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Review

Application of solid-phase microextraction for determination of organic vapours in gaseous matrices

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Abstract

This paper reviews the practical applications of solid-phase microextraction (SPME) in the analysis of organic vapours which are pollutants of atmospheric air, indoor air and workplace air. Applications to headspace of solids and liquids such as different waters, soils, food, etc., are also included. Problems related to calibration in SPME analysis of gaseous matrices are also dealt with. Calibration procedures and apparatus for generation of standard gaseous mixtures are described. Advantages and limitations of SPME based gas chromatographic methods of air organic pollutants are discussed.

Keywords: Reviews; Solid-phase microextraction; Air analysis; Headspace analysis; Environmental analysis; Volatile organic compounds

Contents

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1. Introduction

A vision of progress, and the pleasure of discoveries and inventions, obscure the accompanying negative effects. Chemicalisation of all areas of human activity, so characteristic for the present world, results in the omnipresence of unwanted chemical substances in air, water, soil and food. Nearly a million of the ca. 12 million known chemical compounds are present in the direct environment of man at concentration levels of above 10^{-10}% (v/v) [1]. The majority are organic compounds, many of which occur in the atmosphere, indoor and workplace air. Problems related to organic air pollutants concern first of all: (1) *human health*, (2) *ozone and other oxidants formation*, (3) *unpleasant odours of human nuisance* [2].

Many organic air pollutants are thought to cause genetic changes in living organisms; some are proved to be carcinogenic, mutagenic and teratogenic. These and other detrimental effects make it necessary to monitor air for their content.

Harmful concentration is compound-dependent and is one of main factors determining the concentration range within which a given pollutant should be monitored. The second important factor is the detection limit, which can be achieved at the current state of the art. Progress in technology in the last 70 years led to development of analytical methods enabling simultaneous determination of many sample components at increasingly lower concentrations [3,4].

Determination of chemical substances in environmental samples is generally a laborious multistep process (Fig. 1). Analytical methods for volatile organic air pollutants should cope with the three basic problems: (1) necessity of analysing very low concentrations; (2) need for analytical standards (to calibrate instruments and test applicability of methods) containing analytes of interest on the level comparable to concentrations in real samples; (3) sample preparation for the final analysis should not add to environmental pollution.

Many methods of air quality control have been developed but, mainly due to insufficient sensitivity, only a few can cope with increasingly difficult analytical tasks. For example, injecting a 1-ml air sample containing benzene at a maximum allowable concentration (maximum allowable concentration according to Polish regulation is 10 $\mu g/m^3$) into a capillary gas chromatograph one generally introduces two-orders of magnitude less benzene than the detection limit of a very sensitive flame ionisation detection (FID) system. Therefore, an analyte enrichment step must be included in the analytical procedure [5,6].

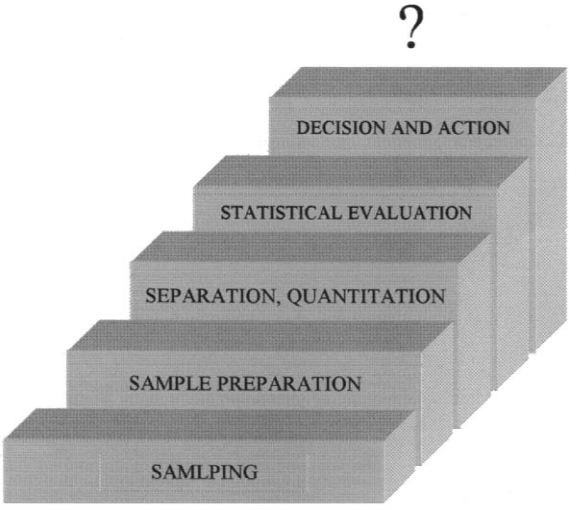

Fig. 1. Steps in the analytical process.

Methods of organic air pollutant enrichment are classified into three basic groups (Fig. 2) [7–9]:

(1) *Dynamic methods*. These are based on passing a sample through a system tube in which components of interest are trapped by freezing out, adsorption, or chemical reaction. The sampling set generally consists of a tube with an enriching medium, a pump equipped with a power supply and volume measuring devices.

(2) *Denudation methods*. The sample is passed through a tube whose walls are covered with trapping medium, reached by components due to diffusion. These methods are applied when vapour enrichments is to be accompanied by particulate separation.

(3) *Passive methods*. In passive methods analytes from the closest surroundings of a sampler reach the trapping medium due to diffusion or permeation processes. Movement of analyte molecules is free

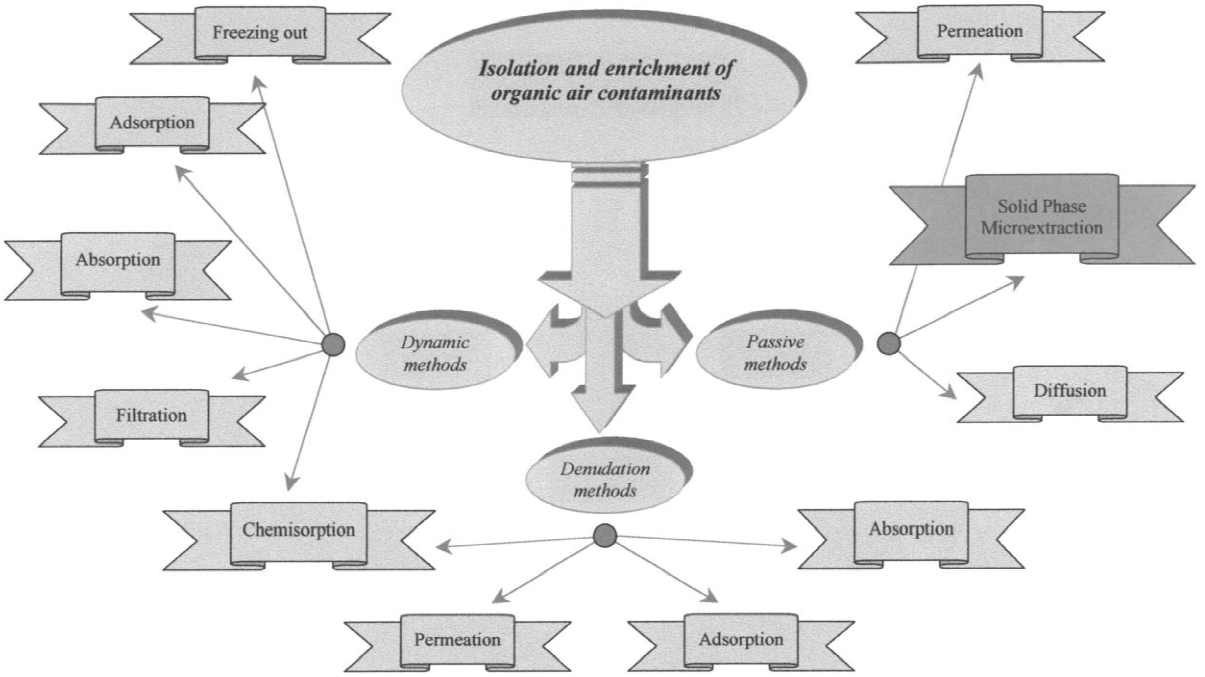

Fig. 2. Enrichment and isolation methods of organic contamination in air.

and no additional devices such as aspirators, rotameters, etc., are needed.

