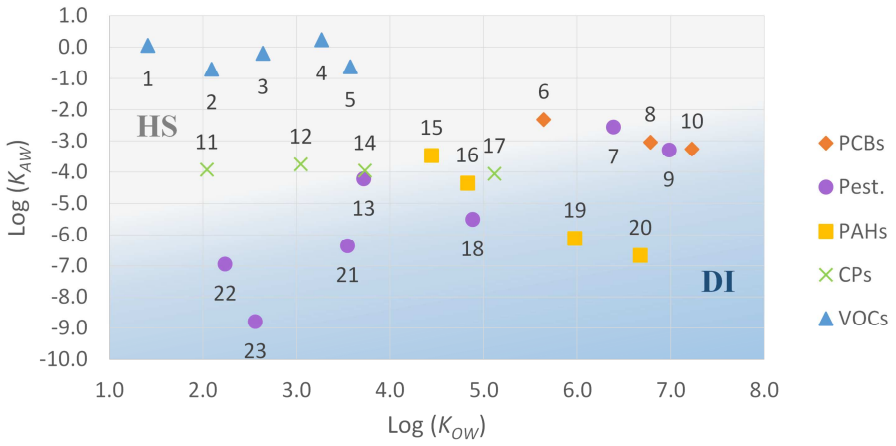

Fig. 3. Logarithm of the air-water partitioning constants (K_{AW}) vs logarithm of the octanol-water partitioning constants (K_{OW}) as a tool to predict the ideal extraction mode: headspace (HS) or direct immersion (DI). HS is recommended for analytes in the grey area and DI for the blue area. In the border between the two extraction modes, the optimal extraction mode cannot be defined, however HS is preferred when possible. Calculated using the UFZ database [15]. Representative analytes from the investigated compound classes are plotted as examples. 1) Chloroethene, 2) Benzene, 3) Trichloroethene, 4) Tetrachloroethene, 5) 1,3,5-Trimethylbenzene, 6) PCB 28, 7) Aldrin, 8) PCB 138, 9) DDT, 10) PCB 180, 11) 2-Chlorophenol, 12) 2,4-Dichlorophenol, 13) Lindane, 14) 2,4,6-Trichlorophenol, 15) Anthracene, 16) Pyrene, 17) Pentachlorophenol, 18) Dieldrin, 19) Benzo[a]pyrene, 20) Benzo[ghi]perylene, 21) Alachlor, 22) Atrazine, 23) Isoproturon.

HS extraction can be performed with all the techniques previously described, however ITEX-DHS would be the technique of choice due to its dynamic extraction mode. Furthermore, desorption is independent of the injector temperature. The method optimization is more complicated than for static techniques, since more parameters need to be studied: the volume and flow of the gas used for extraction and desorption and the number of extraction strokes also have to be considered [3, 9]. However, for ITEX-DHS, optimization strategies including a flow chart for an accelerated method development are thoroughly described by Laaks et al. [18].

PAL SPME Arrow and SBSE are the recommended techniques for DI extraction. SBSE typically achieves better sensitivities due to the higher phase volume available. However, for the same reason it usually requires a significantly longer time to reach equilibrium and strong matrix effects can sometimes be observed [1, 7]. On the other hand, multiple samples can be extracted simultaneously if enough stir bars are available, as they can be stored before being measured. Only two commercially available coating materials are available, limiting the spectrum of analyte polarities that can be analyzed, and one of them (EG/Silicone) is rarely discussed in literature. If the optimal phase is not available in the SBSE format, or full automation is required, PAL SPME Arrow is recommended. The classical SPME can also be used, however, due to the smaller phase volume, it is the technique with the lowest sensitivity. Furthermore, due to the fragility of the fiber, its lifetime is shorter than for other techniques

