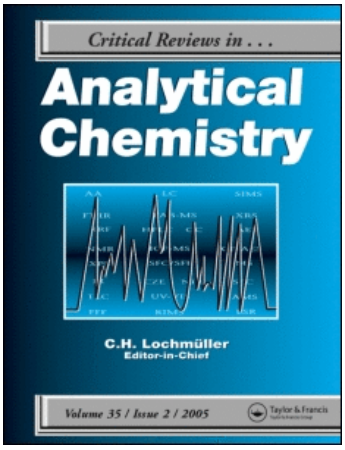

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Solid Phase Microextraction — A Convenient Tool for the Determination of Organic Pollutants in Environmental Matrices

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ABSTRACT: This article reviews the application of solid phase microextraction (SPME) for determination of organic pollutants in gaseous, liquid, and solid environmental samples. Practical aspects of direct and headspace SPME sampling and combination of SPME with other techniques of sample preparation are discussed.

The application range can be widened by derivatizing analytes. SPME can combined with other related techniques of sample preparation.

I. INTRODUCTION

From among 12 millions defined chemical compounds almost a million can be found in an immediate environment of man on level of ca. 10^{-10}% and above.[1] Many organics present in the environment is suspected to cause a genetic change in living organisms, some of them have prove cancerogenic and mutagenic activity.

The concentration level, from which one can speak about harmfulness, differs from substance to substance. This concentration is one of the factors determining the limits from which presence of a given toxic substance should be monitored in the environment. The second important parameter is a detection limit with respect to a given substance depending on an analytical technique,[1] and also on sample preparation. In environmental analysis, stages of sampling and sample preparation for final analysis should be as short as possible. The latter involves isolation of components of interest from a generally complex environmental mixture and their enrichment to a level making quantitative analysis possible. This part of an analytical procedure should be devoid of steps in which losses of analytes are significant, which can often happen when a multistep sample preparation procedure is applied. This problem has been dealt with in a number of books and monograph papers.

To a wide spectrum of the modern sample preparation techniques belong those based on extraction. Conventional extraction techniques such as liquid — liquid and liquid — solid extractions carried out at mild temperatures by shaking with an organic solvent or in a Soxhlet apparatus are often increasingly replaced by such that belong to the latest achievements in analytical chemistry (varieties of solid phase extraction — SPE, membrane extraction — ME, supercritical fluid extraction — SFE, accelerated solvent extraction — ASE, microwave-assisted extraction — MAE or ultrasonic extraction). Characteristics of a particular technique determine the frequency of its use in analytical laboratories. Typical disadvantages of conventional techniques are a large consumption of solvents and that they are laborious and time consuming. Their great advantage is relatively low price of necessary apparatus; this means that they are commonly used to extract analytes from environmental samples. In the case of the latest techniques, on the other hand, the cost of apparatus is often so high, that despite the obvious advantages they are not widely spread. In distinction from the conventional techniques, the newest ones are generally quicker and simpler and demand considerably smaller quantities of solvents.

Nowadays special attention is focused on such techniques, which are characterized by a consid-

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erable reduction or a complete elimination of organic solvents from sample preparation. When studying developmental trends (both methodical and instrumental), one can notice that special attention is paid to so-called solvent-free sampling and analyte isolation and enrichment techniques in which organic solvent is not used at all. This is connected with two aspects, that is, protection of the environment against additional quantities of solvents (dangerous sewage, pollution of laboratory air); and analysis cost reduction due to elimination of very pure and therefore expensive solvents.

Classification of existing solvent-free methods of sample preparation are given in Figure 1. None of the methods is ideal. For example, the techniques of analyte extraction by means of gas (e.g., static and dynamic headspace) are limited to volatile and relatively volatile organic compounds, membrane extraction is adequate for rather volatile nonpolar compounds, while solid phase extraction (SPE) to compounds of relatively low volatility. Among solvent-free methods of sample preparation, which are already widely used, we can find solid phase microextraction (SPME). It is a comparatively new technique of preparing of environmental samples (and also other samples) for analysis, which proves to be a very interesting and promising alternative to traditional methods.

Since the first papers on SPME were published in the years 1987 to 1989,[2, 3] more and more information on SPME use in routine analysis[4-8] has been appearing and also new possibilities of the technique have been showed.[9-12] When studying literature on the topic it would be difficult to pass over the changes in construction of an SPME device. At present, devices introduced by Supelco reign on market. Details of construction of these devices have already been given in many papers and will not be discussed here.[13, 14]

The SPME device can be used to perform the following analytical operations: sampling, isolation, and enrichment of analytes in one stage (analyte extraction from on investigated medium), and analyte introduction to a measuring apparatus (analyte desorption). Analytes sampling is based on their transport to and sorption in a thin film of stationary phase coated on an SPME fiber. The quantity of a given component trapped depends on its partition between phases (a sample and a stationary phase on the fiber). A partition coefficient is a measure of ability of a stationary phase to extract an analyte from the medium analyzed.

II. PRACTICAL ASPECTS OF SPME APPLICATION IN ENVIRONMENTAL ANALYSIS

A. Sampling — Analyte Extraction from the Investigated Medium

In the case of SPME, a sampled analyte and matrix determine the way of sampling. Two basic methods of sampling can be distinguished, that is, direct and indirect. This is schematically presented in Figure 2.

