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Review

Solid-phase microextraction coupled to gas chromatography: a new method for the analysis of organics in water

Ralf Eisert*, Karsten Levsen

Department of Analytical Chemistry, Fraunhofer Institute of Toxicology and Aerosol Research, Nikolai-Fuchs-Strasse 1, D-30625 Hannover, Germany

Abstract

Methods developed for the analysis of organic compounds from aqueous samples by solid-phase microextraction (SPME) coupled to gas chromatography (GC) are reviewed with special emphasis on the determination and monitoring in environmental samples contaminated by organic micropollutants, i.e., benzene, toluene, ethylbenzene and xylene isomers (BTEX), pesticides, phenols and polycyclic aromatic hydrocarbons (PAH).

Keywords: Solid-phase microextraction; Reviews; Environmental analysis; Water analysis; Pesticides; Phenols; Polynuclear aromatic hydrocarbons; Aromatic hydrocarbons

Contents

* Corresponding author.

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1. Introduction

In general, most organic pollutants of interest in aqueous environmental samples, i.e., pesticides, have to be extracted and enriched before their instrumental determination. This isolation from a sample matrix is often achieved by sampling and extraction steps separate from the instrumental analysis. In the past, sample preparation was dominated by the conventional liquid–liquid extraction, a time-consuming multi-step method for which large amounts of solvents were necessary. Today, many sampling and extraction methods are still based on classical techniques, such as the common Soxhlet extraction method [1]. Liquid–liquid extraction has been largely replaced in the past few years by solid-phase extraction (SPE) using a variety of different sorbents [2–6]. An optimized selectivity could be achieved by using analyte-specific sorbents for different compound classes. These SPE methods are simple, and less time-consuming than classical liquid–liquid extraction as many samples can be enriched in parallel. Moreover, inexpensive and less (toxic) solvents are needed. The full automation of the extraction process in combination with the control of the gas chromatographic system is possible. However, SPE is still a multi-step process that is prone to loss of analytes if it is not fully automated and still needs toxic organic solvents for the elution step. Furthermore, SPE is limited to semi-volatile compounds because the boiling points of the analytes must be substantially above that of the solvents. By coating the sorbent on a fine rod of fused-silica (a kind of inverted fused-silica capillary column, where the polymeric film is on the outside) the limitations of SPE may be overcome. This new extraction technique, solid-phase microextraction (SPME), was recently introduced by Pawliszyn and co-workers [7]. The SPME method, which is described in more detail in section 2, is based on an immobilized liquid phase (i.e., polydimethylsiloxane or polyacrylate polymers) as a stationary phase and is used for the direct extraction of organic trace compounds from water by simply dipping the fibre into the aqueous sample. Hence sampling, extraction and concentration are focused in a single step. After absorption, the fibre is transferred into the heated injector of the gas chromatograph and exposed for a given period of time, where the organic compounds are thermally desorbed from the polymeric phase. The total amount of extracted sample is used for the determination by gas chromatography (in contrast to conventional extraction methods). The fibre can be used repeatedly for many extraction cycles. Very small sample volumes, 1–5 ml, are often sufficient for the analysis. This method represents a further important advance in the efficient extraction of organic pollutants from aqueous samples at trace levels. So far, SPME has been applied to the extraction of organic compounds from different matrices including air [8], water [9] and soil [10]. The SPME method shows several attractive features: it is very simple, fast, easy to automate by use of a commercially available auto-sampler [11,12]. Finally, and this seems to be a completely new aspect for the extraction process, no solvent is necessary for the extraction. The operation principle of any sample preparation technique is the partitioning of the analytes between the sample matrix and an extracting phase. Therefore, sample preparation methods have become available which use little or no organic solvent. These solvent-free techniques can be subdivided into three major classes: gas-phase extraction, membrane extraction, and sorbent extraction [13]. SPME, like SPE, belongs to sorbent extraction methods but works completely solvent-free. Therefore, it becomes one step

nearer to an ideal instrument which performs sampling or sample preparation and, when coupled to GC, separation, quantification, and evaluation without human intervention.

This article reviews the various papers devoted to SPME analysis of organics from environmental aqueous samples. Most studies have dealt with four compound classes determined in water, namely, aromatic hydrocarbons (e.g., BTEX), pesticides, phenols and polycyclic aromatic hydrocarbons (PAH). This review cites all important articles in which SPME has been used for the monitoring of organic water pollutants.

2. Extraction

Solid-phase microextraction consists of two steps: first, the absorption of the analytes from the (aqueous) matrix by dipping the SPME fibre into the matrix, and second, the desorption of the analytes from the polymeric layer into the carrier gas stream of the heated GC injector. An illustration of both steps is shown in Fig. 1. A linear relationship is expected between the amount of analyte absorbed by the fibre and its concentration in the solution [14].

2.1. Theory

The partitioning of analytes between an aqueous sample and the polymeric film on the fibre is the main principle on which SPME is based. A mathematical model for the dynamics of the absorption process was developed by Louch et al. [15]. The amount of analyte absorbed by the polymeric phase at equilibrium (infinite volume assumed) is proportional to the concentration in the aqueous solution and is determined by the partition coefficient. As shown in Eq. 1:

$$n = \frac{K_{fs} V_f C_0 V_s}{K_{fs} V_f + V_s} \quad (1)$$

where n is the number of moles of the analyte absorbed by the stationary phase, K_{fs} is the partition coefficient of an analyte between the stationary and the aqueous phase, V_f and V_s are the volumes of the stationary phase and the sample and C_0 is the initial concentration of the analyte in the aqueous phase.