The following parameters influence the extraction efficiencies of all the techniques previously described: sorbent material and dimensions, sample/air ratio, stirring speed, incubation, extraction and desorption temperatures and times, salt and organic modifier addition and pH [1-3, 7, 10, 18]. For SBSE-LD the organic solvent needs to be optimized instead of desorption temperature. Salt addition can potentially improve the performance of the extraction step, particularly for more polar compounds. However, if more hydrophobic analytes are of interest as well, up to 20 % of an organic modifier such as methanol could be added to minimize absorption to the walls [19]. Moreover, salt addition can also damage certain phases if DI extraction is performed [20, 21], and is therefore seldom considered when using this extraction mode. If possible, when optimizing pH the ionic strength should be kept constant by adjusting the salt content. Extraction time also affects the efficiency for all techniques, except ITEX-DHS and SPDE, which are affected by the number of extraction cycles instead.

Independent of the technique, the use of isotope labelled internal standards is strongly recommended when using GC-MS, both for the optimization step and for the analysis of real samples, since it corrects not only for matrix effects, but also for the degradation of the sorbent material after extended use. Furthermore, it could also correct for acid/base catalyzed hydrolysis that might be favored at higher temperatures.

Finally, all of the extraction phases presented here should be carefully conditioned before their first use and, in order to avoid carry over, after each sample run.

3 APPLICATIONS

Representative compound classes from the aforementioned regulations were selected, and, to the best of our knowledge, the most recent (maximum 10-15 years old) and detailed literature (both in terms of the description of the microextraction technique, and of the validation method carried out) were compared. It should be kept in mind that this is not a comprehensive review of all the literature available, and that for some of the analyte classes presented here, only a few of the techniques previously described have been used.

Considering that these techniques are based on the partitioning of analytes from the aqueous sample into the extraction phase, only neutral analytes (either samples with an adjusted pH or non-ionizable substances) were studied. To represent the true capabilities of the different microextraction techniques, publications where either SPME was performed manually, non-commercial sorption materials were used, or complex derivatization steps were needed, were excluded from this review. Finally, the focus of this review was on publications that use gas chromatography-mass spectrometry (GC-MS) for the analysis of water samples, since the vast majority of microextraction-related publications use this technique.

The experimental conditions and the validation results of the publications mentioned in the following sections are summarized in Table 2 and Table S4. Unfortunately, the lack of a standardized procedure regarding the method validation and the reporting of figures of merit hinders the direct comparison of many of the publications presented here. That is particularly the case for the calculation and reporting of limits, since several alternatives such as the method detection limits (MDLs), the limits of detection (LODs), and the limits of quantification (LOQs)

295 can be used, and different calculation possibilities exist. Furthermore, the use of instruments with
296 inherently different noise levels and sensitivities complicates the comparison even more.
297

Table 2. Applications of the microextraction techniques discussed in this review for the analysis of environmentally relevant compound classes in water samples: chlorophenols (CPs), pesticides (Pest.), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), short chain chlorinated paraffins (SCCPs) and volatile organic compounds (VOCs).

