Potential of Solid-Phase Microextraction Fibers for the Analysis of Volatile Organic Compounds in Air

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Abstract

This work presents the usefulness of five different solid-phase microextraction fibers in the screening of volatile organic compound (VOC) traces in air samples. The performances of these fibers are compared by studying the sorption kinetics in an equimolar gaseous mixture of eleven VOCs. For each fiber, static and dynamic sampling are compared. It is shown that repeatability is better for the dynamic mode (less than 6% for dynamic sampling and 10% for static sampling). The equilibrium time and the sensitivity vary considerably from one fiber type to another. As an example, the classical polydimethylsiloxane (PDMS) coating presented the shortest equilibration time (5 min) but also the poorest sensitivity, whereas the PDMS–Carboxen showed the longest extraction time but the greatest sensitivity. The estimation of the quantity of VOCs fixed on the target fiber allows for the determination of the different affinities of the compounds with the involved sorbent and relates them with physicochemical properties of the molecules. Competitive sorption is observed for the fibers involved with the adsorption process (i.e., PDMS–divinylbenzene and PDMS–Carboxen fibers). These competitions can lead to SPME calibration problems and thus bad quantitative analysis.

Introduction

Volatile organic compounds (VOCs) are pollutants of environmental interest because they can be responsible for health hazards (1); therefore, they must be determined in the atmosphere at very low levels. This goal can be achieved by using sorbent tubes (2) or cryogenic trapping (3), but these techniques require the use of specific and expensive equipment (automatic thermal desorber). An advancement in sample preparation for trace analysis is the solid-phase microextraction (SPME) method, which has been described elsewhere (4). No specific equipment is needed because extracted analytes are directly thermally desorbed in the heated injection port of a gas chromatograph (GC).

SPME has been extensively used in water analysis (direct or headspace), especially for benzene toluene ethylbenzene xylene (BTEX) compounds (5), phenols (6), halogenated compounds (7), pesticides (8), or various VOCs (9). Pollutants in soils (10), PCBs (11), and beverage aromas (12) have also been investigated. However, this technique has been tested to a lesser extent in air analysis.

In this area, one of the main difficulties exists in generating standard atmospheres to check the performances of the SPME fibers. The first experiments described in the literature were done in static mode. Gaseous samples were prepared by spiking gas-sampling bulbs with liquid standards (13). In order to generate sufficiently low concentrations, it is necessary to prepare a standard stock solution in which analytes are dissolved in a solvent that can interact with the sorption of analytes. As shown by Pawliszyn et al. for BTEX analysis (14), it results in a distortion when studying the sorption's phenomena on SPME fibers. An alternative solution consists of first spiking a gas-sampling bulb with neat analytes, then taking a gaseous aliquot and diluting it into a second gas-sampling bulb (15). However, these experiments are tedious, time consuming, and not sufficiently reproducible.

In order to be as accurate as possible in SPME–GC calibration, the most reliable approach would be to expose SPME to gaseous standards that are similar to the real-air sample. Static sampling can be representative of ambient or workplace air monitoring, but not circumstances of industrial stream emissions. There are two main ways to generate polluted air streams. Permeation tube techniques have been used for SPME studies. For example, Mangani et al. (16) achieved low concentrations and a wide range of linearity over a wide concentration range for BTEX mixtures and halogenated hydrocarbon mixtures. Namiesnik et al. used a home-made apparatus based on permeation (17) to sample xylene, toluene (Tol), and *n*-decane. The major drawback of permeation tubes is temperature control. By changing the temperature by 1°C, the permeation rate changes by 10% (18). Another drawback is the need for an accurate scale to measure weight loss leading to the permeation rate. Also, equilibrium of the permeation rate is reached between a few hours and several weeks (19). Finally, if one considers working on a mixture of approximately ten analytes, the apparatus will quickly become cumbersome.

Martos et al. (20,21) used the syringe-injection method to build a standard gas-generating device. By continuously injecting a

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liquid mixture of hydrocarbons in an air stream with the assistance of a syringe pump, Martos et al. created dynamic polluted atmospheres. They validated this standard gas generating device by analyzing the effluent with National Institute for Occupational Safety and Health methods 1500 and 1501. Therefore, the syringe injection method was chosen in this study.