Among the passive methods solid-phase microextraction (SPME) can be included. It is a relatively new sampling preparation technique invented in the years 1987–1989 [10,11]. An increasing number of papers deal with routine use of the technique [12–20] as well as with new designs and applications.

The technique incorporates sampling, isolation and enrichment into one step; the analytes are trapped on a thin fused-silica fibre coated with a liquid polymer or solid sorbent and then are desorbed into a chromatographic mobile phase directly in an injection port of a liquid or gas chromatograph. An important characteristic of the technique is that it is solvent-free (Fig. 3). Excluding a few special situations, SPME does not assure quantitative analyte extraction; generally at equilibrium analyte concentration in a sample is not negligible. SPME is an equilibrium method and calibration, a crucial step of analysis, requires special care.

2. Calibration – a crucial step of an analytical procedure

2.1. General remarks

SPME–gas chromatography (GC)-based analytical procedures (sorption of analytes on a fibre, their desorption in a GC injection port, separation in a chromatographic column, detection and quantitation) [21,22] require careful calibration. Qualitative and quantitative calibration can be distinguished; in the former a compound is related to a given instrument signal, in the latter analyte content (concentration, amount) is related to an instrument response value [23]. If the calibration step is not properly made then results can be correct only accidentally; most often, they could be a source of serious misinformation.

The calibration step generally consists of: (1) preparation of proper standard mixtures; (2) the calibration proper, i.e., conducting a given analytical process for standard mixtures; (3) establishing the

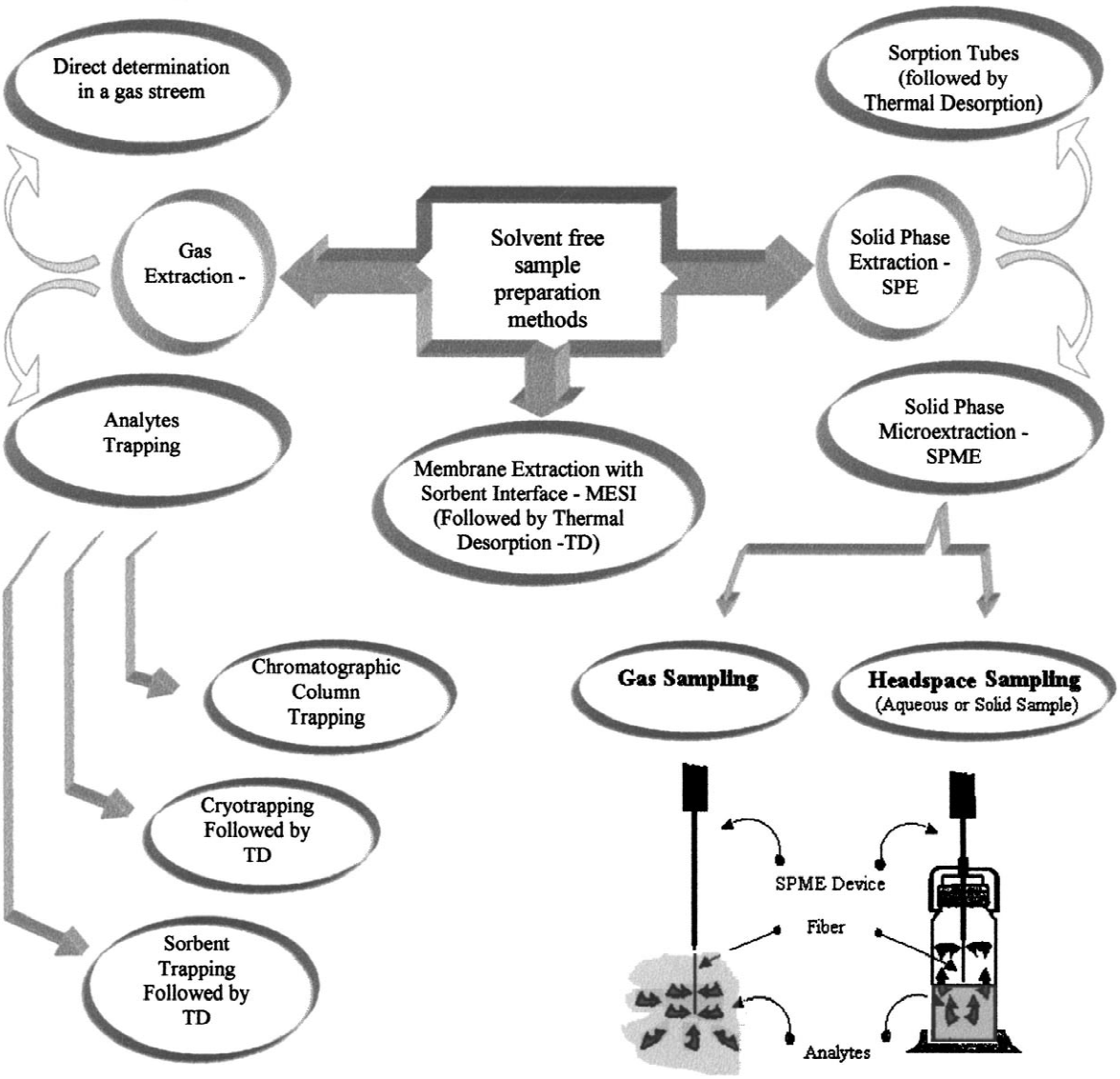

Fig. 3. Solvent-free sample preparation methods.

relationship between final instrument response and analyte content (concentration, amount) in a sample.