Analyte/ Analyte group	Matrix	Method	Phase material	Phase dimensions	Instrument	LOD/ ng/L	LOQ/ ng/L	Linear range/ ng/L	Ref.
CPs	River water	DI-SPME	PA	85 µm	GC-MS[a]	40-50[1]	200-250[1]	500-2000	[22]
	Pure water	HS-SPME	CAR/PDMS	85 µm	GC-MS[a]	8.8-42.3[2]	35.3-171.5[2]	50-1000	[23]
	Pure water	SBSE-LD	PDMS	1 cm x 0.5 mm	GC-MS[a]	6-65[2]	NR	20-8333	[24]
PAHs	Groundwater	DI-PAL SPME Arrow	PDMS	250 µm	GC-MS[a]	0.1-0.8[2]	NR	NR	[11]
	Wastewater	HS-SPME	PA	85 µm	GC-HRMS[d]	NR	0.05-5[2]	1-1500	[17]
	Seawater Sewage water River water Groundwater	SBSE-LD	PDMS	1 cm x 0.5 mm	GC-TOF	0.12-5.97[3]	NR	1-1000	[19]
	Surface water	DI-SPME	PA	85 µm	GC-HRMS[d]	NR	0.1-15[4]	0.1-1500	[20]
	Surface water	DI-SPME	PDMS	30 µm	GC-MS[a]	0.9-3.6[5]	3-11[5]	10-1000	[25]
	Airport wastewater	HS-SPME	PDMS	100 µm	GCxGC-TOF	0.23-2.2[6]	0.68-6.5[6]	10-1000 10000-100000	[26]
	Seawater	SBSE-TD SBSE-LD	PDMS	2 cm x 0.5 mm	GC-MS[a]	0.14-1.15[7]	NR	NR	[27]
	Seawater	SBSE-TD	PDMS	2 cm x 1mm	GC-MS[a]	0.011-2.50[3]	NR	0.5-500	[28]
	Seawater Tap water Surface water	SBSE-TD	PDMS	2 cm x 1mm	GC-MS[b]	0.04-1.5[8]	0.1-4.9[8]	20-600	[29]

Analyte/ Analyte group	Matrix	Method	Phase material	Phase dimensions	Instrument	LOD/ ng/L	LOQ/ ng/L	Linear range/ ng/L	Ref.
PCBs	Wastewater	HS-SPME	PA	85 µm	GC-HRMS[d]	NR	0.01-0.09[2]	0.1-150	[17]
	Seawater Sewage water River water Groundwater	SBSE-LD	PDMS	1 cm x 0.5 mm	GC-TOF	0.01-0.49[3]	NR	1-1000	[19]
	Surface water	DI-SPME	PA	85 µm	GC-HRMS[d]	NR	0.1-5[4]	0.1-100	[20]
	Seawater	SBSE-TD	PDMS	2 cm x 1mm	GC-MS[a]	0.011 - 0.061[3]	NR	0.5-500	[28]
	Bottled water	SBSE-TD	PDMS	2 cm x 0.5 mm	GC-MS/MS[b]	NR	5-14[9]	5-450	[30]
Pesticides									
Alkamides	Surface water Groundwater	DI-SPME	PDMS/DVB	65 µm	GC-MS[a]	17[3]	50[3]	50-5000	[31]
Benzamides	Groundwater	DI-SPME	PDMS/DVB	60 µm	GC-MS[b]	25[10]	75[10]	5-250	[32]
Benzofuranes	Surface water Groundwater	DI-SPME	PDMS/DVB	65 µm	GC-MS[a]	30[3]	100[3]	50-5000	[31]
Benzonitriles	Groundwater	DI-SPME	PDMS/DVB	60 µm	GC-MS[b]	4[10]	12[10]	5-250	[32]
Carboxamides	Surface water Ground water	DI-SPME	PDMS/DVB	65 µm	GC-MS[a]	20[3]	50[3]	50-5000	[31]
Chloroacetamides	Surface water Groundwater	DI-SPME	PDMS/DVB	65 µm	GC-MS[a]	20[3]	50[3]	50-5000	[31]
	Groundwater	DI-SPME	PDMS/DVB	60 µm	GC-MS[b]	6-19[10]	19-58[10]	5-250	[32]
Chloronitriles	Surface water Groundwater	DI-SPME	PDMS/DVB	65 µm	GC-MS[a]	17-30[3]	50-100[3]	50-5000	[31]
	Groundwater	DI-SPME	PDMS/DVB	60 µm	GC-MS[b]	10[10]	30[10]	5-250	[32]
Cyclodienes	Wastewater	HS-SPME	PA	85 µm	GC-HRMS[d]	NR	0.01[2]	5-100	[17]
	Surface water	DI-SPME	PA	85 µm	GC-HRMS[d]	NR	5[4]	15-150	[20]
	Groundwater	DI-	PDMS/DVB	60 µm	GC-MS[b]	8[10]	26[10]	5-250	[32]

