Review

Sorptive Extraction Techniques for Trace Analysis of Organic Pollutants in the Aquatic Environment

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Abstract

Environmental water analysis requires the determination of organic contaminants down to the low ng L^{-1} range which makes efficient sample preconcentration and sample clean-up mandatory prior to high-performance separation techniques combined with selective detection. Solid-phase extraction has become one of the most important sample pre-treatment procedures in environmental analytical chemistry, based on either single equilibration or multiple equilibration of analytes between the aqueous sample and the sorbent. Procedures based on a single partitioning step between sample and sorbent phase (such as solid-phase microextraction, stir bar sorptive extraction and related variants) are generally called sorptive extraction techniques. The increasing popularity of these techniques is due to reduced time-consumption and increased cost-effectiveness. In this review paper, the current state of sorptive extraction with respect to organic trace analysis in water samples is discussed regarding both the theoretical aspects as well as the applications for organic xenobiotics in the aquatic environment. The ongoing acceptance of sorptive extraction techniques into official methods clearly indicates that they offer satisfactory reliability and robustness for routine monitoring purposes.

Keywords: sample preparation, sorptive extraction, water analysis, organic trace analysis

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1. Introduction

Monitoring of water quality and the necessity of proper risk assessment requires the availability of reliable analytical methods for trace analysis of organic pollutants with determination limits in the low ppt or even sub-ppt range. Gas and liquid chromatography in combination with mass spectrometric detection are state-of-the-art techniques in environmental analysis. Unfortunately, direct analysis of organic pollutants in water samples by chromatographic procedures is hardly feasible. The low concentration levels make the availability of efficient sample preconcentration steps mandatory, which can selectively extract and enrich the analytes from the aqueous matrix.

One of the most widely used sample treatment technique in water analysis is the extraction of the analytes by means of a solid sorbent. This extraction procedure can be equilibrium-based or exhaustive in nature. The latter technique is well-known as solid-phase extraction (SPE). Typically, the aqueous sample is passed through a small cartridge filled with an appropriate stationary phase that retains the analyte completely. Afterwards, the analyte is eluted with a volume of organic solvent much smaller than the original sample volume. The applications of SPE in environmental water analysis are almost endless and the present review will not focus on that area. Instead, attention will be paid to equilibrium-based sorptive extraction techniques which are attractive due to their simplicity and can be used in the lab to process water samples as well as in the field as passive samplers.

Equilibrium-based sorptive extraction includes solid-phase microextraction (SPME), stir-bar sorptive extraction (SBSE), and several related variants. SPME was introduced by Pawliszyn and coworkers in the early 1990s.[1,2] SBSE was first reported several years later by Baltussen et al. and commercialized under the trade name Twister by Gerstel.[3,4] Originally, both techniques were based on polydimethylsiloxane (PDMS) as material for trapping trace analytes from a water sample due to the partition equilibrium established between the aqueous matrix and the PDMS phase. In the meantime, new sorptive materials have been investigated and the field of applications has been widened considerably. In several cases, these new materials exploit adsorption equilibria between the aqueous phase and the surface of the solid sorbent rather than partition equilibria encountered for PDMS sorbents.

2. Basics of Sorptive Extraction

Assuming a partitioning equilibrium of the analytes between the aqueous phase and the sorbent (and neglecting any equilibrium of analytes between the aqueous phase and the gaseous headspace phase), the amount n of an analyte in the sorbent can be easily calculated by using the law of conservation of mass and expressed in the following way:[5]

$$n = \frac{K_e V_e V_s}{K_e V_e + V_s} c_s^\circ . \quad (1)$$

V_e is the volume of the sorbent, V_s is the volume of the sample, c_s° is the original concentration of the analyte in the sample, and K_e is the partition coefficient:

$$K_e = \frac{c_e}{c_s}, \quad (2)$$

with c_e and c_s being the equilibrium concentrations of the analyte in the sorbent and in the aqueous phase, respectively. Strictly speaking, Eq.1 would be true for a (liquid) polymeric phase such as PDMS in contact with a water phase. If the sorbent is a solid that extracts analytes from the water phase by adsorption, the mathematical treatment would be analogous (as long as the analyte concentration is not too high) because the total surface available for adsorption is proportional to the coating volume.

When V_s is considerably larger than KV_e, (which becomes true if the volume of sorbent is very small in comparison with the sample volume) Eq.1 can be simplified:

$$n = K_e V_e c^\circ_s . \quad (3)$$

Eq.3 indicates that the extracted amount becomes independent of the sample volume. In this case, the extracted amount is not increased when the volume of the sample is further increased.

On the other hand, when V_s is considerably smaller than KV_e, Eq.1 can be written in the following way:

$$n = V_s c^\circ_s . \quad (4)$$

In this case, the extracted amount increases with the sample volume. This may be true if the partition coefficient is very high and the sorbent volume not too low.

From Eq.1 it can also be easily deducted that the percentage extracted from the sample increases when V_s decreases and V_e and K increase. Nevertheless, in reality one has to maximize the extracted amount n and not the percentage, because the parameter actually measured by subsequent chromatography is the amount of analyte in the sorbent.