Louch et al. [15] showed that, in the case of $V_s \gg K_{fs} V_f$, the amount of analyte extracted by the polymeric film is given by:

$$n = K_{fs} V_f C_0 \quad (2)$$

and is not related to the sample volume. Thus, there is a linear relationship between the concentration of the analytes in aqueous samples and the amount absorbed by the fibre. This leads to a linear response of the GC detector when the absorption conditions in the sample and the desorption conditions in the injection port of the gas chromatograph are reproducible (Eq. 2).

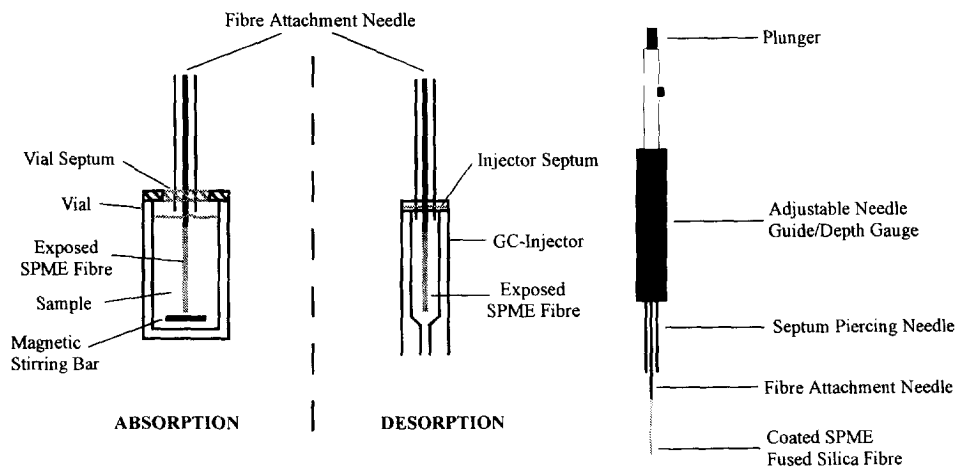

Fig. 1. Illustration of the SPME process and sampling equipment.

They assume that the dynamics of extraction and thus the extraction times are a diffusion-controlled process.

$$\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2} \quad (3)$$

Based on Fick's second law (Eq. 3), they calculated time profiles for perfectly stirred and unstirred samples of infinite volume. They demonstrated that the time for reaching the equilibrium concentrations in a perfectly agitated sample is relatively short.

Without intensive mixing of the aqueous solution, the equilibration time increases considerably. In this static case, transport of the analyte is limited by the diffusion in both the aqueous phase and the aqueous layer at the fibre surface; during the absorption process, the concentration gradient at this layer is steadily decreasing, thus reducing the flux into the fibre. In the dynamic case (extensive stirring), a layer of water still remains on the surface of the polymeric fibre so that the final equilibration time is determined by diffusion through this layer. A typical example for the influence of intensive stirring of the aqueous solution on the extraction efficiency is shown in Fig. 2. Usually the amount absorbed on the fibre may be easily increased by a factor of ca. 5 with stirring of the aqueous sample [10].

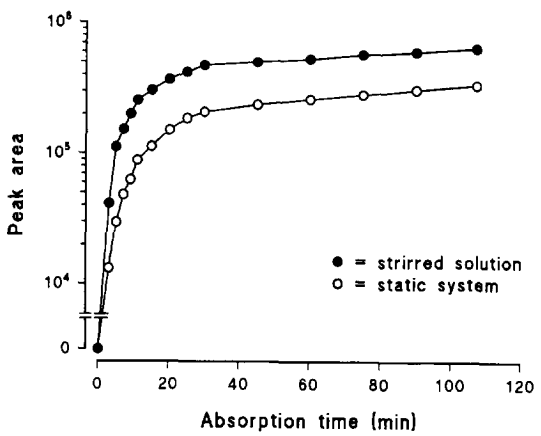

Fig. 2. Time dependence for equilibration of propachlor (herbicide) between the aqueous and the polyacrylate phase. The extraction was performed from a sodium chloride saturated aqueous solution spiked with propachlor at 24 ng/ml. Two exposure time profiles are shown: one with intensive stirring of the aqueous sample and the other without mixing.

2.2. The extraction of organics from aqueous samples

Two approaches have mainly been used for extraction of organics from aqueous samples by solid-phase microextraction. First, the direct extraction of the aqueous matrix, where the SPME fibre is directly exposed to the aqueous matrix. This method is usually used for semi-volatile compounds, e.g., polar pesticides such as triazines [9]. Second, the exposure to the headspace above the aqueous sample, which is used for the extraction of more volatile organic compounds (VOCs), e.g., BTEX [16] or phenols after in-situ derivatization and extraction of their acetates from the headspace over the water [17]. The absorption times of the analytes will increase if the fibre is exposed into an aqueous media. The diffusion coefficients in water are lower by several orders of magnitude compared to extraction from the gas phase. Therefore, the kinetics in solution are slow compared to gas-phase transport. Thus, the equilibria of the analytes between the gas phase and the polymeric fibre are achieved, normally, in a few minutes. The time necessary for reaching the absorption equilibria from aqueous solutions are, in general >1 h. However, there is no need to achieve complete equilibrium concentrations if only the exposure time of the fibre is kept exactly constant. Furthermore, up to 70–80% of the maximum amount extracted after reaching the equilibrium of the investigated compound will be extracted in the first 20% of the total equilibration time. There are other parameters, e.g. mixing the aqueous solution, which have a pronounced effect on the kinetics and therefore the total amount extracted after a certain time of exposure.