Analyte/ Analyte group	Matrix	Method	Phase material	Phase dimensions	Instrument	LOD/ ng/L	LOQ/ ng/L	Linear range/ ng/L	Ref.
		SPME							
Dinitroanilines	Wastewater	HS-SPME	PA	85 µm	GC-HRMS[d]	NR	0.02[2]	0.1-50	[17]
	Surface water	DI-SPME	PA	85 µm	GC-HRMS[d]	NR	5[4]	5-150	[20]
	Groundwater	DI-SPME	PDMS/DVB	60 µm	GC-MS[b]	16[10]	50[10]	5-250	[32]
Organochlorines	Wastewater	HS-SPME	PA	85 µm	GC-HRMS[d]	NR	0.01-0.1[2]	0.5-150	[17]
	Seawater Sewage water River water Groundwater	SBSE-LD	PDMS	1 cm x 0.5 mm	GC-TOF	0.01-3.08[3]	NR	1-1000	[19]
	Surface water	DI-SPME	PA	85 µm	GC-HRMS[d]	NR	1-15[4]	1-300	[20]
	Seawater	SBSE-TD	PDMS	2 cm x 1mm	GC-MS[a]	0.275-37.5[3]	NR	0.5-500	[28]
	Seawater Tap water Surface water	SBSE-TD	PDMS	2 cm x 1mm	GC-MS[b]	0.1-10.2[8]	0.4-36.1[8]	20-600	[29]
	Groundwater	DI-SPME	PDMS/DVB	60 µm	GC-MS[b]	4-32[10]	12-97[10]	5-250	[32]
	River water	TD-SBSE	PDMS	2 cm x 0.5 mm	GC×GC-TOF	0.010-0.044[11]	NR	NR	[33]
Organophosphorus	Wastewater	HS-SPME	PA	85 µm	GC-HRMS[d]	NR	1-5[2]	5-1500	[17]
	Seawater Sewage water River water Groundwater	SBSE-LD	PDMS	1 cm x 0.5 mm	GC-TOF	0.03-0.1[3]	NR	1-1000	[19]
	Surface water	DI-SPME	PA	85 µm	GC-HRMS[d]	NR	15[4]	15-150	[20]
	Seawater Tap water Surface water	SBSE-TD	PDMS	2 cm x 1mm	GC-MS[b]	0.1-0.8[8]	0.5-2.7[8]	20-600	[29]
	Groundwater	DI-	PDMS/DVB	60 µm	GC-MS[b]	11-26[10]	33-78[10]	5-250	[32]