Eq.1 neglects possible additional partition equilibria of an analyte between the aqueous phase and suspended solids or dissolved organic materials. The amount of suspended solids is generally expressed as amount of organic carbon (OC) present in the solids, and the amount of dissolved organic material is generally given as dissolved organic carbon (DOC). Therefore, these additional partition equilibria can be described by the following partition coefficients K_{OC} and K_{DOC}:

$$K_{OC} = \frac{c_{OC}}{c_s}, \quad (5)$$

$$K_{DOC} = \frac{c_{DOC}}{c_s}, \quad (6)$$

with c_{OC} and c_{DOC} being the concentrations of the analyte in the suspended solids and in the dissolved organic material, respectively. It has been shown that the consideration of these equilibria leads to the following equation:[6]

$$n = \frac{K_e V_e (V_s + \theta)}{K_e V_e + V_s + \theta} c_s^\circ . \quad (7)$$

where θ is $K_{OC}m_{OC} + K_{DOC}m_{DOC}$, with m_{OC} and m_{DOC} being the masses of organic carbon present in suspended solid and dissolved organic material, respectively.

If Eq.2 is rearranged into

$$n = c_s K_e V_e , \tag{8}$$

then Eqs.8 and 7 obviously yield

$$\frac{c_s}{c_s^\circ} = \frac{V_s + \theta}{K_e V_e + V_s + \theta} . \tag{9}$$

Eq.9 demonstrates that the increase of the sample volume finally leads to a situation where $(V_s + \theta) >> K_e V_e$, so that the ratio of c_s/c_s° approaches unity. Under such conditions, the concentration of the analyte in the aqueous phase remains practically unchanged during the sorptive extraction process. Therefore, partition equilibria between analytes and suspended solids or dissolved organic material are not affected and the method allows the selective determination of the concentration of the free analyte in the sample. This technique has also been called negligible depletion sorptive extraction.[7] Since free and bound species may exert different effects in the environment, methods for measuring selectively the free analyte are of considerable interest.

It should be clear that the equations mentioned above refer to equilibrium conditions and do not give any information about the time necessary to reach these equilibrium conditions. For routine analysis it may be possible to work even under conditions that do not represent the equilibrium state.

In the equations given above, any gaseous headspace phase acting as an additional phase with affinity for the analyte has been neglected (which may be appropriate for less volatile analytes and/or small volumes of the headspace phase). If the headspace should be taken into consideration, the law of conservation of mass leads to the following equation:

$$n = \frac{K_e V_e V_s}{K_e V_e + V_s + K_h V_h} c_s^\circ \tag{10}$$

K_h is the partition coefficient between the headspace and the aqueous phase (Henry´s constant) and V_h is the headspace volume. The amount extracted is proportional to the initial sample concentration, and this is true whether the extraction phase is located in the aqueous sample or in the headspace.

Quantification of sorptive extraction can be done by external calibration (in those cases when sample composition is quite constant and the matrix of samples and standards quite similar), by internal calibration (ideally using an isotopically labelled analyte as the internal standard), or by standard addition.

Eq.3 indicates that it is possible to use the principle of sorptive extraction for passive samplers. This aspect is discussed in detail in part 7 of this review.

3. Solid-Phase Microextraction (SPME)

SPME procedures include fibres SPME and in-tube SPME. Fibre SPME employs a fibre coated with a thin film of sorbent. Silica-based fibres have been used for many years as substrate for the coating, whereas more recently titanium wires and nickel-titanium alloys have been developed so that unbreakable assemblies can be produced that provide increased robustness of the SPME procedure.[8,9] The extraction of analytes from the aqueous sample can be done by direct immersion of the fibres (DI-SPME) or by exposing the fibre to the vapour phase (headspace) of the liquid sample (HS-SPME). DI-SPME is the more widely applicable technique whereas HS-SPME may be more appropriate when volatile compounds are to be extracted. In both cases, the preconcentrated analytes must be desorbed from the fibre for a subsequent GC or HPLC analysis. For GC analysis, desorption is a straightforward process based on heating the fibre in the injection port of the GC instrument. HPLC analysis requires desorption of the analytes by a small amount of solvent in a suitable desorption chamber. This desorption process can be done off-line or in an on-line coupling configuration with the HPLC injector.[10]

Commercially available SPME fibres include polydimethylsiloxane (PDMS) as the most popular sorbent, polyacrylates, copolymers of PDMS with divinylbenzene (DVB), copolymers of polyethylene glycol (Carbowax, CW) with DVB, and mixtures of carboxen (an inorganic adsorbent) with PDMS or DVB.

Various procedures based on sol-gel technologies have been reported in the literature for preparation of coated fibres. This technique was introduced by Malik and coworkers and allows the incorporation of organic polymers like PDMS into an inorganic polymeric structure like silica.[11] Furthermore, fibres coated with polyethylene glycol,[12,13] polyphenylmethylsiloxane,[14] PDMS/crown ethers,[15–18] PDMS/hydroxyfullerene,[19] PDMS/diallyltriethylene glycol,[20] PDMS/poly(vinyl alcohol),[21] PDMS/calixarenes,[22–24] or PDMS/polymethacrylates[25,26] have been prepared by the sol-gel technology. Recently, Liu et al. reported the development of a PDMS-coated fibre based on a sol-gel process that uses alumina instead of silica as the inorganic polymeric structure.[27] Olesik and coworkers prepared silica particles coated with glassy carbon that were immobilized on a fibre by a sol-gel process.[28,29]

An alternative approach to the preparation of coated fibres consists in the deposition of coatings on a conductive support by electrochemical procedures. Polypyrrole and polyaniline are typical examples for this kind or sorbents.[30–32]

One should be aware of the fact that most routine applications of SPME reported so far are based on those few sorbents that are commercially available, whereas the potential of alternative materials for trace determination of organic pollutants in water samples is still not fully exploited.