Analytes can be directly sampled from such media as atmospheric air, indoor air, workplace air, drinking water, and water for food industry and surface waters. The fraction of an analyte extracted from a medium depends on a partition coefficient and a volume ratio of a stationary phase and a sample.

In indirect sampling an SPME fiber is inserted in the sample headspace; this is applied in the case of liquid samples of very complex matrix and solid samples. Analysis of headspace differs little from analysis of gaseous samples; in the former analytes undergo distribution among three phases: a sample (liquid or solid), headspace, and stationary phase on a fiber; the concentration in the sample is derived from the quantity extracted to the fiber and determined by, for example, gas chromatography.[15] In headspace sampling a limiting factor is transport of analytes from the sample to the headspace.[16]

It was also shown,[13] that indirect analysis is more selective than direct analysis. High selectivity is especially important when isolating components from very complex matrices. An additional advantage of HS sampling is that column contamination with high-molecular-mass components possibly present in a sample can be avoided.

On the other hand, however, headspace analysis can give erroneous results due to non-

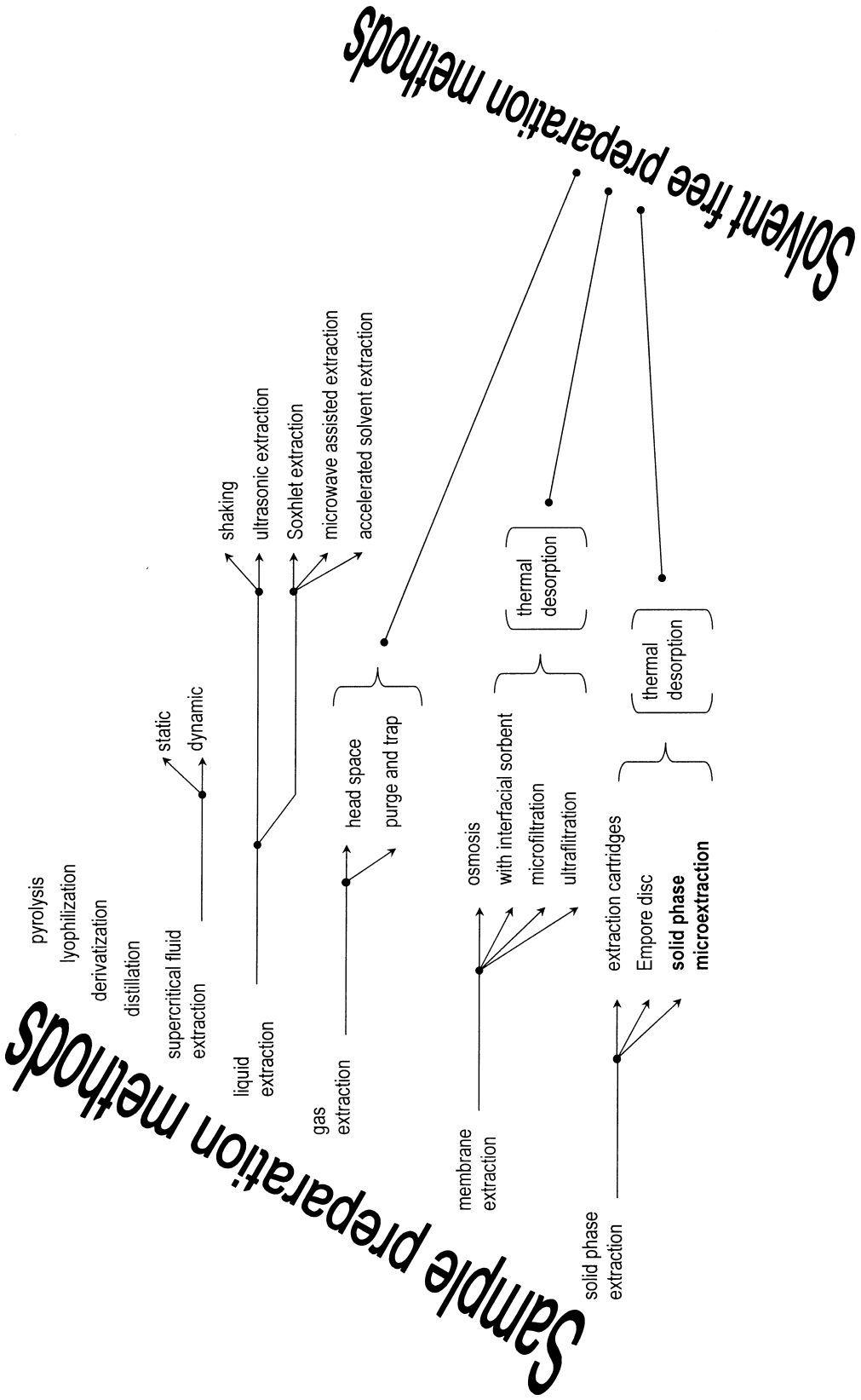

FIGURE 1. Sample preparation methods.