Analyte/ Analyte group	Matrix	Method	Phase material	Phase dimensions	Instrument	LOD/ ng/L	LOQ/ ng/L	Linear range/ ng/L	Ref.
		SPME							
Pyrethroids	Seawater Sewage water River water Groundwater	SBSE-LD	PDMS	1 cm x 0.5 mm	GC-TOF	0.4-7.36[3]	NR	1-1000	[19]
	Groundwater	DI-SPME	PDMS/DVB	60 µm	GC-MS[b]	10-22[10]	31-66[10]	5-250	[32]
Sulfamides	Groundwater	DI-SPME	PDMS/DVB	60 µm	GC-MS[b]	32[10]	97[10]	5-250	[32]
Thiocarbamates	Surface water Groundwater	DI-SPME	PDMS/DVB	65 µm	GC-MS[a]	20[3]	50[3]	50-5000	[31]
	Groundwater	DI-SPME	PDMS/DVB	60 µm	GC-MS[b]	13[10]	39[10]	5-250	[32]
Triazines	Wastewater	HS-SPME	PA	85 µm	GC-HRMS[d]	NR	200-350[2]	300-1500	[17]
	Seawater Sewage water River water Groundwater	SBSE-LD	PDMS	1 cm x 0.5 mm	GC-TOF	0.11-17.73[3]	NR	1-1000	[19]
	Surface water	DI-SPME	PA	85 µm	GC-HRMS[d]	NR	30-50[4]	50-1500	[20]
	Seawater Tap water Surface water	SBSE-TD	PDMS	2 cm x 1mm	GC-MS[b]	0.1-8.6[8]	0.4 - 28.6[8]	20-600	[29]
	Surface water Groundwater	DI-SPME	PDMS/DVB	65 µm	GC-MS[a]	20[3]	50[3]	50-5000	[31]
	Groundwater	DI-SPME	PDMS/DVB	60 µm	GC-MS[b]	31[10]	93[10]	5-250	[32]
Ureas	Surface water Groundwater	DI-SPME	PDMS/DVB	65 µm	GC-MS[a]	20[3]	50[3]	50-5000	[31]
SCCPs	MilliQ/Sea water/ Surface water	HS-SPME	PDMS	100 µm	GC/ECNI-MS[b]	4/50/30[12]	120/200/150[12]	200-1000	[34]
	MilliQ/Surface water	SBSE-TD	PDMS	1 cm x 0.5 mm	GC-QqQ-MS/MS[c]	20/20[13]	60/80[13]	5-3000	[35]
VOCs	MilliQ water	ITEX-	Tenax TA	-	GC-MS[a]	0.9-9.1[14]	NR	1-10000	[16]

Analyte/ Analyte group	Matrix	Method	Phase material	Phase dimensions	Instrument	LOD/ ng/L	LOQ/ ng/L	Linear range/ ng/L	Ref.
		DHS							
	MilliQ water	HS-PAL SPME Arrow	PDMS	100 µm	GC-MS[a]	0.9-4.8[14]	NR	1-10000	[16]
	MilliQ water	HS-SPME	PDMS	0.6 µL	GC-MS[a]	0.5-79.6[14]	NR	1-10000	[16]
	Drinking water Surface water Industrial effluent	HS-SPME	CAR/PDMS	75 µm	GC-MS[b]	190-510[10]	450-207[10]	250-5000	[36]
	Sea water River water Treated water	HS-SPME	PDMS/DVB	65 µm	GC-MS[b]	0.5-1[3]	2-3.33[3]	NR	[37]
	Tap water River water	HS-SPME	PDMS	100 µm	GC-MS[a]	10-1170[3]	NR	100-100000	[38]
	Drinking water	HS-SPME	PDMS/DVB	65 µm	GC-MS[b]	1.7-6[3]	6-20[9]	50-150000	[39]
	Groundwater	SPDE	PDMS/AC	50 µm	GC-MS[b]	12-870[15]	NR	12-8300	[40]
	Snow	SPDE	PDMS/AC	50 µm	GC-MS[b]	19-63[15]	58-188[15]	NR	[41]
	Pond, reservoir Tap water	ITEX-DHS	Tenax TA	-	GC-MS[b]	1-70[16]	NR	2-5800	[42]

a = SIM; b = Scan; c = MRM, Multiple reaction monitoring; d = Multiple ion detection

LODs and LOQs calculations: 1 = Not reported; 2 = n x standard deviation (SD) of the lowest calibration level, with n = 3 for LOD and 10 for LOQ; 3 = 3 x signal to noise (S/N); 4 = lowest concentration level in which RSD ≤ 20% and 80 - 120% recoveries; 5 = n x SD of the lowest calibration level, with n = 3 for LOD and 9 for LOQ; 6 = n × SD/b, with n = 3.3 for LOD and 10 for LOQ and b = the slope of the calibration curve; 7 = S/N > 4; 8 = n x standard deviation of a 20 ng/L solution, with n = 3 for LOD and 10 for LOQ; 9 = 10 x S/N, or, in the case of blank contribution, 10 x SD + the mean of the blank concentration; 10 = n × $S_{y/x}$/b, with n = 3 for LOD and 10 for LOQ; 11 = 3 x SD of a 100 pg/L solution; 12 = n x SD + mean of the blank concentration, with n = 3 for LOD and 10 for LOQ; 13 = n x SD a 0.1 µg/L, with n = 3 for LOD and 10 for LOQ; 14 = US EPA 821-R-16-006; 15 = DIN 32645; 16 = t x SD, with t = student's t value for the one-tailed test with a confidence level of 99% and six degrees of freedom.