In-tube SPME uses capillaries internally coated with the sorbent. Pieces of commercial GC capillaries with a wide range of stationary phases can be used. The capillary is filled with the aqueous sample (or the headspace phase) and the analytes are trapped in the sorbent; desorption is either done thermally or by flushing with an organic solvent.[33–35] An in-tube SPME technique based on a syringe with a needle coated on the inner surface has been developed under the name solid-phase dynamic extraction (SPDE) and has been commercialized for automated sample preparation.[36,37]

In-tube extraction procedures using a packed capillary represent a smooth transition to traditional solid-phase extraction techniques and will not be addressed in this review.

4. Stir-Bar Sorptive Extraction (SBSE)

Generally, Eq.1 indicates that the amount extracted from the sample will increase upon an increase of the volume of the sorbent (V_e). An increase of V_e can be realized by using stir bars coated with a layer of sorbent such as dimethylpolysiloxane. The basic principles of SBSE are the same as for SPME. The stir bar is added to the sample which is subsequently stirred for a defined time. Afterwards, the stir bar is removed from the sample and transferred to a GC instrument equipped with a dedicated thermal-desorption injection system. Alternatively, desorption can be achieved by a small volume of solvent followed by HPLC analysis.

Recently, a similar technique has been introduced which uses a polydimethylsiloxane rod (e.g. 5 cm length and 2 mm diameter) instead of the coated stir bar.[38] The sample solution is shaken to support the extraction into the rod. The subsequent analysis by thermal-desorption GC (or HPLC) is the same as in the case of a coated stir bar. A partition equilibrium is hardly reached during the extraction step due to the relatively big volume of the sorbent and the slow diffusion velocity of the analyte within the sorbent. Nevertheless, this fact does not necessarily impair the reliable and reproducible quantification. An advantage of the use of silicon rods are the low costs of this material, so that even a one-way use becomes economically reasonable. An application of silicon rods to the de-

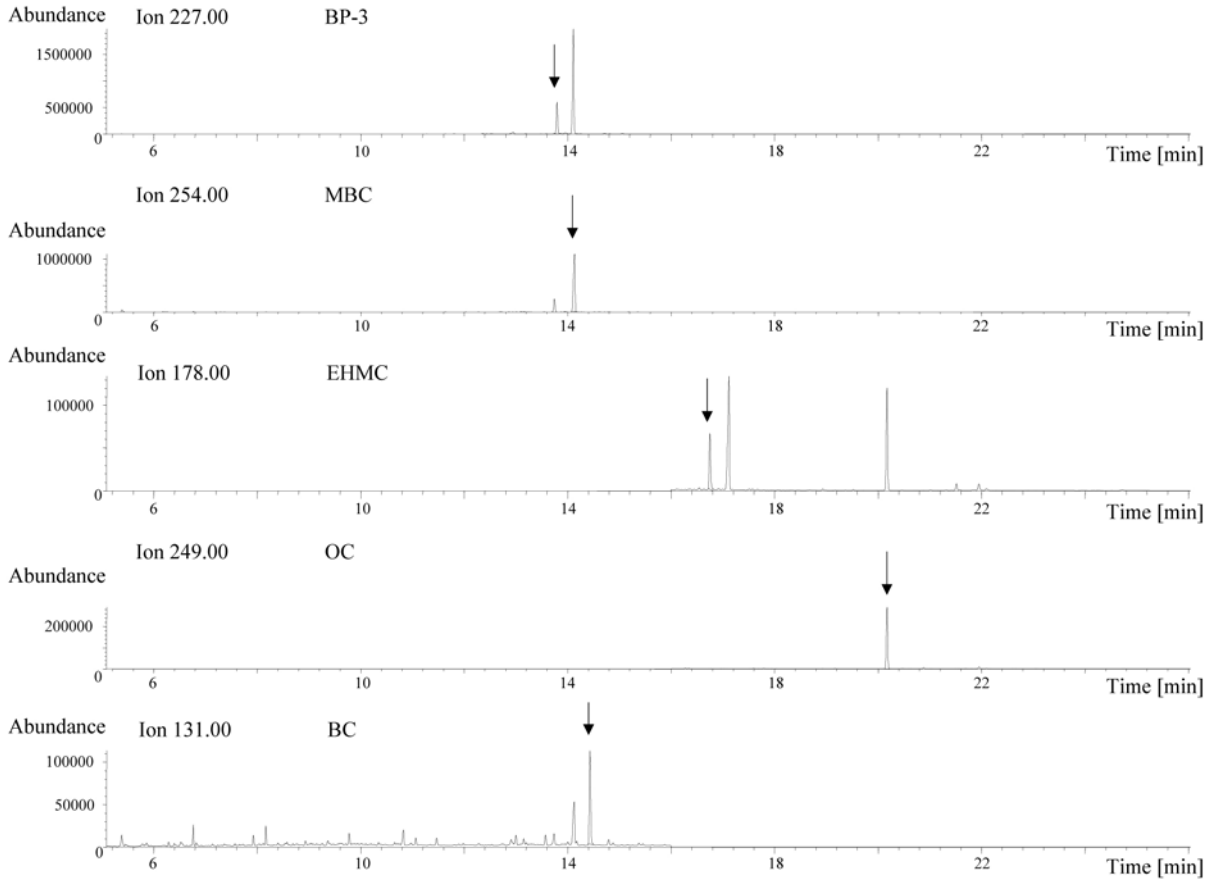

Figure 1. Determination of residues of UV filters in surface water by GC-MS after SBSE. Peaks: BP-3 benzophenone-3 (54 ng L^{-1}); 4-MBC 4-methylbenzylidene camphor (202 ng L^{-1}); EHMC ethylhexyl methoxy cinnamate (4 ng L^{-1}); OC octocrylene (59 ng L^{-1}); BC benzyl cinnamate (internal standard). Sample volume: 250 mL.