2.3. In-line coupling to gas chromatography

Solid-phase microextraction can be easily coupled with gas chromatography. The heated split/

splitless injector, septum programmable injector (SPI) or the on-column port of the gas chromatograph can be used for the thermal desorption of the analytes from the fibre. The SPME fibre is drawn into the syringe needle when the plunger is retracted. This protects the fibre when the syringe needle is used to pierce the septum of a sample vial or, in this case, of the GC injector. The plunger can then be pushed down to expose the fibre to the GC carrier gas stream during thermal desorption (see Fig. 1). The optimization of the desorption time is one of the first steps to be done if a new SPME method is to be developed. The SPME fibres are conditioned prior to use at a certain temperature (e.g., 300°C for the 85-μm polyacrylate fibre) under helium for several hours to reduce bleeding. This can be achieved very simply by exposure of the fibre to a split/splitless injector while the purge is open. The desorption of the analytes takes from a few seconds up to several minutes depending on the compound class. In general, there is no need for further trapping steps. However, the initial oven temperature should be 60–90°C below the boiling point of the first eluting compound. For VOCs such as CS_2 cryogenic cooling at, for example, −20°C focusses the analyte at the beginning of the column [18,19]. The thermal desorption in the GC injector facilitates the SPME technology for thermally stable compounds. Otherwise, the thermally labile analytes might be determined by SPME–GC, e.g., if an in-situ derivatization step in the aqueous medium is performed prior to extraction.

2.4. Analysis

The calibration for the SPME analysis is achieved by standards containing the target compounds in organic cosolvents such as methanol which are spiked into water at different amounts. Calibration performed in this way includes both the extraction and instrumental determination. If matrix effects are not reproducible, the use of deuterated standards should be included. Optimum quantification may be achieved if isotopically labelled standards of target compounds are available which show a very similar chemical and physical behaviour to the target analytes themselves [20]. Although SPME depends strongly on some basic parameters such as pH or concentration of salts (which influences the ionic strength of the sample) [20,21], equal extraction conditions can be obtained only when these parameters are standardized for the SPME method. Maximum selectivity for monitoring environmental matrices may be achieved if instrumental coupling techniques such as GC–MS are used for identification and quantification of the analytes in these samples.

Selectivity is further gained by proper choice of the sorbent (polymeric phase) used for extraction which is shown in more detail in section 2.2. The instrumental selectivity which is very important for the unequivocal identification of organics, especially, in unknown samples enhances the specificity of the SPME–GC analysis [22,23]. If industrial wastewaters are to be monitored, there is a need for selective detection by GC–MS. Often observed matrix effects are reduced by SPME analysis because the interfering matrix compounds can be only enriched on the fibre until their partitioning equilibria are reached. But there are still other interfering effects from the matrix itself which determine the free amount of analytes present in the aqueous sample. However, this is not an effect which is significant for SPME analysis, it prones all the other extraction techniques from water. It is conceivable that solid-phase microextraction is less effective if environmental samples are analysed, as in this case many often unknown matrix components compete with the analytes for absorption by the polymer. Therefore, compounds first tentatively identified by less specific detection methods such as GC–NPD should be later confirmed by GC–MS, where under selected-ion SIM conditions several characteristic masses of a compound of interest may be monitored and used for confirmation of the results. The selectivity achieved by using a polymeric phase specific for the investigated compounds (see section 2.5) should be enhanced by more selective detection systems when complex and heavily contaminated samples will be analysed.

2.5. Commonly used fibres

Since SPME was offered to analytical researchers in 1989 [7] the variety of different coating materials for SPME fibres has increased. For organic compounds the basic principle of 'like dissolves like' applies. Polar compounds are more likely to be extracted by polar coatings, and vice versa. Today, four different types of commercially available fibres are used for more selective determination of different compound classes. They are summarized in Table 1. In general, the thicker SPME phases show a higher capacity for the extracted organics. The polydimethylsiloxane (PDMS) fibres were the first polymers used for SPME [7]. They show excellent selectivity for non-polar compounds such as BTEX [24]. The reduction of the film thickness from 100 to 7 μm produces a bound phase which is more stable at higher temperatures and allows the analysis of compounds with higher boiling points. Thus, the desorption process is much faster since the diffusion out of the 7-μm coating is much easier than desorption out of the 100-μm coating. These phases are not amenable for the more polar compounds such as phenols and several pesticides, e.g., triazines. The new polyacrylate fibre represents a breakthrough in the extraction of polar compounds. This fibre coating is obviously more hydrophilic, thus facilitating the extraction of polar analytes from water. This is demonstrated for pesticides and phenols in sections 4 and 5.