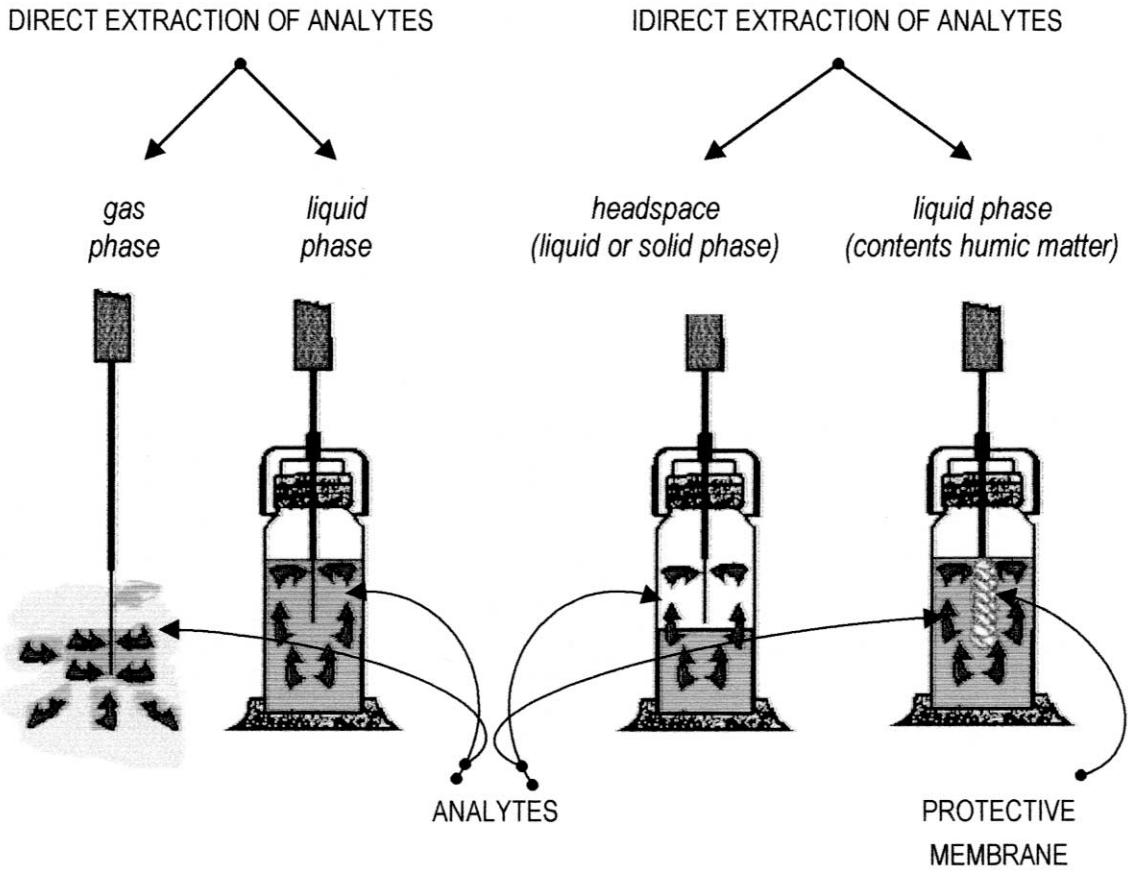

FIGURE 2. Direct and indirect extraction SPME.

controlled analytes losses through cracks in membranes[17] used to seal vials.[18-20] The cracks result from piercing the membrane with an SPME device needle. Some authors[17] have noticed that use of "open cup vials", whose PTFE (polytetrafluoroethylene) caps contain a narrow diameter capillary, permits to considerably decrease and control analyte losses. The advantage of this approach complies with a rule, that it is better to have a constant, foreseeable loss than a lower uncontrolled loss through membrane cracking.

Figure 2 also represents indirect sampling based on inserting to an original sample a fiber protected by semipermeable material.[21] In this manner, analytes, for example, PAHs (polycyclic aromatic hydrocarbons) can be extracted from a heavily contaminated medium without a risk of sorption on a fiber of large mass components such as humic acids generally present in surface waters.

1. Influence of Kind and Volume of the Stationary Phase on the Quantity of the Analyte Extracted

When withdrawing the fiber from an SPME device needle into a sample, components undergo partitioning between the stationary phase on a fiber and the sample. Both kinds of stationary phase and its volume (film thickness on a fused silica fiber) affect the extracted analyte fraction. Supelco offers fibers with coatings of different chemical nature and film thickness (Table 1). Thickness of typical coatings phase ranges from 7 to 100 μm. The sensitivity of an extraction step increases with film thickness because the quantity of the analyte extracted increases. This, however, lengthens sampling time because equilibration is slower in such a case.

The type of coating material has also essential influence on extraction selectivity and yield. As shown by Chai and Pawliszyn,[22] of the three common coatings (PDMS — polydimethylsiloxane,

TABLE 1
The Species of SPME Cover Fibers Proposed by SUPELCO (Bellefonte, USA)

Fiber coating	Thickness	Target analyte	Working max. temp. [°C]	Rocommended operating temp. [°C]	Conditions	
					Temp. [°C]	Time [h]
Polydimethylsiloxane (PDMS)	100 µm	volatile	280	200-270	250	1
	30 µm	non-polar semivolatile	280	200-270	250	1
	7 µm	semipolar, non-polar semivolatile	340	220-320	320	2-4
Polydimethylsiloxane /Divinylbenzene (PDMS/DVB)	65 µm	polar volatile	270	200-270	260	0.5
Polyacrylate (PA)	85 µm	polar semivolatile	320	220-310	300	2
Carboxen/ Polydimethylsiloxane (CAR/PDMS)	75µm	polar semivolatile	320	240-300	280	0.5
Carbowax/ Divinylbenzene (CW/DVB)	65 µm	polar	265	200-260	250	0.5
Carbowax/Templated Resin (CW/TPR)	50 µm	polar	-	-	-	-
Divinylbenzene /Carboxen/ Polydimethylsiloxane (DVB/CAR/PDMS)	50/30 µm	polar	270	230-270	270	4