termination of polycyclic aromatic hydrocarbons in water samples demonstrated that their performance was similar to that of coated stir bars.[39]

Another alternative to a coated stir bar has been reported by Pettersson et al. who used a glass rod (diameter 3 mm, length 58 mm), onto which a PDMS tube (outer diameter 3 mm, wall thickness 0.5 mm) was mounted.[40] This sampling probe was inserted into a stirred sample solution and treated in the same way as coated stir bars or silicon rods.

PDMS-coated stir bars for sorptive extraction have also been prepared by sol-gel technology similar to fibres for SPME discussed in the previous part.[41]

As mentioned above, SBSE techniques have almost exclusively been based on PDMS as sorbent. The higher the hydrophobicity of the analyte, the better becomes the extraction efficiency. A typical example for analytes well suited for sorptive extraction by PDMS is the residue analysis of sunscreen agents (UV filters) in water. Figure 1 shows a typical chromatogram of a real sample after SBSE. On the other hand, recoveries of polar compounds are generally poor. An interesting approach to improved recoveries of polar analytes has been reported by Bicchi et al.[42] They used so-called dual-phase stir bars consisting of a PDMS tube filled with an additional adsorbent like activated carbon. Regarding applications in environmental chemistry, the recovery of atrazine from a water sample was about 80% higher with the dual-phase stir bar than with a conventional PDMS stir bar.

Comparing SPME and SBSE, the latter technique generally yields better detection limits. On the other hand, SPME can be fully automated which is not yet completely true for SBSE.[43]

5. Derivatization and Sorptive Extraction

Derivatization of the analyte can improve the performance of sorptive extraction procedures considerably in those cases when the original analyte exhibits a poor partition coefficient between the aqueous sample and the sorbent. Furthermore, the derivatization step can improve the properties of the analytes for the subsequent chromatographic procedure. Generally, the derivatization reaction can be carried out in the aqueous sample solution prior to the extraction step or on/in the sorbent phase.

Derivatization in the aqueous sample solution is hampered by the fact that many common derivatization reagents require non-aqueous conditions. Among water-compatible reagents, alkylchloroformates are attractive reagents for phenols, amines or carboxylic acids. Butylchloroformate has been used for determination of phenoxy acids and their phenolic degradation products.[44] Recently, we could successfully employ this reagent for trace determination of the antidepressant fluoxetine in surface water by SBSE and GC. The detection limits were in the mid ppq range. A typical example is given in Fig. 2.