Abbreviations: AC, Activated carbon; CAR, Carboxen; DVB, Divinylbenzene; GC/ECNI-MS, Gas chromatography/electron capture negative ionization-mass spectrometry; GC-HRMS, Gas chromatography-high resolution mass spectrometry; GC-MS, Gas chromatography-mass spectrometry; GC-MS/MS, Gas chromatography-tandem mass spectrometry; GC-QqQ-MS/MS, Gas chromatography-triple quadrupole-mass spectrometry; GCxGC-TOF, Comprehensive two-dimensional gas chromatography-time of flight mass spectrometry; NR, Not reported; PA, Polyacrylate; PDMS, Polydimethylsiloxane.

3.1 Chlorophenols

CPs are widely used in plastics, drug manufacturing, dye preservatives, biocide production and household products. Their endocrine disrupting properties, although weak, lead to major concerns as they are found in the environment in rather high concentrations due to their poor biodegradability. Furthermore, the US-EPA includes 2-Chlorophenol, 2,4-Dichlorophenol and 2,4,6-Trichlorophenol in their list of priority pollutants as they are highly toxic [22, 23], and pentachlorophenol can be found in all of the aforementioned conventions.

Gallego et al [22] studied five different chlorophenols in river water. The optimized extraction procedure was validated for a linear range of 0.5-20 µg/L and LODs of 0.04-0.05 µg/L. Yuan et al. [23] studied eleven estrogenic and odorous compounds in pure water, from which seven were chlorophenols. The extraction conditions were optimized, and the method was validated with respect to the linearity (50-1000 ng/L) and LODs (8.8-42.3 ng/L). As Gallego et al. used DI-SPME for surface water and Yuan et al. used HS-SPME for pure water, less matrix effects and lower LODs are expected for the latter (Fig. 3). However, the recovery for Gallego et al. was tested at a higher concentration level (500 ng/L vs. 100 ng/L) which leads to a better recovery range for their analytes (91.8-96.7 % vs. 69-98 %) [22, 23].

In comparison to SPME, the extraction of phenolic compounds using SBSE is very time consuming. After 240 min of extraction, the analytes are desorbed with ethyl acetate before being introduced into the GC system. The experiments lead to similar LODs (6-65 ng/L) and good repeatability (below 20 %) [24].

3.2 Polycyclic aromatic hydrocarbons

PAHs are one of the rare groups of compounds for which a standard SPME-based method for water analysis exists (US EPA 8272, see SI, A2) [43]. It was developed for the interstitial pore water in sediment samples, however, parameters like extraction temperature, stirring rate, etc., were not explicitly defined.

In the studied literature, PDMS fibers were predominantly used, despite theoretical calculations showing PA as a better sorbent material [44]. The phase thickness varied greatly [11, 25, 26] and the extraction time was typically 30 min [25, 26], however, for thicker phases

longer times were needed [11]. To reduce matrix interferences, HS extraction is also possible, but in that case salting out and higher extraction temperatures were needed [26].

SBSE also provides an excellent way of extracting PAHs from water matrices. 20 mm long stir bars coated with 0.5 mm PDMS were used to extract analytes from 25 – 200 mL of sample. The extraction time is usually long, up to 14 h [19], but in the case of higher concentrations where equilibrium is not needed, shorter extractions can also be performed [27].