2.2. Gaseous standard mixtures

The term ''standard gaseous mixture'', though seems quite unambiguous, can be a source of misunderstanding. A gaseous mixture must satisfy some requirements to be a standard mixture. The basic are the following [24,25]: (1) concentration of analytes of interest should be known with sufficient accuracy (2–5-times better than that of a calibrated instrument or method); (2) analyte concentration should be constant for a long time (stability should be specified

in a certificate). The stability requirement is difficult to fulfil for components which are unstable, reactive and considerably differing in volatility (possible stratification); (3) availability of the same mixture throughout all planned experiments; (4) possibility of calculating concentration from such basic quantities as mass, temperature and pressure.

Usually standard mixture preparation is not an easy task, especially if trace (ppm, ppb) and ultratrace (ppt, ppq, and lower) components are of interest. In environmental analysis and monitoring this is very often the case [26].

Though static and dynamic methods can be used for gaseous standard mixture generation, the latter are decidedly more common for low concentrations [24,27–30]. Many dynamic methods are known and new methods being developed. Very promising is the approach based on thermal decomposition of surface compounds obtained by chemical modification of silica gel [31–34].

Nowadays commonly used are dynamic methods based on permeation of analytes through semipermeable membranes, most often made of PTFE, polyethylene and silicone rubber [35]. Membrane material should be characterised by high permeation coefficient, selectivity and homogeneity. Transport of analytes from a container with a substance to a diluting gas through the membrane generally depends on the three phenomena: (1) dissolution and/or sorption on inner surface of the membrane; (2) permeation through the membrane (dissolution and diffusion); (3) desorption or evaporation from outer surface of the membrane to the diluting gas.

The final concentration of analytes in the gaseous mixture is a function of material, thickness and surface area of the membrane and of permeation temperature and flow-rate of diluting gas.

Permeation techniques are used for analytes which are gases, liquids and, in some cases, even solids under standard conditions. They are very convenient to prepare gaseous standard mixtures for calibration of SPME–GC-based methods of analysis of volatile organic components in gaseous environmental samples.

In studies on SPME sampling static and dynamic methods of standard mixtures generation were used. They are presented in Table 1.

2.3. Calibration of solid-phase microextraction–gas chromatographic analytical methods for volatile organic air pollutants

SPME is an equilibrium process and, in most experiments, total amount of an analyte originally present in a gaseous sample is not introduced into a GC system for analysis. Calibration of an SPME–GC–MS system, a necessary step in such a situation, can be performed in two ways generally used in SPME–GC measurements of organic vapours in gases.

(1) In one, GC response is first related to absolute mass of a given analyte introduced into the GC system by injection of standard liquid solutions. To calculate the analyte concentration in real sample the relation between the amount adsorbed by the fibre and concentration of an analyte in the gaseous mixture must be known. This dependence can be found if the stationary phase volume coated on the fibre and partition coefficients K_{fg} (a ratio of analyte concentration in stationary phase coated on fibre and in gaseous sample at equilibrium) are known or can be calculated from some other available quantities. In field experiments sampling is generally performed at ambient temperature which can differ from site to site and from experiment to experiment and therefore, the dependence of K_{fg} on temperature should also be known.

The problem of predicting K_{fg} values and their temperature variability on the basis of some other thermodynamic quantities was thoroughly studied by Matros and Pawliszyn [28]. Use was also made of isothermal retention times [36,37] and linear programmed retention indices [38,39] to calibrate polydimethylsiloxane (PDMS) for air sampling. Using this approach, GC should be first calibrated with respect to analyte mass by injecting known volumes of the standard solution of analytes in a convenient organic solvent.

The above approach can give reliable results provided that the influence of any other parameters of the sampled air is negligible or known with good accuracy. Thermodynamic considerations and experiments show that logarithm of K_{fg} changes linearly with a reverse of absolute temperature. Though the effect of sampled air humidity in the air analysed on

Table 1
Generation of gaseous standard mixtures for SPME–GC analytical procedures calibration

Analyte	Matrix	Method of standard mixture generation	Ref.
Volatile chlorinated hydrocarbons	Atmospheric air	*Static* To flasks of 1 l and 0.5 l containing methanol gaseous standards were added. Equilibration time: 5 min. Temperature effect on extraction studied in the range of 0°C–25°C. Conditioning time: 10 min. Humidity effect studied at 25°C. Each water portion (50 μl) increased humidity by 25%	[40]
BTEX, chloromethane, chloroethanes	Air	*Static* To a 1-l flask a standard solution was injected through semipermeable membrane. The flask was kept at a temperature of 100°C for 10 min., then cooled to room temperature for analysis. Calibration was made starting from the lowest concentration. Gaseous standards were prepared just before analysis	[27]
Ethanol, acetone	Human breath	*Static* To a 1-l flask required amounts of analytes (ethanol and acetone) and 39.7 μl water were added – mixture became saturated with water vapour. Mixture kept at 35±0.2°C (water bath) for 30 min	[41]
BTEX, mesitylene, α-pinene, *d*-limonene, *n*-pentane, *n*-hexane, *n*-undecane	Environmental samples	*Dynamic* Methods based on dilution of volatile compounds vapours diffusing from vial of 1.8 ml volume. Gaseous mixture generation set comprises air compressing system, 20 l mixing chamber and flow-rate meter, temperature and pressure controllers. Diffusers were used to give required humidity to the mixture	[28]
Formaldehyde	Indoor air, workplace air	*Dynamic* Kin–Tek gaseous standard mixture generator applied. Nitrogen was a diluting gas; Kin–Tek permeation tubes supplied formaldehyde to the diluting gas at a constant rate. The system was equipped with diluting gas flow-rate meter and temperature controller. HCHO permeation tubes were NIST certified	[42]
Benzene, toluene, chlorobenzene, xylenes, carbon tetrachloride, *n*-decane	Indoor air, laboratory air	*Dynamic* Permeation based generation of gaseous standard mixtures. Assumed humidity was given to the mixture by passing it through two thermostated gas washers filled with saturated aqueous salt solutions (CH_3COOK, KNO_3, $NaNO_3$ at 20°C, 45°C, 66°C; respectively). For dry air measurements, humidifying washers were removed and drier packed with 5A molecular sieve was installed at a diluting gas inlet. Facility to regulate gas mixture temperature was regulated	[29,43]

the K_{fg} values has been dealt with in a few papers the situation in this respect is not fully clear.

(2) In another calibration approach, gaseous standard mixtures containing analytes of interest at the appropriate concentration are used. The sample and standard gaseous mixture are subjected to the same analytical operations; calibration becomes an integral part of an analytical procedure. The result obtained when using this calibration approach are expected to satisfy quality assurance (QA) requirements. When operating in a linear range of the SPME–GC system the final result can be calculated from ratios of the instrument response to an analyte in a real sample and in standard samples.