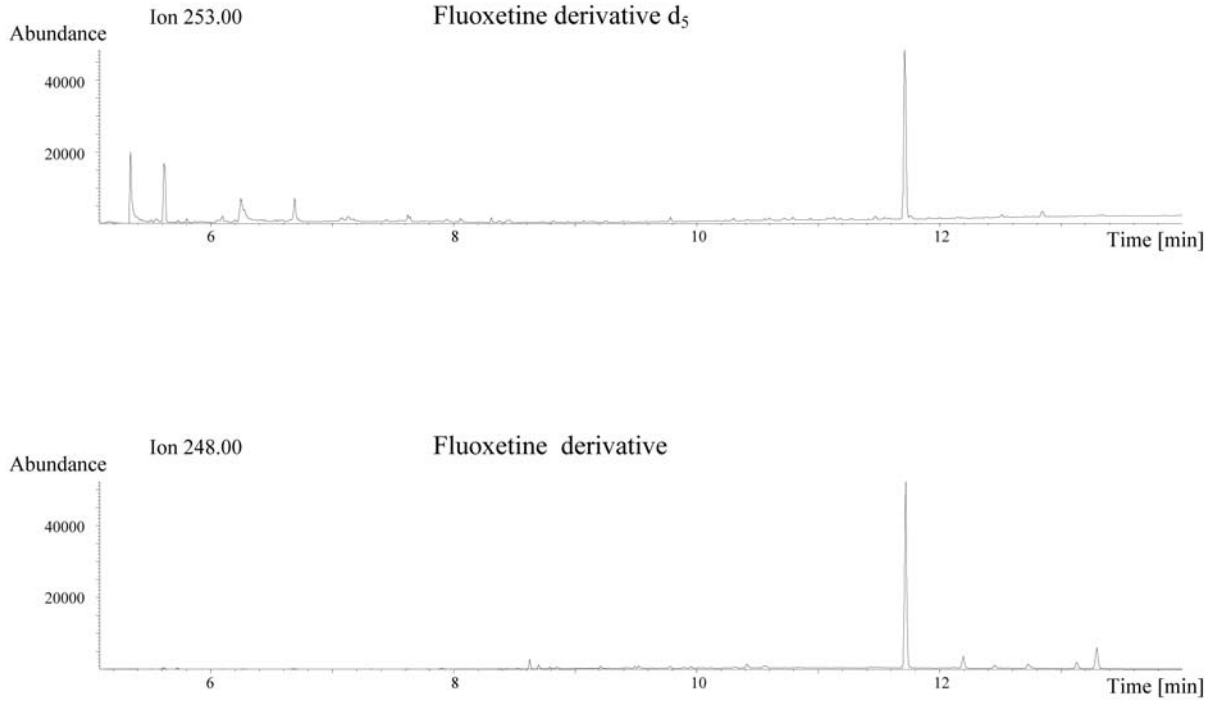

Figure 2. Determination of residues of the antidepressant fluoxetine in surface water by GC-MS after derivatization with isobutyl chloroformate and SBSE. Upper chromatogram: internal standard (deuterated fluoxetine); lower chromatogram: fluoxethine (21 ng L^{-1}). Sample volume: 250 mL.

Table 1. Applications of solid-phase microextraction for trace analysis of organic contaminants in water samples.

analyte	SPME material	analytical technique	detection limits	comments	literature
pharmaceuticals and personal care products					
fluoroquinolones	carboxen 1010 (in-tube)	HPLC/MS	7 … 29 ng L^{-1}		64
selective serotonin reuptake inhibitors	PDMS/DVB (fiber)	GC/MS	15 … 75 ng L^{-1}	acetylation prior to SPME	55
anti-inflammatory drugs	PA (fiber)	GC/MS	12 … 20 ng L^{-1}	derivatisation with MTBSTFA prior to GC	65
anti-inflammatory drugs	PA (fiber)	GC/MS	12 … 40 ng L^{-1}	derivatization with MTBSTFA prior to GC	66
triclosan and metabolites	PA or PDMS/DVB (fiber)	GC-MS	2 … 7 ng L^{-1}	derivatization with MTBSTFA prior to GC	67
sunscreen agents	PDMS or PA (fiber)	GC-FID or GC-MS	0.6 …4.4 µg L^{-1}	DI- or HS-SPME	68
synthetic musk compounds	CAR/PDMS or PDMS/DVB (fiber)	GC-MS	0.1 …9 ng L^{-1}	HS-SPME	69
synthetic musk compounds	PDMS/DVB (fiber)	GC-MS	14 … 22 ng L^{-1}		70
parabens	PA (fiber)	GC-MS	1 … 25 ng L^{-1}	derivatization with MTBSTFA prior to GC	71
estrogens, xenoestrogens and steroid hormones					
estrogens	DHPMM (coated hollow fiber)	GC-MS	0.03 … 0.8 ng L^{-1}	derivatization with MSTFA prior to GC	72
estrogens	Supel-Q (in-tube)	HPLC-MS	2.7 … 11.7 ng L^{-1}		73
estrogens	PA (fiber)	GC-MS	0.2 …3 ng L^{-1}	derivatization with MSTFA prior to GC	74
steroid hormones and xenoestrogens	PA (fiber)	GC-MS	2 … 378 ng L^{-1}	derivatization with BSTFA prior to GC	75
estrogens and xenoestrogens	PA (fiber)	HPLC-ED	60 … 80 ng L^{-1}		76
estrogens and xenoestrogens	PA	GC-MS	40 … 1000 ng L^{-1}		77
nonylphenolethoxylates	DVB/CAR/PDMS	GC-MS	30 … 150 ng L^{-1}		78
PAHs and related compounds					
PAHs	PDMS (fiber)	GC-MS	1 … 29 ng L^{-1}		79
PAHs	PDMS (fiber)	HPLC-FL	1 … 6 ng L^{-1}		80
PAHs and alkyl-PAHs	PDMS (fiber)	GC-MS	low ng L^{-1} range		81
Nitro-PAHs	PDMS/DVB (fiber)	GC-MS	4 …60 ng L^{-1}		82
flame retardants					
brominated phenolic compounds	CAR/PDMS or PDMS (fiber)	GC-MS	1.3 … 46 ng L^{-1}	acetylation prior to SPME	83
Polybrominated diphenyl ethers and polybrominated biphenyls	PDMS (fiber)	GC-MS	7 … 190 ng L^{-1}	HS-SPME	84
pesticides					
pyrethroides	PDMS (fiber)	GC-ECD	0.05 … 2.18 ng L^{-1}		85
phenoxy acid herbicides	PA (fiber)	GC-MS	4 … 28 ng L^{-1}	derivatization with MTBSTFA prior to GC	86
phenoxy acid herbicides	CW (in-tube)	HPLC-MS	5 … 30 ng L^{-1}		87
triazines	PDMS/DVB (fiber)	GC-MS	2 … 17 ng L^{-1}		88
phenylurea herbicides	PA (fiber)	GC-MS	0.3 … 1 ng L^{-1}	solid-phase extraction and derivatization with iodoethane and sodium hydride prior to SPME	89
herbicides	PA (fiber)	GC-MS	20 … 110 ng L^{-1}		90
organochlorine pesticides	PDMS (fiber)	GC-ECD	10 … 40 ng L^{-1}		91
organochlorine pesticides	DVB/CAR/PDMS	GC-ECD	2 … 70 ng L^{-1}	HS-SPME	92
priority pesticides	PDMS (fiber)	GC-TID or MS	3 … 90 ng L^{-1}		93
31 pesticides of different groups	PDMS/DVB (fiber)	GC-MS	1 … 56 ng L^{-1}		94
44 pesticides of different groups	PDMS/DVB (fiber)	GC-MS	low ng L^{-1} range (except for dimethoate)		95