CAR — carboxen, and CPB — carbopack B), PDMS is the most effective for extraction of BTEX. However, the fiber coated with a mixed PDMS/ CAR stationary phase is more selective.[23] Acetone, ethanol, isoprene, and terpenes best sorb on PDMS/ DVB (polydimethylsiloxane/ divinylbenzene).[24, 25] The overall recovery of these compounds in the enrichment process is even better than when using a very polar PA (polyacrylate) coating. In fiber selection the general rule: "like dissolves like" should be helpful. Table 1 presents application of available fibers in the analysis of various classes of chemical compounds.

2. Ways to Improve Extraction

Besides suitable selection of stationary phase, some other factors are also used to improve SPME extraction.

a. Internal Cooling of the Extraction Fiber

This approach was applied in the analysis of very volatile components in heavily contaminated liquid samples and solid samples. The sample is heated to increase analyte equilibrium concentrations in the headspace, while the fiber is kept at low temperature to increase sorption. This promotes analyte extraction.[7, 26-28]

b. Sample Agitation

Stirring the sample considerably improves extraction effectiveness.[29] The way of agitation is important. The three basic techniques generally applied are magnetic stirring, sonication, and intrusive stirring studied by Motlagh and Pawliszyn,[8] who showed that intrusive and ultrasonic ways of agitation are more effective,

although the latter is accompanied by disadvantageous temperature increase. Likewise, fiber vibration was also helpful;[30, 31] it increases precision and speeds up the extraction process.[32] The extraction process could be also accelerated by fiber.[33] It was experimentally proven that fiber rotation and vibration give like effects, although the former is simpler to use.

c. Salting Out Effect

Adding an electrolyte to the sample increases ionic strength. This decreases analyte solubility and makes HS-SPME (headspace SPME) extraction more effective.[29, 34-43]

d. pH of the Solution Analyzed

By changing pH ionisable compounds (e.g., phenols) can be converted to a nonionized form and are much bettering extracted by non-polar and weakly polar stationary phases.[29, 40, 42-46]

e. Derivatization

In a derivatization process analytes are converted to other compounds as a result of the reaction with a characteristic derivatizing reagent. Derivatives should have properties that make them GC analyzable and SPME extractable;[44] derivatives should be characterized by higher volatility, better thermal solubility and lower polarity than original analytes. For derivatization such reactions should be used, which are fast and give a single product with practically 100% yield. Derivatization is generally used in analysis of carboxylic acids, alcohols, phenols, amines and some pesticides. This is presented in Table 2.

Several derivatization approaches are used for SPME:

- **In situ derivatization**. It is based on adding derivatizing reagent to a sample and SPME extraction of the derivatives from the headspace.[37]
- **Derivatization in a GC injector port**. Derivatization process proceeds at high temperature in an injector port of a GC [49].
- **Derivatization in an SPME fiber coating**. Transformation of analytes to their derivatives takes place in the stationary phase coated on the fiber of an SPME device.[61] The fiber is immersed in a reagent solution and then in a sample. The analyte is extracted and converted to a derivative in the coating. The reverse order can also be applied; first analytes are extracted into the fiber and then the fiber is immersed in the reagent solution for derivatization.

Derivatization should be applied only, when it is really necessary, because it increases time and cost of analysis and can be a source of additional analytical errors.

3. Influence of Matrix on Effectiveness of Extraction

The presence of organic matter and inorganic compounds, which is very common for real environmental samples, can create some problems in the process of extraction (especially in the case of direct analysis where the fiber is immersed directly in the examined medium).[62] The presence of humic and fulvic acids[63] lowers the fraction of the analytes extracted. This results from the interaction of dissolved organic matter with analytes and with the coating of the extraction fiber.[64] Samples with a large content of dissolved organic matter are characterized by considerable viscosity, and analytes diffusion is slowed down and extraction time lengthened.[65]

B. Precautions Against Analytes Loss as a Result of Uncontrolled Desorption from the Fiber

Typical SPME devices have been designed for laboratory operations. Pawliszyn[14]

TABLE 2
Derivatization Approaches Used for SPME

DERIATIZATION	ANALYTE	DERIVTIZING REAGENT	REF.
in situ	phenols	acetic anhydride	47
	chlorinated acetic acids	methanol	48
	fatty acids C_1-C_2	2,3,4,5,6-pentafluorobenzyl bromide, 1-(pentafluorophenyl) diazoethane	49
	degradation products of chemical warfare	N-methyl-N-(tertbutyl - dimethylsilyl) with tertbutyl dimethylsilyl chloride	50
	inorganic lead	sodium tetraethylborate	51-53
	inorganic tin	sodium tetramethylborate	54
	carbonyl compounds	o-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride	29
	haloacetic acids	ethanol	55
in port GC	fatty acids C_{10}-C_{22}	tetramethylammonium hydroxide, tetramethylammonium hybrogen sulfate	49
	bisphenol A	N,N-bis(trimethylsilyl) trifluoro-acetamide	56
on fiber	formaldehyde	2,4-dinitrophenylhydrazine, o-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride	57, 58
	ttiodiglycol, 2-(diisopropylamino) ethanol	N,O-bis(trimetylosililo) trifluoro-acetamide	59
	acids herbicides	diazomethane	60
	short chain fatty acids	1-phenyl diazomethane	49

proposed some modification for remote monitoring.