Calibration based on identical interchangeable analysis of real samples and a gaseous standard mixture could be very convenient provided that the gaseous standard mixture of accurately known and constant concentration is available, the mixture generating apparatus makes it possible to sample analytes in an easy manner, and parameters of the mixture such as temperature, humidity and analyte concentration can be controlled in a simple way. If this is the case calibration SPME–GC can be nearly as easy as finding a relation between GC response and analyte mass by injecting liquid standard solutions. When using the same fibre for calibration and for analysis of real samples many errors related to

fibre characteristics are eliminated. This approach was described in a number of papers dealing with analysis of various organic vapours in gaseous samples.

3. Practical applications of a solid-phase microextraction technique

Depending on matrix and analyte of interest two ways of sampling can be distinguished: direct and indirect. Analytes can be directly sampled from gases and from relatively clean aqueous matrices. In the case of solid matrices and aqueous samples containing some solids, oils and some other fibre coating unfriendly components, volatile analytes can be sampled from headspace (Fig. 3). Technically sampling from gaseous matrices and from head space are very similar. However, an equilibrium between a condensed phase (solid or liquid) and head space must be taken into account to derive analyte concentration in a sample from the amount trapped on the SPME fibre [44]. An important step in the process is analyte transport from the sample to the head space [45].

Transfer of analytes from the medium studied to the GC column with use of SPME consists of two steps: extraction of analytes from a sample and their desorption in an instrument for final analysis.

3.1. Extraction

For analyte extraction, the fibre is withdrawn form a needle of an SPME sampling device and immersed in a sample. Analytes undergo distribution between a matrix and fibre coating. Both type of coating and film thickness influence the extraction. An increase in film thickness improves sensitivity (for a given equilibrium concentration in a sample, amount extracted is proportional to coating volume) but lengthens sampling time (equilibration time is increased). Extraction is strongly influenced by fibre coating; volatile organics from air matrices are commonly extracted with use of PDMS, Carboxen and Carbopak B. BTEX (benzene, toluene, ethylbenzene, xylenes) are most effectively extracted by PDMS [27] but a mixture of PDMS and Carboxen is more selective with respect to these aromatic hydrocarbons [46]. Polar acetone, ethanol, isoprene and terpenes are very effectively sorbed on a PDMS–divinylbenzene (DVB) coating [41,47]; recovery is even better than with use of very polar polyacrylate (PA). Table 2 presents applications of various SPME fibre coatings to analysis of different organic air pollutants.

Extraction can be improved by internal fibre cooling, salting out and derivatization.

Fibre internal cooling [22,55,59,81] is useful in extraction from headspace (HS) when sample temperature must be increased to improve analytes transfer from a liquid or solid sample to the head space. To maintain high fibre coating/HS coefficients fibre temperature must be kept low. This approach ensures increased sensitivity due to increase in partition coefficients of HS/sample (increase temperature) and fibre/HS (decrease temperature) and hence increased ratio of analyte concentration in the fibre coating and the sample.

Salting out [52,62,78,82,83] is used to decrease solubility of analytes of interest (including polar ones) in liquid samples. This results in better HS extraction and the increased overall SPME/sample partition coefficient.

Derivatization is based on analyte conversion to another compound by reaction with a specially selected reagent. An analyte derivative should be characterised by better and/or more selective SPME extraction and by polarity, volatility and thermal stability which make its thermal desorption from a fibre and gas chromatographic analysis possible. Generally reactions which are quantitative and give only one product are used for derivatization. Typical analytes analysed in this way are carboxylic acids, alcohols, phenols, amines and some pesticides. In SPME sampling from gases usually two derivatization approaches are used.

(1) *In-matrix derivatization* is based on addition of a derivatizing reagent to a container with a sample and extraction of a derivative from HS [82]. This approach was used to analyse chloroacetic acids in water as methyl derivatives [72] and C_1–C_2 fatty acids in air by derivatizing them with solutions of perenyldiazomethane and (pentafluorophenyl)diazoethane. Other applications include determination of lead ions in water by converting them to tetraethyllead in reaction with sodium tetra-

Table 2
Published applications of SPME for gaseous matrices[a]

	Matrix	Fibre coating	Target analyte	Extraction and desorption conditions	LOD [ppb or (ppt)]	RSD (%)	Final analysis	Ref.
Atmospheric air	Environmental samples	PDMS, 100 μm	BTEX	E<3 min, D=2 min, T_D=220 °C	0.05–2.0	1.5–6	GC–ECD	[27]
	Environmental samples	PDMS, 100 μm	Ethylbenzene, xylenes, alkylnaphthalenes	E=20 min, D=3 min, T_D=260°C	1.3–273.9	3	GC–MS	[48]
	Air in underground parking garage	GCB	BTEX, hexane, isooctane, methylcyclohexane	E=3 min, D=1 min, T_D=240°C	<357	<1.5	GC–FID	[49]
Indoor air	Air in flats	PDMS, 100 μm	Toluene, chlorobenzene, carbon tetrachloride, *p*-xylene, *n*-decane	E=15 min, D=1 min, T_D=250°C	0.002–0.205	*)	GC–MS	[29,50]
	Air in swimming pool	PDMS, 100 μm	Volatile halogenated hydrocarbons	E=5 min, D=1 min, T_D=230°C	0.02	3.2	GC–MS	[51]
	Not specified	PDMS, 95 μm	Volatile halogenated organic contaminants	E=5 min, D=3 min, T_D=200°C	0.01–1.0	<5	GC–ECD	[52]
	Chemical laboratory	PDMS, 95 μm	Volatile chlorinated hydrocarbons	E=10 min, D=3 min, T_D=200°C	0.01–1.0	1–7	GC–ECD, GC–MS	[40]
	Indoor air inside buildings, trains and cars	Carboxen/ PDMS, 75 μm	BTEX	E=1–60 min, D=0.5 min, T_D=300°C	(0.4)–(2)	<15	HRGC–FID	[17]
Industrial air	Occupational exposures	PDMS–DVB, 100 μm	Formaldehyde	E=2 min, D=1 min, T_D=210°C	4.6	<12	GC–FID	[42]
	Perfume and fragrances	PDMS, 100 μm	*cis*-7,*trans*-11-Hexadecadienyl acetate, *cis*-7,*cis*-11-hexadecadienyl acetate	E=35 min, D=6 min, T_D=290°C	*)	<7	GC–FID	[18]
	Different air matrices (air inside furniture, etc.)	PDMS, 7 μm	Formaldehyde	E=1 min, D=1 min, T_D=250°C	0.17	9.6	GC–ECD	[53]
	Not specified	PA, 80 μm	Fatty acids (C_2–C_5)	E=10 min, D=3 min,	0.025–0.3	*)	GC–FID	[54]
Headspace (HS)	Clay sludge, wastewater	PDMS, 340 μm	BTEX	T_D=300°CE=2–5 min, T_B=110°C, 80°C D=1 min, T_D=150°C	<(0.3)	<10	GC–MS	[55]
	Water accommodated fraction samples generated from crude oils	PDMS, 100 μm	BTEX, propylbenzene, butylbenzene, naphthalene	E=20 min, T_B=95°C, D=3 min, T_D=260°C	(1.3–273.9)	<15	GC–MS	[48]
	Wine aromas	PDMS, 100 μm	Ethyloctanoate, ethyldecanoate, terpene alcohols, β-phenylethanol	E=10 min, T_B=20°C, D=5 min, T_D=250°C	<(1)	*)	GC–MS	[56]