3. Volatile organic compounds

The first compound class studied by SPME were the benzene, toluene, ethylbenzene, and the xylene isomers (generally referred as the BTEX compounds). They were used as volatile model compounds to investigate the theory and principles of SPME processes [14,25]. Thus, analytical methods for the determination of VOCs such as

Table 1
Commonly used SPME fibres

Fibre	Property
100 μm Polydimethylsiloxane (PDMS)	High capacity Max. exposure temperature[a] 220°C recommended desorption temperature 200°C For volatile, low-, mean-boiling (<220°C) and apolar compounds (e.g. VOCs), tolerates concentrations of organics up to 1%
30 μm Polydimethylsiloxane (PDMS)	Characteristics between the 100-μm and the 7-μm fibre Max. exposure temperature[a] 280°C recommended desorption temperature 200–270°C
7 μm Polydimethylsiloxane (PDMS)	Bound phase for higher desorption temperatures Max. exposure temperature[a] 340°C recommended desorption temperature 220–320°C For semivolatile, high-boiling (>200°C) and apolar compounds (e.g. PAHs), tolerates concentrations of organics up to 1%
85 μm Polyacrylate	High capacity Max. exposure temperature[a] 310°C recommended desorption temperature 220–300°C For both polar and non-polar compounds (e.g. hydrophilic pesticides and phenols), tolerates concentrations of organics up to 10%

[a] Max. temperature recommended by the manufacturer.

Table 2
Comparison of distribution constants for liquid and gas phases with tabulated K_{ow} constants (from Ref. [8])

Compound	Log K_{ow}	Log K_{aq}	Log K_g
Chloroform	1.97	2.6	2.6
1,1,1-Trichloroethane	2.18	3.4	3.1
Carbon tetrachloride	2.83	3.0	2.8
Trichloroethane	2.3	3.1	3.1
1,2-Dichloropropane	2.28	2.8	2.4
Bromodichloromethane	1.88	2.7	3.4
1,3-Dichloropropane	1.41	1.3	3.4
1,1,2-Trichloroethane	2.18	3.0	3.3
Tetrachloroethane	2.6	3.9	3.1
Dibromochloromethane	2.08	3.5	3.0
Bromoform	2.30	2.8	3.5
1,1,2,2-Tetrachloroethane	2.39	1.8	3.3

BTEX and halogenated hydrocarbons were reported first in the literature [26–33]. BTEX are common contaminants in ground and surface water. Special detection techniques such as direct exposure of the SPME fibre to raman spectrometry were carried out by Wittkamp et al. [34]. Pawliszyn and co-workers have shown that the octanol–water partitioning coefficient K_{ow} can be used as an approximation for the partitioning constant K_{fs} in Eq. 2 if using a non-polar polymer, e.g., PDMS as a stationary phase [8]. This correlation is shown in Table 2 from Ref. [8]. In general, the aqueous-fibre distribution constants K_{aq} are lower than the corresponding gaseous-fibre distribution constants K_g [8].

3.1. BTEX

3.1.1. Direct extraction from water

Potter and Pawliszyn reported in 1992 a direct analysis of the BTEX using the 100 μm PDMS fibre combined with gas chromatography–ion trap mass spectrometry (GC–IT-MS). They achieved a limit of quantification (LOQ) of 50 pg/ml benzene in water. This corresponds to an absolute amount of 5 pg extracted by the SPME fibre. The LOQs for the other BTEX were all $\leq$50 pg/ml as summarized in Table 3 from Ref. [26]. The method was linear over at least four orders of magnitude and the precision was in general <8% at a concentration of 50 pg/ml

Table 3
Distribution constants, limits of detection, limits of quantification, precision of SPME, K_{ow} values, and method detection limits (MDL) as required by MISA and USEPA regulations (from Ref. [26])

Analyte	$\log_{10}K^a$	$\log_{10}K_{ow}$	LOD (pg/ml)	LOQ (pg/ml)	Precision 50 pg/ml (%)	Precision 15 ng/ml (%)	MDL	
							MISA (pg/ml)	USEPA (pg/ml)
Benzene	2.30	2.13	15	50	7.3	5.3	500	30
Toluene	2.88	2.69	5	15	6.7	3.2	500	80
Ethylbenzene	3.33	2.84	2	7	7.2	3.6	600	60
m- and *p*-Xylene	3.31	3.20 *meta* 3.15 *para*	1	4	6.5	6.5	1100	90
o-Xylene	3.26	2.77	1.5	5	5.5	2.7	500	60

[a] Experimentally determined.

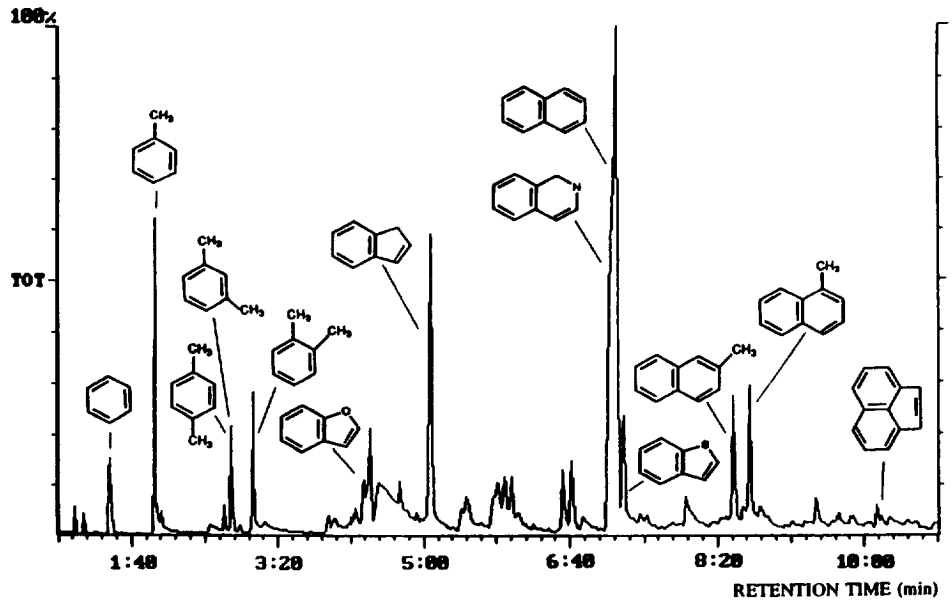

Fig. 3. Total ion chromatogram showing organics detected and identified in a coal gasification wastewater sample (from Ref. [26]).