In field sampling it is very important to preserve extracted analytes on a fiber for a longer time and to protect the coating from contamination. As Chai and Pawliszyn[22] showed the capping of a needle with a polymeric septum prevents even light analytes from losses, but only if stored for a short time. Cooling to –70°C enables much longer storage time considerably. Organic analytes can dissolve in polymeric material, and the approach based on metal to metal sealing appears more appropriate.[14]

By adding a tube with a small opening to cover a needle, Groth and Pawliszyn[24] obtained a convenient design for breath analysis.

C. Desorption of Analytes

After a definite time of sampling the fiber is withdrawn into an SPME needle and the device transferred to a measuring instrument.

Most frequently it is a gas chromatograph coupled with a suitable detector. The SPME device needle is at once introduced through a septum into a hot injector port, where, after drawing the fiber out of the needle, thermal desorption of analytes proceeds. Desorption should be fast and therefore conducted at possibly high temperature. On the other hand, the maximum desorption temperature is limited by thermal resistance of the stationary phases used and by other factors. So sometimes, it is necessary to desorb analytes at lower temperature for a longer time, what neces-

sitates the focusing of the bands of released analytes. In another approach the fiber is internally heated, what speeds up desorption and enables self — focusing of analytes bands.[66]

In the focusing process it proves helpful to place an additional element between a GC injector and column. Generally, it is a heated glass tube with a diameter a little greater than the diameter of a column. Even such a small element ensures sufficient focusing for majority of cases of increased desorption rates. The higher flow rates of carrier gas can be used in such situations that shorten analysis time, for example, to tens of seconds for BTEX,[66,67] and to 10 min for some chloroorganic pesticides.[68]

A liquid chromatograph can also be used as a measuring instrument. In this case the needle of the SPME device is introduced to an injector, where the fiber is immersed in a stream of liquid eluent that desorbs analytes and later transports them to a HPLC column. HPLC creates new possibilities and widens the application range of SPME to nonvolatile and thermally labile compounds. An example can be the determination of alkylphenol ethoxylate surfactants in water.[69] The selection of a suitable fiber and desorption and chromatographic conditions permit obtaining detection limits on a ppb level.[70]

D. Final Analysis

Analytes released from the fiber are separated with use of a gas or liquid chromatograph equipped with a suitable detector. The chromatographic systems used include GC–FID (flame ionization detection), GC–MS (mass spectrometry), GC–ITMS (ion trap mass spectrometry), GC–ECD (electron capture detection), GC–NPD (nitrogen — phosphorus detector), and HPLC–UV (high performance liquid chromatography–ultraviolet detection),[71] HPLC–ESMS (electrospray/mass spectrometry)[72] and HPLC–PAD (photodiode array detector).[73] Detection limits of SPME–chromatography based procedures depend on analytes, extraction fibers, and also on the chromatographic detectors used. For many analytical tasks detection limits of the order of ppb were obtained when FID as a GC detector was used.[3,47,74-77] In some cases detection limits of ppt were obtained when ITMS was applied for GC detection.[61,78-80] SPME-based analytical procedures were also developed in which less popular coupled systems such as GC-AED (atomic emission detection)[81,82] and GC–IR (infrared spectroscopy)[83, 84] were used.

III. ENVIRONMENTAL APPLICATIONS OF SPME

Environmental pollutants analysis concerns such media as air, water, soil, sewages, etc; aqueous samples are analyzed most often.[64]

The basic steps in SPME-based analysis are the following:

- Development of extraction technique: selection of method of sample preparation for extraction (e.g., derivatization, extraction with water at high temperature and pressure); mode of sampling — indirect or direct; way of sample agitation;
- Optimization of conditions of chromatographic analysis (separation, detection, analyte desorption from the fiber);
- Determination of extraction parameters on the basis of model matrices (sample volume, time and temperature of extraction, pH and salt addition);
- Method validation (linearity, precision, detection limit, etc.);
- Analysis of real samples.

A. Air Analysis

The SPME method can be used for the determination of organic compounds in atmospheric air, indoor air, industrial air, etc.; usually a wide spectrum of compounds can be isolated from these media. Table 3 presents the applications. The fibers used were generally coated with PDMS (polydimethysiloxane); PDMS with addition of DVB (divinylbenzene); and PDMS with CB (carbowax) for rather polar compounds. The number of publications on the subject is, however, comparatively low. Perhaps this can result from