Wine aromas	PDMS, 100 μm	Ethylacetate, alcohols (methanol, ethanol)	E=10 min, T_B=20°C, D=5 min, T_D=250°C	<1	*)	GC–MS	[56]
Water polluted with petroleum hydrocarbons	PDMS, 100 μm	Isoalkanenes, aromatic naphthenes	E=3 h, T_B=25°C, T_D=250°C	*)	15	GC–FID	[39]
Aqueous media	PDMS, 100 μm	Benzene, *tert*.-butylmercaptan, *n*-butylmercaptan	E=30 min, D=2 min, T_D=200°C	0.2-5	4–14	GC–FID	[45]
Ground coffee, fruit juice beverage, butter flavour in vegetable oil	PDMS, 100 μm	Limonene, ethyl butyrate, ethyl hexanoate, *cis*-3-hexenyl acetate	E=2–60 min, T_B=25°C, D=3 min, T_D=200°C	*)	0.5–18	GC–MS	[57]
Wastewater, aqueous sluge, sand	PDMS, 100 μm	1,1-Dichloroethane, chloroform, carbon tetrachloride, trichloroethane, dibromochloroethane, chlorobenzene,	E=1–5 min, T_B=50°C, 100°C D=1, 2 min, T_D=200°C, 300°C	(2–550)	2–14	GC–FID or GC–MS	[58]
Aqueous, sand and clay matrices	PDMS, 100 μm	BTEX	E<5 min, T_B=110°C, 80°C D=1 min, T_D=150°C	(0.12–0.32)	7–17	GC–MS	[59]
Soils	PDMS, 100 μm	Chloroanilines, nitroanilines, chlorobenzenes, nitrobenzenes, anilines, benzenes	E=30 min, T_B=80°C, D=5 min,T_D=250°C	<1	*)	GC–ECD	[60]
Single flower honeys	PDMS, 100 μm	Specific compounds	E=30 min, T_B=70°C D=3 min,T_D=240°C	*)	*)	GC–MS	[61]
Millard reaction and sugar thermal degradation compounds	PDMS, 100 μm	Pyrazines, pyridynes, furans, thiazoles	E<10 min, T_B=25°C D=1 min, T_D=250°C	1000–2000	<8	GC–MS	[62]
Human body fluids (blood, urine)	PDMS, 100 μm	Nitrogen–phosphorous pesticides	E=20 min, T_B=100°C D=1 min, T_D=180°C	1.6–200	<40	GC–NPD	[64]
Herbal medicines herb extracts	PDMS, 100 μm	β-Myrcene, β-pinene, limone, menthol	E=0, 5–40 min, T_B=20°C D<5 min, T_D=250°C	210–74 200	<5	GC–MS	[63]
Aqueous solutions, foods, beverages	PDMS, 100 μm	33 Halogenated volatile contaminnts	E=30 min, T_B=4–(−20°C) D=15 min,T_D=250°C	0.002–1.5	2.8–15.2	GC–ECD	[65]
Drinking water in PET bottles	PDMS, 100 μm	Acetaldehyde	E=25 min, T_B=20°C D=5 min, T_D=260°C	1	*)	GC–FID	[66]
Water	PDMS, 100 μm	Tetraethyllead, ionic lead	E=10 min, T_B=105°C T_D=250°C	(200)	5	GC–MS	[67]