When working in single ion monitoring (SIM) mode or using time of flight (TOF) detector, SPME allows LODs of 0.23-8.8 ng/L [25, 26]. PAL SPME Arrow is slightly more sensitive (LODs 0.1-0.8 ng/L) [11], similarly to SBSE if relatively short extraction times are used [27]. It is reported that SBSE can achieve even lower LODs (down to 0.04 ng/L) [19]. Better reproducibility than 13.5 % with the same SPME fiber, or better than 30 % with varying fibers can be expected [26].

3.3 Polychlorinated biphenyls

PCBs are chemically and thermally stable compounds used until the 1970s in industrial applications. However, despite the existing regulations on a worldwide scale, these compounds can still be found in the environment due to their persistency and mobility, therefore being a typical example of legacy pollutants.

Domínguez et al. studied 26 PCBs together with pesticides, PAHs and brominated diphenyl ethers, both in surface (DI-SPME) and in wastewater samples (HS-SPME) [17, 20]. They optimized the extraction procedure and calculated, from matrix matched calibrations, limits of quantification (LOQs) ranging from 0.1 to 5 ng/L (DI) and from 0.01 to 0.09 ng/L (HS). Unfortunately, due to the differences regarding the calculation approach, the matrices studied and the experimental conditions, these results can hardly be compared.

Similar or worse limits were achieved with SBSE despite the fact that more sample and longer extraction times were needed (see SI, A3) [19, 28, 30]. This could be explained by the fact that different phases were used: PA showed generally better or similar results than other phases for SPME, and only PDMS was tried for SBSE [20, 30]. This behavior can be explained (and predicted) by calculating the different partitioning constants, i.e. K_{PDMSW} and K_{PAW}

(polyacrylate-water partitioning constant), with the help of polyparameter linear free energy relationships (PP-LFERs) models (see SI, A1).

3.4 Pesticides

Solventless microextraction techniques are mainly used for the determination of triazine and chloroacetamide herbicides, and organochlorine and organophosphorus insecticides. The analysis of pesticides in drinking, ground or surface water is possible by DI-SPME and it is standardized in a form of DIN EN ISO 27108:2013-12 method (Table S1) [45].

In order to select the phase that works optimally for all analytes of interest, phases of wide range of polarities should be tested due to the very different chemical properties of the different pesticides [31, 32, 46, 47]. Similarly, pH can have a drastic influence on the extraction efficiency, for example fenpropidin (pKa of corresponding acid = 10.13), shows a significantly better extraction efficiency at basic pH values [31]. However, in some cases the optimal pH is extremely difficult to predict: for compounds with several pKa values, like triazine herbicides, the best way of selecting the proper pH comes down to testing several different values [31, 46, 47]. Due to their typically low volatility, pesticides are generally analyzed by DI (Fig. 3), thus the use of SPDE or ITEX-DHS is not recommended. However, as it can be seen in Fig. 3, organochlorine pesticides, such as aldrin or lindane, can also be successfully extracted from the HS. This is at the expense of sensitivity for other compounds, such as triazines [17].

For most pesticides, the lowest detection limits reported with SPME are around 10 ng/L [20, 31]. SBSE allows for lower detection limits of about 0.1 ng/L [29]. Lower limits, down to 0.01 ng/l, have been reported [19, 33], however the method used for the calculation raises the question of overestimation of the instrumental capabilities.

3.5 Short chain chlorinated paraffins

Chlorinated paraffins behave similarly to PCBs, particularly in terms of their chemical stability and flame retardant capabilities, and partially replaced them after the 1980s [34]. SCCPs, with 10 to 13 carbon atoms, are of special interest since they are the most toxic of the compound class [35].

Gandolfi et al. [34] optimized the HS-SPME step for the analysis of SCCPs with GC/ECNI-MS using experimental design. They achieved LOQs of 0.2 and 0.15 µg/L for sea and river water respectively. Tölgyessy et al. [35] obtained lower LOQs of 0.08 µg/L for river water with SBSE GC-MS/MS, however, they used a 10 times higher sample volume and a significantly longer extraction time (16 h). Both techniques reported LODs equal or better than those obtained when using LLE or SPE [48].