BTEX in water. The authors used an absorption time of 30 min for complete equilibration and for desorption a septum programmable injector (SPI) with a heating programme of 250°C/min from 25 to 150°C, where the final temperature was held for 3 min. The column was held at −5°C for the first two minutes to achieve sharp peaks. No significant carryover of BTEX on the fibre could be observed after a 1.5 ng/ml standard was measured. A total ion chromatogram showing organics, such as benzene and toluene besides several PAHs, detected and identified in a coal gasification wastewater sample is demonstrated in Fig. 3 from Ref. [26]. Sarna et al. investigated the same compounds by using a carbon-layer open tubular capillary column for GC. All BTEX were separated without focussing the analytes by cryogenic trapping [33]. The authors used splitless injection at 220°C for 2 min.

3.1.2. Headspace exposure

The second extraction mode for SPME is the extraction from the gas phase or introduction into the headspace above an aqueous sample [16,35]. Volatiles are extracted from the gas matrix; furthermore they are concentrated in the coating of the fibre. Thus, an increase in the sensitivity by this sampling method is assumed and limits of detection are therefore in the ppt range [16,36]. MacGillivray et al. reported in 1994 their results from a comparison of headspace SPME versus purge and trap for the determination of BTEX in water [35]. Fig. 4 from Ref. [35] shows the correlation of the results

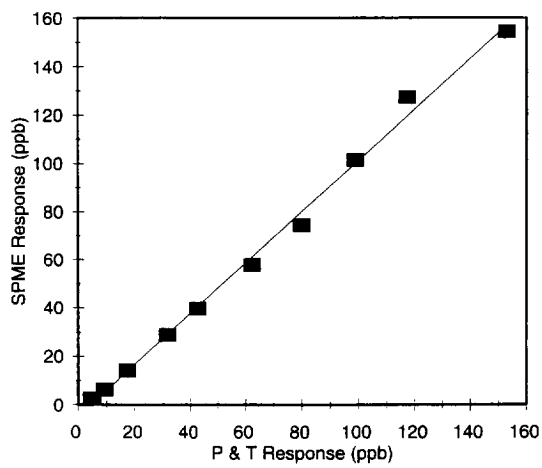

Fig. 4. Headspace solid-phase microextraction response versus purge and trap response for toluene in water (from Ref. [35]).

observed from both techniques. The coefficients of correlation for all investigated compounds in these SPME versus purge and trap diagrams are usually >0.99. LODs of both methods are very similar using optimized techniques, but slightly lower for SPME.

3.1.3. Thin film fibres and fast GC

The use of thin film fibres, i.e. 56 μm PDMS, was described by Arthur et al. [25]. Górecki and Pawliszyn tested two modes for heating the fibre in the injector, continuous and flash heating [37]. The latter method is an important alternative if high-speed separation is to be achieved. Fast GC allows the separation of BTEX compounds in less than 20 s after desorbing from a 56 μm PDMS fibre. A 15-μm fibre needs about 12 s for complete separation when sampling from headspace [37]. This sets new dimensions in the in-time monitoring of target compounds although the method is still too expensive for widely used routine analysis.

3.1.4. Internally cooled SPME fibre

A recently published work by Zhang and Pawliszyn overcomes the main problems of headspace SPME by using an internally cooled SPME device for quantitative extraction [38]. A very steep temperature gradient from the heated aqueous sample to the internally cooled SPME fibre accelerates the kinetics of the extraction process and therefore the mass transport to the fibre. Quantitative extraction was achieved with this device in less than 5 min for BTEX. LODs are in the sub ppt range for the investigated compounds [38]. Finally, they developed a thermodynamic theory for calculation of coating/gas-phase partition coefficients of the analytes.

3.2. Halogenated VOCs

Page and Lacroix described a SPME-GC method using a hall electrolytic conductivity detector for determination of 33 halogenated volatile hydrogens [30]. They used a PDMS fibre equilibrated in the headspace. Furthermore, they performed standard addition for analysis of beverages and selected foods. A SPME–GC–ECD method for determination of these halogenated compounds was developed by Chai et al. for both air and water matrices [8]. LODs in the range of 1–130 ng/l extracting the liquid phase were achieved. The method was linear over at least three orders of magnitude and shows relative standard deviations of 1–5%. In air they observed LODs in the ppt range (v/v). The linearity is at least two orders of magnitude with relative standard deviation of 1–7%. Absorption needs 10 min for the gas phase and 20 min in the aqueous phase. In general, very volatile compounds absorb much faster, reaching their equilibrium in the gas phase than in the liquid phase. Typical equilibration times are summarized for twelve VOCs in Table 4 from Ref. [8]. In the aqueous phase, analytes must diffuse through a static layer of water next to the fibre which reduces the flux as described in section 2.1. In the gas phase, the diffusion rates are significantly higher by about four orders of magnitude which increase the extraction time [8]. The amount absorbed by the fibre decreases with increasing temperature and humidity [8]. Very similar results for sampling VOCs in environmental air are reported by Chai et al. [39].