Table 2. Continued

	Matrix	Fibre coating	Target analyte	Extraction and desorption conditions	LOD [ppb or (ppt)]	RSD (%)	Final analysis	Ref.
	Water	PDMS, 100 μm	Polychlorinated biphenyls	E=30 min, T_B=90°C D=2 min	<(1)	3–11	GC–ECD	[68]
	Water	PDMS, 56 μm	BTEX	E=50 min, T_B=40°C D=2 min, T_D=180°C	(0.19–0.70)	20	GC–FID	[69]
	Water	PDMS, 15 μm	BTEX	E=2 min, T_B=150°C D=0,2 min, T_D=250°C	*)	<17.4	High-speed isothermal GC–FID	[70]
	Drinking water	PDMS, 95 μm	60 Volatile organic compounds	E<30 min, T_B=20°C, 80°C, D=5 min, T_D=200°C	(20–200)	*)	GC–MS	[71]
	Drinking water	PDMS, 30 μm	Chlorinated acetic acids	E=2 min, T_B=100°C D=0.5 min, T_D=250°C	1.6–400	*)	GC–ECD	[72]
	Water rich in humic organic mater	PDMS, 7 μm	Polycyclic aromatic hydrocarbons, phenols	E=90–180 min	*)	4–13	GC–MS	[73]
	Cosmetics, building products	PDMS–DVB, 100 μm	Formaldehyde	E=2 min, T_B=25°C D=1 min, T_D=210°C	<40	<12	GC–FID	[42]
	Fruit juice	PDMS–DVB, 65 μm	Flavour volatiles	E=30 min, T_B=40°C D=5 min, T_D=220°C	0.27–26.9	11.3	GC–ion-trap MS	[47]
	Groundwater near leaking underground storage tanks with gasoline	PDMS–porous carbon	BTEX, methyl-*tert.*-butyl ether, ethyl butyl ether	*)	0.36–0.63	10	C2DGC–FID	[74]
	Groundwater	Carboxen–PDMS, 80 μm	BTEX C_1–C_2 halocarbons	E=30 min, T_B=25°C, D=2 min, T_D=300°C,	(50–60) (0.1–13)	*)	GC–FID GC–ECD	[46]
	Drinking water in PET bottles	Carbowax–DVB, 65 μm	Acetaldehyde	E=25 min, T_B=20°C D=5 min, T_D=260°C	1	*)	GC–FID	[66]
	Human body fluids	Carbowax–DVB, 65 μm	Ethanol, isobutanol	E=15 min, T_B=70°C D=2 min, T_D=200°C	<20 000	*)	GC–MS	[75]
	Flue–cured tobacco grades	Carbowax–DVB, 65 μm PA, 85 μm	Isovaleric, valeric, hexanoic, benzoic, phenyloacetic, heptanoic, octanoic	*)	*)	*)	GC–MS	[76]
	Wastewater discharges	PA, 85 μm	Chloroform, saturated carboxylic acid, alkylobenzenes, phenol, benzonitryle, benzofuran	E=30 min, T_B=25°C, 60°C D=2 min, T_D=220°C	10–170	<10	GC–MS	[77]
	Local tap water, bi-distilled, deionized	Activated charcoal	BTEX	E=15 min, T_B=25°C, 50°C, 75°C	(1.5–2)	<8.5	GC–FID	[78]
	Human blood	GCB	BTEX, hexane, isooctane, methylcyclohexane	E=25 min, T_B=25°C D=1 min, T_D=240°C	1–10	4–7	GC–FID	[49]
Others	Gaseous mixture	PDMS, 100 μm	71 Compounds containg 1–16 carbon atoms and a variety of functional groups	E=30 min, T_B=25°C, D=0.5 min, T_D=200°C	3000–0.04	*)	GC–FID	[37]
	Propane–butane gas mixture, nitrogen	PDMS, 100 μm	Thiophene, dimethyl sulphide, diethyl sulphide	E=10 min,D=3 min, T_D=200°C	100	*)	GC–FPD	[79]
	Human breath	Carbowax–DVB, 65 μm	Ethanol, isoprene, acetone	E=1 min, T_B=36, 6°C D=20 s, T_D=200°C	<0.30	<13	GC–ion-trap MS	[41]
	Mainstream smoke	PA, 80 μm	Phenolic compounds	E=60 min, D=2 min T_D=275°C	(3.8–300)**	<12	GC–SIM-MS	[80]

[a] E=Fibre exposition time, T_B=bath temperature, D=desorption time, T_D=desorption temperature; BTEX=benzene, toluene, ethylobenzene, xylenes; C2DGC=comprehensive two-dimensional GC; PET=polyethylene terephthalate; ECD=electron-capture detection; FID=flame ionisation detection; FPD=flame photometric detection; GCB=graphitised carbon black; HR=high resolution; LOD=limit of detection; RSD=relative standard deviation; PA=polyacrylate; PDMS=polydimethylsiloxane; SIM=selected ion monitoring. *=Not given; **=amount (ng/cigarette).

ethylborate and extracting it from HS [67,84] and tin [85].

(2) *On-fibre derivatization*: Derivatization is conducted directly in SPME fibre coating [86]; the fibre is immersed in reagent solution and then exposed to an analysed gaseous medium. Examples of this approach is determination of formaldehyde [42,53] and low-molecular-mass organic acids in air [87].

3.2. Introduction of analytes into a gas chromatographic column

After exposition to a sample, the fibre is withdrawn into a needle of on SPME device and introduced into an injection port of a gas chromatograph by piercing the needle through a septum. The fibre is extended from the needle in a hot GC injector, analytes thermally desorbed and transferred with carrier gas into the column. The injector temperature should be high enough to ensure quantitative and fast desorption (analyte band is then narrow). The upper desorption temperature is limited by thermal stability of coating and analytes. To speed up desorption and obtain narrower bands special SPME devices with internal fibre heating are sometimes used [88]. For desorption band focusing special tubes placed between the injector and the column can also be applied [70,88].

3.3. Final analysis

To identify and quantitate analytes isolated and enriched by SPME and then separated in the chromatographic column different detectors were used. Detector selection depends on required sensitivity and selectivity to perform a given analytical task. For analysis of many typical volatile organic pollutants in air on a level of μg/l SPME was combined with GC equipped with FID [11,89–93]. In some special cases a level of ng/l was achieved with ion-trap MS detection [59,67–69,87,94–96].

3.4. Special designs

Typical SPME devices have been designed for laboratory operations. Pawliszyn [97] proposed some modification for remote monitoring. By adding a tube with a small opening to cover a needle, Groth and Pawliszyn [41] obtained a convenient design for breath analysis.

In field sampling it is very important to preserve extracted analytes on a fibre for a longer time and to protect the coating from contamination. As Chai and Pawliszyn [27] showed capping a needle with a polymeric septum prevents even light analytes from losses but only for short time. Cooling to (−70)°C extends the storage time considerably. Organic analytes can dissolve in polymeric material and more appropriate approach is based on metal to metal sealing [97].

3.5. Coupling of solid-phase microextraction with other preconcentration methods

Many present day analytical tasks consist in simultaneous determination of trace components of different polarity and volatility in complex matrices. Generally no single sample preparation technique can be satisfactory in such situation and combined systems are used. For simultaneous determination of volatile and semivolatile analytes supercritical fluid extraction (SFE), solid-phase extraction (SPE) and HS-SPME were combined [97].

The authors propose combination of passive dosimeters and HS-SPME to determine trace BTEX (below 1 $\mu g/m^3$) in air [17]. Temperature and humidity of the studied air have then a smaller effect on results. Generally analytes are stable after passive sampling and can be stored for a relatively long time before they are subjected to HS-SPME analysis.

3.6. Comparison of solid-phase microextraction with other sample preparation methods

SPME is an alternative method for the isolation and enrichment of volatile and semivolatile analytes directly in liquid and gaseous matrices and in liquids and solids by sampling headspace. In many situations HS-SPME gives comparable or lower detection limits than static HS or PT [71]. Generally it is simpler and faster than PT technique and more sensitive than static HS.