multi-class pesticides	PA (fiber)	GC-MS	mid ng L^{-1} range	HS-SPME	96
antifouling biocides	PDMS/DVB (fiber)	GC/ECD or TID or MS	2 … 20 ng L^{-1}		97
organometallic compounds					
organotin compounds	PDMS (fiber)	GC/MS	0.4 … 1.5 ng L^{-1}	derivatization with sodium tetraethylborate prior to headspace SPME	98
14 organotin compounds	CAR/PDMS (fiber)	GC/PFPD	0.03 … 56 ng L^{-1}	derivatization with sodium tetraethylborate prior to headspace SPME	99
Butyltin species	PDMS (fiber)	GC/AED	1 … 5 ng L^{-1}	derivatization with sodium tetraethylborate prior to headspace SPME	100
speciation of mercury	CAR/PDMS (fiber)	GC/ICP-MS	0.027 … 0.27 ng L^{-1}	derivatization with sodium tetraethylborate prior to headspace SPME	101
speciation of lead	PDMS (fiber)	GC/MS	83 … 130 ng L^{-1}	derivatization with deuterium-labeled sodium tetraethylborate prior to headspace SPME	102
phenols					
19 chloro phenols	CW-TPR (fiber)	HPLC-ED	3 … 8 ng L^{-1}		103
30 alkyl and chloro phenols	CAR/PDMS or PDMS (fiber)	GC-MS	1 … 61 ng L^{-1}	acetylation prior to headspace SPME	49
disinfection by-products					
trihalomethanes	PDMS (fiber)	GC-MS	< 100 ng L^{-1}	headspace-SPME	104
haloalkanes	PA (fiber)	GC-ECD	0.3 … 120 ng L^{-1}		105
iodinated phenols	CAR/PDMS (fiber)	GC/ICP-MS	0.07 … 0.12 ng L^{-1}		106
haloacetic acids	CAR/PDMS (fiber)	GC-MS	10 … 450 ng L^{-1}	derivatization mit dimethyl sulphate prior to head-space SPME	58
aldehydes	DVB/PDMS (fiber)	GC-ECD	50 … 400 ng L^{-1}	derivatization with PFBHA prior to SPME	61
phthalate esters					
	PDMS/DVB (fiber)	GC-MS	2 … 103 ng L^{-1}		107
	PA (fiber)	GC-ECD	1 … 50 ng L^{-1}		108
	PDMS/DVB (fiber)	GC-MS	3 … 30 ng L^{-1}		109
	CW/DVB (fiber)	GC-MS	20 … 600 ng L^{-1}		110
miscellaneous					
aromatic amines	PDMS/DVB (fiber)	GC/MS	2 … 38 ng L^{-1}	diazotation and iodination prior to SPME	56
perfluorocarboxylic acids	PDMS (fiber)	GC-MS	20 … 750 ng L^{-1}	ion-pair SPME, esterification during GC injection	111
alkylbenzenesulfonates	PDMS (fiber)	GC-MS	160 … 800 ng L^{-1}	ion-pair SPME, esterification during GC injection	112
BTEX	PDMS (fiber)	GC-FID	80 … 600 ng L^{-1}	headspace SPME	113
explosives	PDMS/DVB (fiber)	GC-MS	0.03 … 1.1 µg L^{-1}		114
explosives	CW/DVB (fiber)	GC-MS	5 …325 ng L^{-1}		115
methyl *tert*-butyl ether	CAR/PDMS (fiber)	GC-MS	10 ng L^{-1}	headspace SPME	116, 117
polychlorinated biphenyls	PDMS (fiber)	GC-MS	low ng L^{-1}	headspace SPME	118
polychlorinated biphenyls	PDMS (fiber)	GC-MS	0.3 … 1.3 ng L^{-1}	headspace SPME	119
polychlorinated biphenyls	PDMS (fiber)	GC-ECD	5 ng L^{-1}		120

Abbreviations for SPME material: CAR carboxen, CW carbowax, CW-TPR carbowax-templated resin, DHPMM dihydroxylated polymethylmethacrylate, DVB divinylbenzene, PA polyacrylate, PDMS polydimethylsiloxane.
Abbreviations for analytical technique: AED atomic emission detector, ECD electron capture detector, ED electrochemical detector, FID flame ionization detector, FL fluorescence detector, ICP inductively coupled plasma, PFPD pulsed flame photometric detector, TID thermionic detector.
Further abbreviations: BSTFA *N,O*-bis(trimethylsilyl)trifluoroacetamide, DI direct insertion, HS head space, MSTFA *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide, MTBSTFA *N*-methyl-*N*-(*tert*-butyldimethylsilyl)-trifluoroacetamide, PFBHA *o*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine.