Table 4
Equilibration times (min) of analytes in the liquid and gas phases (from Ref. [8])

Compound	Liquid phase	Gas phase
Chloroform	5	1
1,1,1-Trichloroethane	10	3
Carbon tetrachloride	15	2
Trichloroethane	10	5
1,2-Dichloropropane	5	10
Bromodichloromethane	7	10
1,3-Dichloropropane	5	10
1,1,2-Trichloroethane	7	5
Tetrachloroethane	5	5
Dibromochloromethane	10	5
Bromoform	7	10
1,1,2,2-Tetrachloroethane	7	10

4. Pesticides

One major field for monitoring water pollutants in the environment is the determination of

pesticides, compounds which are used extensively in agriculture throughout the world to protect plants against insects, fungi, and weeds. Their analysis was reviewed by Sherma [40]. If not biodegraded within the soil, these pesticides may move through the soil profile and cause a pollution of ground water [41]. These agents may persist for years, thus representing a possible risk where ground water is the source of drinking water. Therefore, the European Union has set in its drinking water regulations a maximum permissible level of 0.1 μg/l per pesticide [42]. Thus, a SPME method using the 85-μm polyacrylate fibre was applied by Eisert and Levsen [9] for the first time to 34 pesticides such as triazines, organophosphorus and 2,6-dinitroaniline compounds, three important pesticide classes of relatively high polarity, at this low level. The extraction efficiency strongly depends on the polarity (or hydrophobicity) of the individual compound, as shown before; i.e., the less polar or the more hydrophobic the compounds, the higher their affinity to the polyacrylate phase, which leads to a peak response after the SPME process which may vary strongly depending on the compound studied even for chemically related compounds such as triazine herbicides [43]. Therefore, an almost linear dependence of the peak response versus the octanol–water partitioning coefficient K_{ow} is observed which is shown for the triazines in Fig. 5. This effect can, however, be overcome by sodium chloride addition which increases the ionic strength of the aqueous phase as demonstrated in Fig. 6. This increases in particular the extraction efficiency for the polar compounds (with low octanol–water partitioning coefficient, K_{ow}), so that almost equal extraction efficiencies are achieved for triazine pesticides [9].

If combined with a gas chromatograph with nitrogen–phosphorus selective detection, very low limits of detection (<0.1 μg/l) can be achieved, as the total amount of extracted analytes is transferred to the gas chromatograph (in-line coupling). Typical results, e.g., for triazines are shown in Table 5. Thus, the limits set by the European Union for pesticides in drinking water can be readily verified.

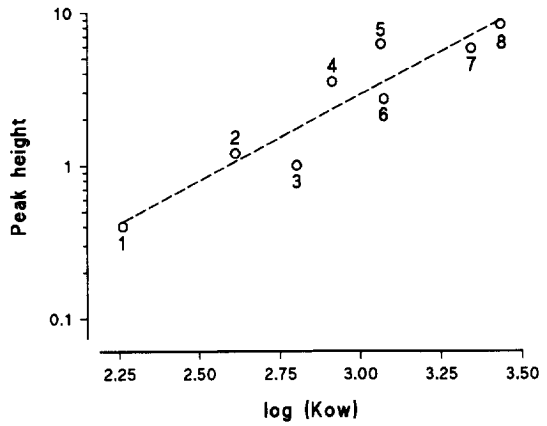

Fig. 5. Dependence of peak response (extraction efficiency) on octanol–water partitioning coefficiency K_{ow} (double logarithmic scale). Assignment: 1 = simazine; 2 = atrazine; 3 = simetryn; 4 = propazine; 5 = terbuthylazine; 6 = ametryn; 7 = prometryn; 8 = terbutryn.

4.1. Selective detection by GC–AED and GC–MS

Even more selective detection methods were applied for SPME analysis such as atomic emission detection, AED [22], and mass spectrometry, MS [23]. While MS is not only a very selective but also a very sensitive method, AED suffers from its relatively poor sensitivity despite

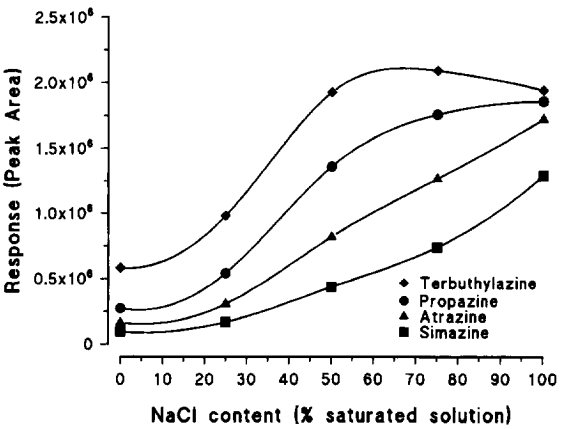

Fig. 6. Dependence of peak response (extraction efficiency) on sodium chloride (NaCl) content which was varied between 0 and 100% saturated solution.