In the case of original gaseous matrices such as air SPME has obvious advantages over passive sampling and dynamic sorption on activated charcoal, what

Table 3
Advantages and drawbacks of SPME

Advantages	Drawbacks
(1) Long lifetime of SPME fibre as compared with sorbent packings used in SPE cartridges (ca. 100 operations) – this decreases analysis costs	(1) A fibre is quite fragile
(2) Solvent-free sampling and analyte introduction into a GC column	(2) If partition coefficient is high and/or a sample is small it can be analysed only once
(3) Wide linearity range and relatively good precision of analysis even in the case of complex matrices	(3) In combination with GC, high mass compounds cannot be analysed
(4) Often elimination of sample clean-up and any sample preparation	(4) Abundance of parameters which can affect precision considerably
(5) Possibility of automating sampling and sample injection into a measuring instrument	(5) In many situations difficulty to select fibre coating of polarity close to polarity of analytes.
(6) No clogging problems met in cartridge SPE	
(7) Short sampling time (2–15 min)	
(8) Applicability to a wide spectrum of analytes in a variety of matrices	
(9) Compatibility with different GC injection ports: splitless, on-column (if equipped with independent heating system), programmed temperature vaporiser	
(10) Easy field sampling	
(11) Applicability to gaseous, liquid and solid (HS) samples	
(12) No need for GC modifications	

was proved, e.g., for BTEX and other benzene derivatives [48].

4. Conclusion

As stressed by many users, the analysis with use of SPME is quite simple and easy. Routine analytical work with use of SPME can be automated [16,18].

Advantages and drawbacks of SPME are presented in Table 3.

References

[1] Z. Witkiewicz, in: Proceedings of the 2nd Polish Chromatographic Seminar, Toruń, 20–21 September 1995, p. 22.
[2] J. Wesołowski, Ochr. Powiet. 26 (1992) 12.
[3] M. Ligor, B. Buszewski, Pol. J. Environ. Stud. 16 (1998) 5.
[4] J. Namiesnik, J. Łukasiak, Z. Jamrógiewicz, in: Handing of Environmental Samples for Analysis, PWN, Warsaw, 1995, p. 14, in Polish.
[5] B. Zygmunt, Sci. J. Technical University Gdańsk Chem. 37 (1997) 1, in Polish.
[6] E. Przyk, B. Zabiegała, J. Namieśnik, Chem. Inż. Ekol. 5 (1998) 1033.
[7] J. Namieśnik, M. Pilarczyk, Toxicol. Environ. Chem. 64 (1997) 203.
[8] J. Namieśnik, Ochr. Powiet. 22 (1988) 114.
[9] J. Namieśnik, B. Zygmunt, B. Kozdroń-Zabiegała, Pol. J. Environ. Stud. 3 (1994) 5.
[10] J. Pawliszyn, S. Liu, Anal. Chem. 59 (1987) 1475.
[11] R.P. Belardi, J.B. Pawliszyn, Water Pollut. Res. J. Can. 24 (1989) 179.
[12] K.D. Buchholz, J. Pawliszyn, Environ. Sci. Technol. 27 (1993) 2844.
[13] R. Eisert, K. Levsen, G. Wünsch, J. Chromatogr. A 683 (1994) 175.
[14] R. Eisert, K. Levsen, GIT Fachz. Lab. 1 (1995) 25.
[15] H. Daimon, J. Pawliszyn, Anal. Commun. 33 (1996) 421.
[16] S. Motlagh, J. Pawliszyn, Anal. Chim. Acta 284 (1993) 265.
[17] K. Elke, E. Jermann, J. Begerow, L. Dunemann, J. Chromatogr. A 826 (1998) 191.
[18] R. Eisert, J. Pawliszyn, G. Barinshteyn, D. Chambers, Anal. Commun. 35 (1998) 187.
[19] M. Ligor, M. Ściborek, B. Buszewski, J. Microcol. Sep. (2000) in press.
[20] D. Gorlo, Ph.D. Thesis, Chemical Faculty Technical University of Gdańsk, Gdańsk, 1998.
[21] H. Prosen, L. Zupancic-Kralj, Trends Anal. Chem. 18 (1999) 272.
[22] D. Gorlo, J. Namieśnik, B. Zygmunt, Chem. Anal. (Warsaw) 42 (1997) 297.
[23] P. Konieczka, Chem. Inż. Ekol. 4 (1997) 37.
[24] J. Namieśnik, Sci. J. Technical University Gdańsk Chem. 28 (1985) 1, in Polish.
[25] J. Namieśnik, J. Chromatogr. 300 (1984) 79.
[26] J. Namieśnik, M. Biziuk, W. Chranowski, W. Wardencki, B. Zygmunt, Chem. Anal. (Warsaw) 40 (1995) 115.
[27] M. Chai, J. Pawliszyn, Environ. Sci. Technol. 29 (1995) 693.
[28] P.A. Martos, J. Pawliszyn, Anal. Chem. 69 (1997) 206.