Another suitable reagent is acetic acid anhydride. Typical applications of this reagent in environmental water analysis include the determination of bisphenol-A,[45,46] hydroxy polycyclic aromatic hydrocarbons,[47] phenols,[46,48–51] estrogens,[52,53] phenolic xenoestrogens,[54] or serotonine reuptake inhibitors.[55] Aromatic amines have been derivatized by diazotation and subsequent iodination.[56] Dimethylsulfate has been used for derivatization of nonylphenol ethoxylates and acidic metabolites into their methyl ethers or esters, and of haloacetic acids into methyl esters.[57,58] Organometallic compounds have been derivatized by tetraethylborate of tetraphenylborate.[59] Pentafluorobenzylhydroxylamine allowed the derivatization of aldehydes either by addition of the reagent to the aqueous sample or by loading the reagent onto the fibre prior to SPME.[60–62] A reagent-loaded fibre was also used for determination of degradation products of chemical warfare agents using *N*-methyl-*N*-(*tert*.-butyldimethylsilyl)-trifluoroacetamide for derivatization.[63]

6. Applications of Sorptive Extraction in Water Analysis

Applications of SPME for trace analysis of organic pollutants in water analysis have been reported right from the beginning of the development of this technique in the early 1990s. During the last years, the detection limits of the procedures have improved, although not necessarily always due to improvements in the SPME procedures themselves but often due to improved sensitivity of chromatographic procedures applied subsequently to the sorptive extraction process. It is practically impossible to give a comprehensive compilation of all applications of SPME published so far. Table 1 summarizes various SPME procedures published mainly within the last 5 years, whereby emphasis is put on multi-methods that include the simultaneous determination of more than just a few analytes.

Table 2 lists recent applications of SBSE in water analysis.

7. Passive Samplers Based on Sorptive Extraction

Passive samplers typically consist of a receiving phase with a high affinity for the analyte, separated from the aqueous sample phase by a diffusion barrier that determines the rate at which analyte molecules are collected in the sorbent. Materials mentioned for SPME and SBSE can be used as receiving phase. The extraction kinetics of the passive sampler can be described in the following way:[135]

$$c_e = c_s^\circ \frac{k_1}{k_2}\left(1 - e^{-k_2 t}\right), \qquad (10)$$

c_e is the concentration of the analyte in the sorbent, c_s° is the concentration of the analyte in the sample (no depletion of the sample takes place), and k_1, k_2 are the uptake and offload rate constants, respectively.

If the exposure time is sufficiently long and equilibrium established, equation (10) reduces to

$$c_e = c_s^\circ \frac{k_1}{k_2}. \qquad (11)$$

The ratio k_1/k_2 is the partition coefficient K_e between the sorbent and the water phase. Therefore, equation (11) is identical to equation (3). Equilibrium passive samplers require response times shorter than fluctuations of the analyte concentrations in the sample medium. To allow a rapid establishment of equilibrium conditions it may be advantageous to use a passive sampler without a diffusion barrier.

Contrary to equilibrium passive samplers, kinetic passive samplers operate with exposure times considerably shorter than necessary for establishing equilibrium conditions. In this case the rate of uptake is linear and desorption from the sorbent negligible. Eq.10 reduces to

$$c_e = c_s^\circ k_1 t. \qquad (12)$$

The advantage of a kinetic passive sampler is its integrative character over a certain time, which can be advantageous in cases when analyte concentrations are variable. This type of sampler yields time-weighted average concentrations.

PDMS-coated SPME fibres have been used as equilibrium passive sampler for persistent chlorinated hydrocarbons.[136] Such a fibre can also be used for time-weighted average water sampling if the fibre is retracted into its needle so that the mass transfer of analyte molecules is governed by diffusion through the static water gap between the needle opening and the fibre coating.[137]

Vrana et al. developed an integrative passive sampler consisting of a PDMS-coated bar enclosed in a dialysis bag.[136,139] This device was called membrane-enclosed sorptive coating (MESCO) sampler.

Pawliszyn and coworkers used a PDMS rod or a PDMS foil without additional diffusion barrier for field-sampling of PAHs.[140,141] A novel standardization technique has been suggested which is based on pre-loading a defined amount of standard on the sorbent and measuring – after exposure of the sampler – the amount of analyte extracted as well as the amount of standard remaining on the sorbent. Thereby, a calculation of the analyte concentration in the sample is possible.[140]

Besides PDMS as receiving phase, solid sorbent particles enclosed in a suitable diffusion barrier have been employed for passive sampling in water analysis. Styrene/divinylbenzene-based resins have been filled into a porous ceramic tube ("Ceramic Dosimeter").[142,143] Alvarez

Table 2. Applications of stir bar sorptive extraction using polydimethylsiloxane for trace analysis of organic contaminants in water samples.