The WFD classified SCCPs as priority hazardous substances and established an annual average quality standard of 0.4 µg/L in surface water [49]. Even though with both techniques the LOQs reported are below that limit, only Tölgyessy et al. achieved a LOQ below the minimum performance criteria for testing new methods of 0.3 times the environmental quality standards (EQSs), or 0.12 µg/L for SCCPs in surface water [34, 35].

In general, the sensitivity achieved for the analysis of SCCPs is much lower than that of other compound classes. This could be due to the fact that the chromatographic separation is complicated because of the large number of isomers (up to 7000), and that there is a lack of suitable standards and matrix reference materials [34, 48].

3.6 Volatile organic compounds

Organic compounds that evaporate easily at normal pressure and temperature are placed in this category. Anthropogenic VOCs often end up in water through wrongful disposal or improper use (such as fuel oxygenates or solvents) or are formed directly in it as a result of disinfection processes (so called disinfection by-products, DBPs). Most VOCs are to some degree dangerous and therefore unwanted in water, and some of them, such as chlorinated ethanes, toluene or halomethanes, are included in some of the aforementioned regulations.

VOCs can be analyzed with a standardized HS-SPME-based method (see SI, A2) [50]. Because of their volatility HS is recommended over DI (Fig. 3), and, for SPME analysis, mixed phases that contain PDMS and Carboxen (CAR) or divinylbenzene (DVB) are preferred, due to their high specific surface area and optimal polarity [14]. With those phases, LODs down to 500 ng/L were reported [36, 37]. Furthermore, PDMS/DVB showed the best results from all mixed-mode fibers tested for the analysis of trihalomethanes, representative DBPs [39].

Although studies dealing with low levels of pollution corroborate the optimal conditions of the standard method [36, 37], the lower capacity of these phases makes their linearity range limited and, at higher concentrations, competition for the adsorption places can become evident [51]. Therefore, for heavily contaminated samples 100 µm PDMS can be used since its linearity range is up to 100 times greater, however, sensitivity would be affected [38].

Being that HS extraction of these compounds is far more efficient than DI extraction (Fig. 3), the application of SBSE for their analysis is not really justifiable, considering the long extraction times, and limited phase choices. For the same reason, SPDE and ITEX-DHS are very useful for their analysis in water. Similar to SPME, optimal extraction phases used for these methods contain activated carbon (AC) or Tenax polymer particles [42]. They typically offer LODs that are 10-50 times lower than SPME and, due to the greater sorption volume, the linearity range of these methods is also broader [9, 38, 40, 41]. For more information on a direct comparison of some of these techniques we refer the reader to [16].

4 CONCLUSIONS

The selection of the optimal technique depends on the analytes of interest, the sample type, and the task at hand (Is sensitivity a priority? Can the sample be filtered?). On the other hand, the selection of the extraction mode (i.e. headspace or direct immersion) depends on the analytes' characteristics, namely the partitioning constants between water, air and the sorbent material. Provided HS is feasible, it is always preferred over DI, since it has lower matrix interferences and faster kinetics. All the microextraction techniques addressed have advantages and drawbacks of their own. In this review, we help the reader make informed decisions.

When studying the available literature, the different ways of validating methods became apparent. This complicates literature comparison, and gives the impression, in some cases, that overestimated LODs and LOQs are reported. A standardized and regulated validation is therefore strongly needed.

For some of these techniques, especially SPME and SBSE, there are established methods for the analysis of diverse compound classes from different matrices. However, the standardization and regulation of the methods is still lacking. Most research is currently being done to develop alternative extraction techniques and find new sorbent materials.

458

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Highlights:

- Automated solventless microextraction techniques for water analysis are compared.
- Selection of the optimal microextraction technique and mode is discussed.
- Application examples for analysis of six relevant compound classes in water are given.