TABLE 3
Published Applications of SPME for Air Samples

	Matrix	Fibre coating	Target analyte	Extraction and desorption conditions *)	LOD [ppb]	Final analysis	Ref.
ATMOSPHERIC AIR	environmental samples	PDMS	BTEX, hexane,	E ≤ 3min,	0,05-2,0	GC-ECD	22, 88
	air in underground parking garage	GCB	isooctane, methylcyclohexane	D= 1-2min T_D=220, 240°C		GC-FID	
	environmental samples	PDMS	ethylbenzene, xylene, alkylnaphthalene	E=20min, D=3min, T_D=260°C	1,3-273,9	GC-MS	89
	ambient air of Algiers		VOCs	E=20min, D=5min, T_D=200°C	-	GC-FID	90
	ambient air	CAR/PDMS	sulfur compounds	E=15, 90min, D=100s, T_D=250°C	0,004-0,05	AED	81, 82
INDOOR AIR	air in flats	PDMS	toluene, chlorobenzene, carbon tetrachloride, p-xylene, n-decane	E=15min, D=1min, T_D=250°C	0,002-0,005	GC-MS	91, 92
	air in swimming pool chemical laboratory	PDMS	volatile halogenated hydrocarbons	E=5min, D=1, 3min, T_D=200, 220, 230°C	0,01-1,0	GC-MS GC-ECD	34, 93, 94
	indoor air inside buildings, trains and cars	CAR/PDMS	BTEX	E=1-60min, D=0,5min, T_D= 300°C	0,0004-0,002	GC-FID	9
INDUSTRIAL AIR	occupational exposures	PDMS/DVB PDMS	formaldehyde	E=1, 2min, D=1min, T_D=250°C	4,6; 0,17	GC-FID GC-ECD	57, 58
	perfume and fragrances	PDMS	cis-7,tras-11-hexadecadienyl acetate	E=35min, D=6min,	-	GC-FID	10
	different air matrices (air inside furniture, etc		cis-7,cis-11-hexadecadienyl acetate	T_D=290°C			
	not specified	PA	fatty acids (C_2-C_5)	E=10min, D=3min, T_D=300°C	0,025-0,3	GC-FID	49
OTHERS	human breath	CW/DVB	ethanol, isoprene, acetone	E=1min, T_B=36,6°C D=20sec, T_D=200°C	< 0,30	GC-ITMS	24
	mainstream smoke	PA	phenolic compounds	E=60min, D=2min T_D=275°C	-	GC- MS	95

*) E - fibre exposition time, T_B - bath temperature, D - desorption time, T_D - desorption temperature

difficulty with calibration. Generally, it is not easy to produce standard gaseous mixtures of the definite content of analytes and moisture for organic trace analysis (analyte content at ppm or even ppt level).[85] There are quite a lot of methods of preparing of standard gaseous mixtures; the most suitable seem to be dynamic methods, where temperature moisture content and analyte concentration can easily be controlled.[86] The calibration problems and gas mixture preparation have been discussed comprehensively by Namieśnik *et al.*[87]

B. Liquid Samples

Aqueous matrices generally analyzed can differ considerably in cleanness. Typical matrices include drinking water, sea and other surface waters, sewages, and other aqueous samples. Depending on contamination level and analyte, direct or indirect SPME can be applied. Table 4 presents examples of pollutants extracted from aqueous samples by means of indirect and direct SPME; extraction conditions and detection limits are also given.

A spectrum of pollutants analyzed in different environmental aqueous samples is very wide: from nonpolar to polar, from volatile to nonvolatile (derivatization).

BTEX (benzene, toluene, ethylbenzene, xylenes) were quite often analyzed with the use of SPME; both direct and indirect (HS-SPME) approaches were used. In combination with modern gas, chromatography detection limits down to a ppt level were reached for these compounds.

The other groups of important water pollutants are **polar solvents**, such as alcohols, ketones, and aldehydes. They are readily soluble in water and hence difficult to isolate. Extraction to nonpolar fiber coating is not effective. The application of polar coatings and salt addition to water samples (salting out effect) make it possible to get relatively low detection limits for the above polar pollutants.[120] Similarly, compounds of medium polarity (e.g., derivatives of phenols, amines, etc.) in natural aqueous matrices determine a serious analytical challenge. In reaching the required detection limit, adjustment of pH, salting out, and selection of rather polar fiber coatings (e.g., PA) can be helpful. In the case of polar compounds, transformation to less polar derivatives can result in lowering the detection limits down to a ppt level.

For semivolatile **nonpolar** and **slightly polar compounds** such as PAHs and PCBs partition coefficients are high, hence extraction yields are large and detection limits low (e.g., a ppt level).[79] These water pollutants, especially PAHs are lipophilic and can undergo adsorption on solid particles and can interact with organic matter possibly present in water. In the case of some surface waters the fraction of PAHs, adsorbed on suspended particular matter can be quite high.[129]

A chemically varied group of pollutants are pesticides. They differ considerably in structure and physicochemical properties; some are nonpolar and relatively volatile, while others are polar and nearly nonvolatile. Despite these differences, SPME was used successfully in the analysis of most pesticides. Extraction times, however, are much different — from several minutes to hours; they can be shortened by suitable agitation and heating of solution (with simultaneous cooling of the fiber to keep detection limits as low as possible).[103, 130, 131]

The last group, discussed here, are some metal ions derivatized to organometalic compounds for SPME isolation.[44, 132] Inorganic ions in the form of volatile derivatives were determined by means of GC–ITMS, while as crown ether complexes by HPLC .[71]

C. Solid Samples

Solid samples can be analyzed exclusively by indirect SPME (mainly, HS-SPME in the case of volatile analytes). Analytes of medium polarity in solid samples can be first extracted with subcritical water (high pressure and high temperature) and then by SPME from the aqueous extract obtained.[7, 133, 134] Examples of compounds analyzed in solid samples and conditions of extraction are presented in Table 5.