analyte	analytical technique	detection limits	comments	literature
PAHs	GC-MS	0.1 … 2 ng L^{-1}		121
PAHs	HPLC-fluorescence	0.1 … 1.2 ng L^{-1}	PDMS rod	39
PAHs	GC-MS	0.02 … 0.09 ng L^{-1}	PDMS tube	40
PAHs	GC-MS	sub ng L^{-1}		122
Hydroxy PAHs	GC/MS	0.27 … 25 ng L^{-1}	derivatization with AA prior to extraction	47
35 pollutants (pesticides and PAHs)	GC-MS	low ng L^{-1} range		123
pyrethroid pesticides	GC-MS	1 … 2.5 ng L^{-1}		124
64 pesticides	GC-MS	0.2 … 20 ng L^{-1}		125
phenols	GC-MS	100 … 400 ng L^{-1}		51
chlorophenols	GC-MS	1 … 2 ng L^{-1}	derivatization with AA prior to extraction	48
alkyl phenols	GC-MS	0.2 … 10 ng L^{-1}	silylation prior to GC	126
alkylphenols and bisphenol A	GC-MS	0.1 ng … 3.2 ng L^{-1}	derivatization with AA prior to extraction	46
phenolic xenoestrogens	GC-MS	0.5 … 2 ng L^{-1}	derivatization with AA prior to extraction	54
bisphenol A	GC-MS	1 ng L^{-1}	derivatization with AA prior to extraction	45
endocrine disrupting chemicals	GC-MS	ng L^{-1} range		127
endocrine disrupters (pesticides)	GC-MS	10 … 240 ng L^{-1}		128
nonylphenol, octylphenol	GC-MS	2 … 20 ng L^{-1}		129
estrogens	GC-MS	0.5 … 2 ng L^{-1}	derivatization with AA prior to extraction	52
17ß-estradiol	GC/MS	0.5 ng L^{-1}	derivatization with AA prior to extraction, silylation prior to GC	53
25 polychlorinated biphenyls	GC-MS	0.05 … 0.15 ng L^{-1}		130
organotin compounds	GC-ICP/MS	100 ng L^{-1}		131
insect repellent	GC/MS	25 ng L^{-1}		132
sunscreen agents	GC/MS	0.5 ... 1 ng L^{-1}		133
polybrominated diphenyl ethers	GC/MS	0.4 … 9.4 ng L^{-1}		134

AA: acetic acid anhydride

et al. developed the "polar organic chemical integrative sampler" (POCIS) which consists of particulate sorbent material contained between two microporous polyethersulfone membranes.[144] A POCIS filled with OASIS HLB particles was successfully used for residue analysis of drugs in effluents of wastewater treatment plants.[145] C18-modified silica particles immobilised by PTFE fibrils (Empore disks) together with a diffusion-limiting membrane have been employed for determination of pesticides in marine environments.[146]

8. New Alternatives in Sorptive Extraction

Frank and Guan developed an approach called sorptive-layer vial extraction (SLVE).[147] The sample is filled into a small vial of a volume of for example 1 mL. The whole inner surface of the vial is coated with a film of PDMS. In this way, the phase ratio can be improved considerably. Sampling, extraction, and thermodesorption/injection for GC takes place within the same vial, so that sources of errors can be reduced.

The "solvent in silicone tube extraction (SiSTEx)" recently described by Janska et al. is another form of sorptive extraction.[148] It uses a piece of PDMS tubing plugged at one end and filled with an organic solvent like acetonitrile. The whole device is inserted into a water sample. Hydrophobic analytes partition into the PDMS phase, and are subsequently extracted into the inner acetonitrile phase. The extract can be used for GC or HPLC analysis. This technique is similar to the concept of "membrane-assisted solvent extraction (MASE)" introduced by Popp et al. who used non-porous polypropylene as membrane material between the aqueous sample and an organic solvent.[149–151] SiSTEx and MASE should not be mixed up with other approaches that use porous membranes enabling the direct contact between the aqueous sample and a water-immiscible extraction solvent. Such a set-up is a true liquid-liquid extraction technique and is different from the basic principles of sorptive extraction.

9. Conclusions

Sorptive extraction techniques like SPME and SBSE have become mature tools for trace determination of organic pollutants in water samples. In many cases, they can replace established methods based on SPE procedures. A comparison of SBSE and SPE for determination of PAHs in water has demonstrated that both sample preparation techniques yield similar repeatabilities and detection li-

mits.[152] Sorptive extraction techniques fulfil the still increasing demands for faster and more cost-effective methods in environmental analysis.

The satisfactory reliability of modern SPME methods has resulted in systematic evaluation of this technique as an alternative within official methods for analysis of organic pollutants in water. Recently, a new SPME method has been added to the German Standard Methods for the Examination of Water, Waste Water, and Sludge (group F, part 34) entitled "Determination of selected plant treatment agents, biocides and breakdown products; Method using gas chromatography after solid-phase microextraction". Furthermore, there is the ASTM D6520-00 method entitled "Standard practice for the solid phase micro extraction of water and its headspace for the analysis of volatile and semi-volatile organic compounds". This clearly demonstrates that SPME has become well-accepted, although it is just fair to mention that SPE might still remain the method of first choice for many applications.

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Povzetek

Pri analizi okoljskih vzorcev vode zahtevamo določitev onesnaževal organskega izvora vse do ng L^{-1}, zato je predkoncentriranje in čiščenje vzorcev nujno potrebno pred uporabo separacijskih tehnik. Ekstrakcija na trdni fazi je postala ena izmed najpomembnejših tehnik in temelji bodisi na enkratni ali večkratni ravnotežni porazdelitvi analita med vzorcem in sorbentom. Postopke, ki temeljijo na enkratni porazdelitvi, kot so mikroekstrakcija na trdno fazo, ekstrakcija na mešalo s sorbentom in sorodne tehnike, imenujemo sorpcijski ekstrakcijski postopki. Naraščajoča priljubljenost teh postopkov temelji na manjši porabi časa in povečani učinkovitosti. V tem članku ponujamo pregled stanja vede na področju sorpcijske ekstrakcije za uporabo pri določanju sledov organskih onsenaževal v vzorcih vode, tako s teoretičnega stališča kot tudi s stališča praktične uporabe. Vse bolj razširjeno sprejemanje sorpcijske ekstrakcije med uradne metode je znak, da nudijo želeno zanesljivost in robustnost tudi za rutinski monitoring.