[29] J. Namieśnik, D. Gorlo, L. Wolska, B. Zygmunt, Analusis 26 (1998) 170.
[30] J. Namieśnik, D. Gorlo, L. Wolska, B. Zygmunt, Chem. Anal. (Warsaw) 44 (1999) 201.
[31] P. Konieczka, J. Namieśnik, J.F. Biernat, J. Chromatogr. 540 (1991) 449.
[32] P. Konieczka, E. Luboch, J. Namieśnik, J.F. Biernat, Anal. Chim. Acta 265 (1992) 127.
[33] P. Konieczka, J. Namieśnik, A. Przyjazny, E. Luboch, J.F. Biernat, Analyst 120 (1995) 2041.
[34] M. Prokopowicz, E. Luboch, J. Namieśnik, J.F. Biernat, A. Przyjazny, Talanta 44 (1997) 1551.
[35] K. Bodzek, Chem. Anal. (Warsaw) 36 (1991) 637.
[36] Z. Zang, J. Pawliszyn, J. Phys. Chem. 100 (1996) 17648.
[37] R.J. Bartelt, Anal. Chem. 69 (1997) 364.
[38] P.A. Martos, A. Saraullo, J. Pawliszyn, Anal. Chem. 69 (1997) 402.
[39] A. Saraullo, P.A. Martos, J. Pawliszyn, Anal. Chem. 69 (1997) 1992.
[40] M. Chai, C.A. Arthur, J. Pawliszyn, R.P. Belardi, K.F. Pratt, Analyst. 118 (1993) 1501.
[41] Ch. Grote, J. Pawliszyn, Anal. Chem. 69 (1997) 587.
[42] P.A. Martos, J. Pawliszyn, Anal. Chem. 70 (1998) 2311.
[43] D. Gorlo, L. Wolska, B. Zygmunt, J. Namieśnik, Talanta 44 (1997) 1543.
[44] T. Górecki, A. Khaled, J. Pawliszyn, Analyst 123 (1998) 2819.
[45] C. Rivasseau, M. Caude, Chromatographia 41 (1995) 462.
[46] P. Popp, A. Paschke, Chromatographia 46 (1997) 419.
[47] M.E. Miller, J.D. Stuart, Anal. Chem. 71 (1999) 23.
[48] M. Llompart, K. Li, M. Fingas, J. Chromatogr. A 824 (1998) 53.
[49] F. Mangani, R. Cenciarni, Chromatographia 41 (1995) 678.
[50] D. Gorlo, B. Zygmunt, M. Dudek, A. Jaszek, M. Pilarczyk, J. Namieśnik, Fresenius J. Anal. Chem. 363 (1999) 696.
[51] J. Czerwiński, B. Zygmunt, J. Namieśnik, Fresenius Environ. Bull. 5 (1996) 55.
[52] C.L. Arthur, M. Chai, J. Pawliszyn, in: K. Saarela, P. Kalliokoski, O. Seppanem (Eds.), Proceedings of the 6th International Conference on Indoor Air Quality and Climate, Helsinki, Indoor Air'93, Vol. 1, 4–8 July 1993, p. 257.
[53] S.V. Bolta, L. Zupancic-Kralj, J. Marsel, Chromatographia 48 (1998) 95.
[54] L. Pan, J. Pawliszyn, Anal. Chem. 69 (1997) 196.
[55] Z. Zhang, J. Pawliszyn, Anal. Chem. 67 (1995) 34.
[56] Z. Penton, Chem. NZ 62 (1998) 41.
[57] X. Yang, T. Peppard, J. Agric. Food Chem. 42 (1994) 1925.
[58] Z. Zhang, J. Pawliszyn, J. High Resolut. Chromatogr. 16 (1993) 689.
[59] Z. Zhang, J. Pawliszyn, Anal. Chem. 67 (1994) 34.
[60] A. Fromberg, T. Nilsson, B.R. Larsen, L. Montanarella, S. Facchetti, J.O. Madsen, J.Chromatogr. A 746 (1996) 71.
[61] M. Guidotti, M. Vitali, in: P. Sandra, G. Devos (Eds.), Proceedings of the 18th International Symposium on Capillary Chromatography, Riva del Garda, 20–24 May 1996, p. 564, Vol. 1.
[62] W.M. Coleman III, J. Chromatogr. Sci. 34 (1996) 213.
[63] J. Czerwiński, B. Zygmunt, J. Namieśnik, Fresenius J. Anal. Chem. 356 (1996) 80.
[64] X.-P. Lee, T. Kumazawa, K. Sato, O. Suzuki, Chromatographia 42 (1996) 135.
[65] B.D. Page, G. Lacroix, J. Chromatogr. 648 (1993) 199.
[66] C.K. Huynh, T. Vu-Duc, Trav. Chim. Aliment. Hyg. 89 (1998) 705.
[67] T. Górecki, J. Pawliszyn, Anal. Chem. 68 (1996) 3008.
[68] J. Koch, P. Völker, Acta Hydrochim. Hydrobiol. 25 (1997) 179.
[69] B. MacGillivray, J. Pawliszyn, J. Chromatogr. Sci. 32 (1994) 317.
[70] T. Górecki, J. Pawliszyn, J. High Resolut. Chromatogr. 18 (1995) 161.
[71] T. Nilsson, F. Pelusio, L. Montanarella, B. Larsen, S. Facchetti, J.O. Madsen, J. High Resolut. Chromatogr. 18 (1995) 617.
[72] B. Aikawa, R.C. Burk, Int. J. Environ. Anal. Chem. 66 (1997) 215.
[73] J. Porschmann, F.D. Kopinke, J. Pawliszyn, J. Chromatogr. A 816 (1998) 159.
[74] R.B. Gaines, E.B. Ledford, J.D. Stuart, J. Microcol. Sep. 10 (1998) 597.
[75] T. Kumazawa, H. Seno, X.P. Lee, A. Suzuki, K. Sato, Chromatographia 43 (1996) 393.
[76] T.J. Clark, J.E. Bunch, J. Chromatogr. Sci. 35 (1997) 209.
[77] K.J. James, M.A. Stack, Fresenius J. Anal. Chem. 358 (1997) 833.
[78] Dj. Djozan, Y. Assadi, Chromatographia 45 (1997) 183.
[79] W. Wardencki, J. Namieśnik, Chem. Anal. (Warsaw) 44 (1999) 485.
[80] T.J. Clark, J.E. Bunch, J. Chromatogr. Sci. 34 (1996) 272.
[81] R. Eisert, K. Levsen, J. Chromatogr. 733 (1996) 143.
[82] L. Pan, M. Adams, J. Pawliszyn, Anal. Chem. 67 (1995) 4396.
[83] C.L. Arthur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145.
[84] T. Górecki, A. Boyd-Boland, Z. Zhang, J. Pawliszyn, Can. J. Chem. 74 (1996) 1297.
[85] Y. Morcillo, Y. Cai, J.M. Bayona, J. High Resolut. Chromatogr. 18 (1996) 767.
[86] A.A. Boyd-Boland, M. Chai, Y.Z. Luo, Z. Zhang, M.J. Yang, J.B. Pawliszyn, T. Górecki, Environ. Sci. Technol. 28 (1994) 569A.
[87] Z. Zhang, J. Pawliszyn, Anal. Chem. 65 (1993) 1843.
[88] T. Górecki, J. Pawliszyn, Anal. Chem. 67 (1995) 3265.
[89] D. Louch, S. Motlagh, J. Pawliszyn, Anal. Chem. 64 (1992) 1187.
[90] C.L. Arthur, L.M. Killam, K.D. Buchholz, J. Pawliszyn, J.R. Berg, Anal. Chem. 64 (1992) 1960.
[91] C.L. Arthur, D.W. Potter, K.D. Buchholz, S. Motlagh, J. Pawliszyn, LC·GC 10 (1992) 656.

[92] C.L. Arthur, L.M. Killam, S. Motlagh, M. Lim, D.W. Potter, J. Pawliszyn, Environ. Sci. Technol. 26 (1992) 979.
[93] K.D. Buchholz, J. Pawliszyn, Anal. Chem. 66 (1994) 160.
[94] D.W. Potter, J. Pawliszyn, J. Chromatogr. 625 (1992) 247.
[95] D.W. Potter, J. Pawliszyn, Environ. Sci. Technol. 28 (1994) 298.
[96] C.L. Arthur, K. Pratt, S. Motlagh, J. Pawliszyn, R.P. Belardi, J. High Resolut. Chromatogr. 15 (1992) 741.
[97] J. Pawliszyn, in: Solid Phase Microextraction. Theory and Practice, Wiley–VCH, New York, 1997, p. 14.