TABLE 4
Published Applications of SPME for Liquid Matrices

	Matrix	Fibre coating	Target analyte	Extraction and desorption conditions	LOD [ppb]	Final analysis	Ref.
DIRECT SPME	oceanic water (Larimore, ND, USA)	PDMS	PCB	E=15min, D=1min, T_D=300°C	0,005	GC-ECD	96
	surface water from river, lakes, canals in Berlin		polycyclic and nitromusk	E=40min, T_B=22°C D=10min, T_D=270°C	<0,01	GC-MS	97
	west water from petrochemical plant in Porto		PAHs	E=30min	<5	HPLC	73
	river water (Elba)		haloethers	E=10min, D=1min, T_D=250°C		GC-ECD	41, 62
	water		chlorinated hydrocarbons	E=20min, D=3min, T_D=220°C	-	GC-MS	98
	octanol/water		chlorinated hydrophobic compounds	E=30min, D=2min, T_D=250, 280°C	-	GC-FID GC-ECD	99
	river water (Tamiza, UK)	PA	1,2-dimethylnaphthalene	E=15min, D=3min, T_D=300°C	-	GC-FID	100
	wastewater		phenols	D=5, 8min, E=60min, T_D=250, 280°C	-	GC-MS GC-FID	43, 65
			chlorination desinfection byproduct	E=15min, D=3min, T_D=200°C	<0,018	GC-MS	101
			bisphenol A	E=20min, D=10min, T_D=320°C	~1	GC-MS	56
			N-butylbenzene sulfonamide, ibuprofen	E=30min, D=5min, T_D=270°C	0,1	GC-MS	42

TABLE 4 (continued

DIRECT SPME	wetland water from production area near Larimore (ND, USA)	PA CW/DVB	bases (pH=12) and acids (pH=2) organic compounds	E=4min, D=1min, T_D=300°C	0,0005-0,05	GC-FID	45
	wastewater from pig farm (Taiwan)	CW/DVB	fatty acids C_1-C_7	E=20min, D=3min, T_D=250°C	0,03-11,5 mM/L	GC-MS	102
	runoff and tile drainage, river water	CW-PDMS PDMS, PA PDMS/DVB	pesticides	E=15-30min, D=1-7min, T_D=250-280°C	0,02-20	GC-MS GC-ECD GC-NPD	40, 60, 63, 68, 103-109
	lake water (Northern Milan), Elba River water	PDMS, PA CW/TPRCAR/DVB PDMS/DVB	polychloro-1,3-butadienes, aromatic amines	E=10-30min, D=4-5min, T_D=240-300°C	≅ 0,001-2	GC-MS HPLC-UV	110-112
	nature and sea water	CW/DVB , PA PDMS PDMS/DVB CAR/PDMS	explosives	E=10, 15min, T_D=250°C D=2-3min	0,001-1 0,001-1	GC-NPD, GC-FID GC-MS	50, 113, 114
	lake water	CW/TPR, PA CAR/DVB, PDMS/DVB	hydroxyaromatic compounds	E=20min, D=3min	0,66-4,2	HPLC-UV	115
	water	CAR/PDMS	VOC	E=30min, D=5min, T_D=250°C	-	GC-MS	116
HEADSPEACE SPME	tap water from Barcelona (Spain)	PDMS	halogenated acetic acids	E=2, 10min, T_B=100°C D=0,5-2min, T_D=250°C	0,01-0,2	GC-ECD GC-ITMS	48, 55
	aqueous media		mercaptans	E=30min, D=2min, T_D=200°C	0,2-5	GC-FID	16
	surface water		alkyl mercury, alkyltin, alkyl lead	E=10min, T_B= to 105°C D=5min, T_D=250°C	0,0001-0,2	GC-ICIMS GC-MS	51, 117
	water		PCB	E=30min, T_B=90°C D=2min	<0,001	GC-ECD	118

HEADSPEACE SPME	local tap water, bi-distilled, deionized; groundwater	PDMS, CAR/PDMS activated charcoal	BTEX, $C_1 - C_2$ halocarbons	E=2-50min, T_B=25- 150^{O}C, D=0,2-2min, T_D=180-300^{O}C	0,0001-0,06	GC-FID GC-ECD	23, 25, 36, 112
	river water, drinking water in PET bottles	PDMS, PDMS/DVB CW/DVB	hydrocarbons, aldehydes, ketones, alcohols	E=25min, T_B=20^{O}C D=5min, T_D=260^{O}C	0,0005 –1	GC-FID GC-ITMS	123, 124
	water rich in humic matter and with petroleum compounds	PDMS, porous layer carbon and methal fiber	BTEX, propylbenzene, butylbenzene, PAHs	E=20min-3h T_B=25-95^{O}C, D=2-5min, T_D=260-350^{O}C	0,001–0,3	GC-FID GC-MS HPLC	89, 120, 125-127
	groundwater near leaking underground storage tanks with gasoline	PDMS/ porous carbon	BTEX, methyl-tertbutyl and ethyl-butyl ether	-	0,36-0,63	GC-FID	128
	treated water	CW/DVB	iodinated trihalomethanes	E=10min, T_B=22^{O}C D=0,5min, T_D=200^{O}C	0,001-0,003	GC-ECD	39
	water	CAR/PDMS, PA	hydrphilic compounds	E=30min, T_B=50^{O}C D=2-4min, T_D=275-310^{O}C	0,1-80	GC-ITMS	119
	westewater	PA	chloroform, saturated carboxylic acids, alkylobenzenes, benzonitryle	E=30min, T_B=25, 60^{O}C D=2min, T_D=220^{O}C	10-170	GC-MS	121