Table 5
Gas chromatographic determination of triazine pesticides after solid-phase microextraction using the 85 μm polyacrylate fibre, coefficients of correlation, limits of detection and precision with $n = 3$

Peak. No.	Retention time (min)	Compound	Coefficient of correlation, r	Limit of detection (μg/l)	Precision[a] (%)
1	11.96	Atraton	0.9993	0.09	4.9
2	12.02	Simazine	0.9996	0.08	7.1
3	12.21	Atrazine	0.9998	0.03	6.1
4	12.31	Propazine	0.99992	0.02	6.0
5	12.57	Terbuthylazine	0.999993	0.01	5.9
6	13.38	Sebuthylazine	0.9994	0.02	5.6
7	13.85	Desmetryn	0.991	0.02	4.8
8	14.38	Simetryn	0.999997	0.015	6.1
9	14.55	Ametryn	0.99998	0.02	6.1
10	14.70	Prometryn	0.999993	0.015	4.2
11	15.16	Terbutryn	0.99995	0.01	4.6
12	16.07	Cyanazine	0.998	0.04	1.3

[a] In triplicate.

a superior selectivity gained from element characteristic chromatography. A gas chromatogram obtained from GC–AED of nine organophosphorus pesticides which were extracted directly from water using a 100 μm PDMS fibre and monitored in the sulphur selective mode at 181 nm is presented in Fig. 7. The analysis of water samples from a ground water well and spiked river water samples were demonstrated. Matrix effects, e.g., by addition of humic acid, were studied in more detail in a recent study [23].

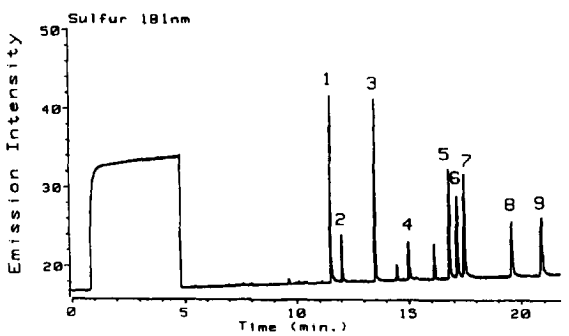

Fig. 7. Sulphur selective chromatogram at 181 nm of nine organophosphorus pesticides (30 ng/ml each) using SPME–GC–AED with the 100-μm polydimethylsiloxane fibre. Assignment: 1 = ethoprophos; 2 = sulfotep; 3 = diazinon; 4 = parathion-methyl; 5 = parathion-ethyl; 6 = bromophos-methyl; 7 = chlorthion; 8 = bromophos-ethyl; 9 = jodfenphos.

4.2. Matrix effects

Humic acids show no significant influence on the extraction at DOC (dissolved organic carbon) concentrations usually observed for surface water samples [23,44]. Moreover, the competition of major and minor components during the SPME process was investigated. It is conceivable that a high content of organics precludes an efficient extraction. To study this effect, different amounts of terbuthylazine, a compound with a high affinity to the 85-μm polyacrylate fibre, were added to a standard mixture of three triazines in concentrations varying over more than three orders of magnitude; no significant decrease in peak response for the other investigated pesticides (kept at constant concentrations) was observed. Thus, the effect of excess concentration of organics with high affinities to the SPME fibre on the extraction efficiency of other analytes in the low ppt to low ppb range is less pronounced than expected. This may be explained by the high capacity of the SPME fibres with thicker phase materials.

4.3. Hexachlorocyclohexanes

Popp et. al. developed a SPME method for the 100 μm PDMS fibre by GC–ECD for the determination of hexachlorocyclohexanes [10]. They found very low limits of detection for the four isomers α-, β-, γ- and δ-HCH ($\leq$32 ng/l by GC–ECD and $\leq$80 ng/l by GC–MS). The samples were collected from highly contaminated surface rivers used for several decades as a wastewater channel by the former East German chemical industry. They were extracted by the SPME method in the direct sampling mode under intensive stirring of the solution which was decided best for equilibration in 20–30 min. β-HCH concentrations up to 4.28 μg/l were detected in surface water samples. This is more than 40 times higher than the level set by the EC for drinking water [42].

5. Phenols

Phenols and differentially substituted isomers of this compound class represent an important group of compounds which are often present in environmental compartments similar to pesticides [45]. Many of these molecules are metabolites from other major pollutants such as explosives [46]. These metabolites are, if they are not thermally labile, amenable to GC and show a high polarity. Thus, they are difficult to extract from water. Methods exist for the extraction of these compounds from aqueous matrices by use of liquid–liquid extraction [45] and more recently by SPE [47]. When the 85-μm polyacrylate fibre became available, many of these polar molecules could be isolated from water by the SPME technique [17,48]. The extraction affinity of these even polar compounds could be enhanced by optimum pH adjustment and addition of salts such as sodium chloride thus increasing the ionic strength of the solution. They show a behaviour similar to that reported for pesticides, i.e. triazines (shown in section 4). Buchholz et al. reported two sampling techniques: first, direct extraction of phenols (including nitro- and chlorophenols) from aqueous media [48], and second, a headspace sampling of their in-situ generated acetates [17] both using a polyacrylate fibre. A precision better than 5% and limits of detection in the sub ppb range were achieved. Analysis in ground- and waste-water was reported. An example of a highly polluted sewage sample where two phenols were identified is shown in Fig. 8 from Ref. [17]. The effect of various pH values and salt concentrations on the extraction efficiency is shown in Table 6 from Ref. [17].

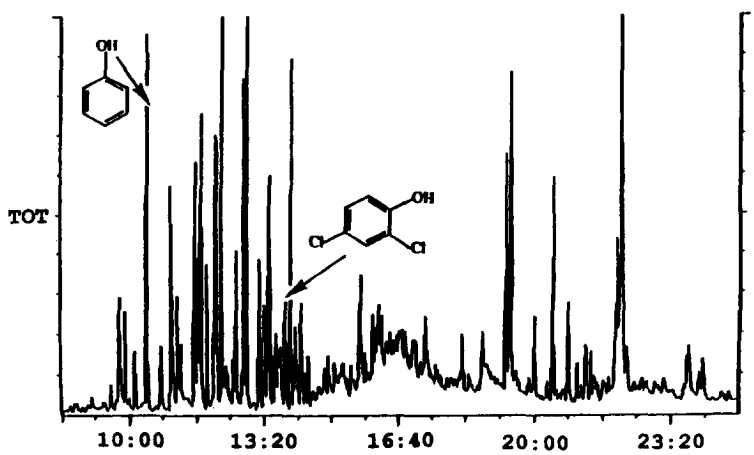

Fig. 8. Sewage sample. Phenol (80 ppb) and 2,4-dichlorphenol (0.3 ppb) were extracted from a sample of primary clarifier effluent (from Ref. [17]).

Table 6
Effect of acid and salt (from Ref. [17])

Compound	Factor increase				pK_a value
	pH 2	salt	pH 2 + salt	pH 2 + salt, 60 min	
Phenol	0.9	5.5	6.0	6.0	9.89
2-Chlorophenol	1.2	1.6	3.8	4.1	8.48
2-Nitrophenol	0.9	0.1	4.3	4.3	7.23
2,4-Dimethylphenol	1.1	5.0	5.6	5.6	10.63
2,4-Dichlorophenol	1.1	0.8	2.0	2.3	7.85
4-Chloro-3-methylphenol	1.1	1.7	1.9	2.3	9.55
2,4,6-Trichlorophenol	1.1	0.1	1.5	1.9	7.42
2,4-Dinitrophenol	10.1	0.2	16.8	17.0	4.09
4-Nitrophenol	0.6	0.1	3.0	3.1	7.15
2-Methyl-4,6-dinitrophenol	4.5	0.1	6.3	6.5	4.35
Pentachlorophenol	1.4	0.2	1.1	1.3	4.74

6. Other organic target compounds of interest

PAHs and nitroaromatics are two compound classes of further interest studied with SPME methods.

6.1. Polycyclic aromatic hydrocarbons

Potter and Pawliszyn used a 15 μm PDMS coating for extraction of PAHs from aqueous samples in this study. The large distribution constants for semi-volatile compounds (e.g. PAHs) lead to very low limits of detection in the ng/l (ppt) range if GC–MS is applied for detection [49]. Headspace SPME procedure is not limited to organic volatile or even semi-volatile compounds; i.e., polycyclic aromatic hydrocarbons are extracted as shown by Zhang and Pawliszyn for naphthalene and acenaphthalene after 5 min extraction time of 40 ppb PAHs [50].

6.2. Nitroaromatic compounds

Nitroaromatics were studied in lake water by Horng and Huang [51] using SPME–GC–FID with a 100 μm PDMS fibre. They used an exposure time of 10 min to extract isophorone and 3 min for nitrobenzene, 2,4-dinitrotoluene and 2,6-dinitrotoluene. The relative standard deviation of the method was usually <5%. LODs were 9 ng/ml for nitrobenzene and 15 ng/ml for the other compounds [51]. Further investigations for extraction of nitroaromatic compounds from water samples monitoring explosives near a former ammunition plant using different PDMS fibres were reported in 1995 by Schäfer [52].

6.3. Caffeine, methadone, and Bi(III)

Besides this upcoming prospect of environmental analysis by the SPME method, there are three further reports in which the SPME method was applied to other analytes. The determination of caffeine in beverages [53], methadone in urine [54] based on SPME analysis is shown. Even inorganic analytes, e.g., the metal ion Bi(III) in aqueous acidic potassium iodine solution, by a PDMS fibre followed by spectrophotometric detection of the yellow-coloured BiI_4^- complex [55] were extracted by the SPME method.

7. Conclusions

Successful SPME–GC of many compound classes from aqueous media are summarized in

this article. The major advantages of this technique are shown in the following list.
(a) The extraction is achieved without the use of solvents.
(b) The methods are very simple and fast.
(c) The methods are very sensitive if coupled in-line to GC and more selective if coupled to hyphenated techniques in GC (GC–MS).
(d) The methods are relatively insensitive to matrix effects if standard parameters, i.e., the ionic strength and pH, are controlled. Thus, relatively high contents of other organics do not interfere with the extraction.
(e) Only a very small sample volume of about 1–10 ml is necessary for SPME analysis.
(f) The fibres can be used repeatedly (in contrast to the normal solid-phase extraction (SPE) where the cartridge is discarded after use).

The small sample volume necessary may be attractive for many applications where the sample volume is limited, e.g., analysis of cloud, rain, or sediment water.

The SPME system can be readily coupled to a gas chromatograph. However, if organic pollutants in the ppt range are to be determined, GC–MS is more selective and even more sensitive at these low concentration levels. Thus, for pesticides the maximum level in drinking water set by the European Union can be verified better by the SPME method coupled in-line to GC–MS than to a GC system.

This review demonstrates that sample extraction and preparation still represents an exciting field of research. Besides a more rational optimization of the extraction methods and understanding the interactions between the analytes and sample matrices, the number of applications using the SPME method is increasing very fast. Furthermore, the development of a completely automated on-line sampling and analysis system based on a SPME procedure might be possible.

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