*) E - fibre exposition time, T_B - bath temperature, D - desorption time, T_D - desorption temperature

TABLE 5
Published Applications of SPME for Solid Samples

	Matrix	Fibre coating	Target analyte	Extraction and desorption conditions *)	LOD [ppb]	Final analysis	Ref.
HEAD SPEACE SPME	clay sludge, wastewater	PDMS	BTEX	E=2-5min, T_B= 110 , 80°C D=1min, T_D=150°C	< 0,0003	GC-MS GC-MS	27
	soil		chloroanilines, nitroanilines, chlorobenzenes, nitrobenzenes, anilines, benzenes	E=30min, T_B=80°C, D=5min,T_D=250°C	0,03-0,1ng/g	GC-MS GC-ECD	136, 137
	sediment samples in Belgium (The Netherlands)		alkyl mercury, alkylin, alkyllead	E=10min, T_D=250°C	< 0,004	GC-ICIMS	117
	borehole sediments, weste water	PDMS PA	chlorinated VOCs	E=1-30min, T_B= to 100°C, T_D= to 300°C, D=1-15min	0,002-0,55	GC-FID GC-MS GC-ECD	131, 138-140
	cosmetics, building products	PDMS/ DVB	formaldehyde	E=2min, T_B=25°C D=1min,T_D=210°C	< 40	GC-FID	58
	soil, organic films on stone monuments	PDMS PA CW/TPR	PAHs, herbicides, polar pesticides	E=30min, T_B=210°C D=4min, T_D= to 300°C	-	GC-MS HPLC-ESI/MS	72, 133

*) E - fibre exposition time, T_B - bath temperature, D - desorption time,T_D - desorption temperature

IV. COUPLING OF SPME WITH OTHER METHODS OF ISOLATION AND ENRICHMENT

Each sample preparation method can be optimal for a definite group of compounds. When analyzing, for example, organic compounds of high and medium volatility it is difficult to avoid losses of very volatile ones. To cope with sophisticated analytical tasks met nowadays, new integrated methods of sample preparation are looked for. The basic trend in this field research is focused on coupling two or more methods. An example of such approach can be coupling of the three widely recognized methods, that is, supercritical fluid extraction, solid phase extraction, and HS–SPME. Such a combined method makes it possible to get reliable results in simultaneous analysis of volatile and semivolatile pollutants.[135]

The Combination of HS–SPME with passive sampling was also proposed.[9] With such a system, a detection limit of 1 ppb and below can be achieved for short-term measurements of BTEX in air. Passive sampling reduces the influence of temperature and humidity on SPME extraction and makes it possible to store sampled analytes for a long time.

V. COMPARISON OF SPME WITH "RELATED" TECHNIQUES OF ISOLATION AND ENRICHMENT

A literature search shows that SPME, quite a new technique, has been widely used to analyze samples of different aggregation state. Due to a number of advantages, it is preferably applied to carry out routine and sophisticated analytical tasks.

In many cases SPME can replace a traditional liquid-liquid extraction, which is still quite common. Depending on the analytes and matrices, extraction efficiency of both techniques can be similar,[28,38,96,141] much higher for SPME (e.g., in the case of haloethers in water[62]), or slightly lower for SPME.[65,113]

The most controversial is SPME analysis of headspace, and in many papers published in specialist journals HS–SPME has been compared with other well-recognized methods of isolation and enrichment.

Analyte sampling from the headspace being at thermodynamic equilibrium with a sample (static HS) is widely used. However, in many cases HS-based determination does not possess a required accuracy. Comparison of the results of conventional static HS sampling with HS–SPME sampling[25] shows that the accuracy of determination of odorants with the latter is three orders of magnitude better. Results of studies on determination of organic analytes of high and medium volatility confirm better sensitivity of methods based on HS–SPME.[25,89]

An efficient method of extraction of volatile analytes from liquid and also from solid samples is purge and trap. The results of determination of benzene in water[122] and also other compounds[20,27] by means of PT and HS–SPME are characterized by similar precision and accuracy; however, the latter is faster and simpler.

HS–SPME is an interesting alternative technique, by means of which concentration of components present in liquid and solid samples can be determined. For volatile and semivolatile analytes for example, in water, an extraction time is shorter than in the case of direct SPME.[16] When compared with dynamic sampling from air on activated charcoal-packed tubes, passive SPME sampling has obvious advantages.[89]

VI. RÉSUMÉ

Up to now, SPME is regarded as a very promising extraction method of preparation of environmental and some other samples for chromatographic determination of trace organic pollutants and in some situations also inorganic pollutants. When both direct and indirect SPME are taken into account a wide spectrum of pollutants can be analyzed in gaseous, liquid and solid samples. With new developments, a number of analytical tasks that can be performed with the use of SPME increase.

SPME is mainly used in combination with gas chromatography. Recently, some papers described a combination of SPME with HPLC, which widens the application range of SPME considerably.

Modifications of construction of an SPME device and application of new polymeric fiber coatings increase application ranges and improve the selectivity and the accuracy of analyzes. The time of routine analysis can be relatively short due to the possibility of automation of SPME.

The facts that costly and environmentally unfriendly solvents are eliminated, time of sample preparation is short, design and operation of an SPME device are simple, progress in SPME development is rapid, and the cost of the device and its use relatively low make SPME a very attractive and promising method of environmental sample preparation. SPME can really replace conventional methods for many analytical tasks in the nearest future.

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