When considering the nature of the SPME fibers for air sampling, it can be observed in the literature that the most common coating used is polydimethylsiloxane (PDMS). Chai et al. (13) obtained detection limits around the parts-per-billion level for BTEX sampling. Other sorbents (such as graphitized carbon black) present interesting performances for the sampling of halogenated hydrocarbons and BTEX (16).

However, although PDMS appears highly suitable for nonpolar and moderately volatile VOCs such as BTEX, other fibers are needed for the most polar and volatile molecules. In this area, four different fibers were compared for the sampling of acetone (Ac), ethanol, and isoprene in human breath (15). It was concluded that the PDMS–divinylbenzene (Dvb) fiber was the most sensitive among PDMS, polyacrylate (PA), and Carbowax (Cwax)–Dvb, but the authors noticed competitive adsorption on the PDMS–Dvb fiber.

Table I. Desorption Temperature and Desorption Time of the Fibers

	Desorption temperature (°C)	Desorption time (min)
PDMS	220	< 1
PDMS–Dvb	240	1.5
Cwax–Dvb	250	1
PDMS–Car	320	2.5
PDMS–Dvb–Car	270	2

Table II. Physicochemical Properties of Adsorbents Used as Coatings*

	BET† surface (m^2/g)	Density (g/mL)	Porosity (mL/g)		
			Micro	Meso	Macro
Car 1006	720	0.47	0.29	0.26	0.23
Dvb	750	0.36	0.11	0.85	0.58

* Data on request from SUPELCO.
† BET, Brunauer, Emmett & Teller.

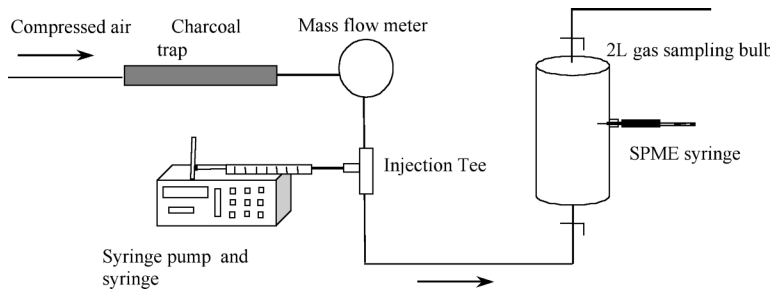

Figure 1. Standard gas generating device.

In these studies, only a limited number of chemical families have been investigated. The aim of this work was therefore to widen air sampling with SPME by comparing the performances of five different coatings for the screening of a wide range of VOCs (methanol, ketones, esters, aromatics, and chlorinated compounds). For each tested fiber, differences between static and dynamic sampling were studied in order to determine whether two calibration modes were necessary to approach air stream and ambient air analysis.

The efficiency of each fiber was evaluated by performing sorption kinetics. In order to unambiguously determine compound affinity with coatings, experiments were carried out using an equimolar gaseous mixture of the model compounds. With this aim in view, it was also necessary to determine the absolute extracted amounts of VOCs by the tested fibers. This is generally performed through an external liquid calibration of the GC. This estimation proved to be suitable, assuming that the liquid injection of the model compounds was as representative as possible of SPME desorption (22). Therefore, the liquid-injection process was carefully examined in this study. Competitive sorptions were also studied in order to determine the usefulness of SPME for quantitative analysis.

Experimental

Chemicals and reagents

The VOCs studied were methanol (MeOH), Ac, dichloromethane (DiClMe), methyl ethyl ketone (MEK), ethyl acetate, (AcEt), dichloroethane (DiClEt), methyl isobutyl ketone (MIBK), Tol, and butyl acetate (AcBu), which were purchased from Carlo Erba Farmitalia (Milan, Italy). Ethyl benzene (EtBenz) and *p*-xylene (pXyl) were supplied by Acros (Geel, Belgium). All of these reagents were of at least 99% purity. A liquid equimolar mixture was prepared with these eleven solvents. It was used in the syringe pump delivery system for generating the standard atmospheres.

The standard solutions for liquid calibration were prepared by dissolving different amounts of the VOC mixture in *n*-butanol (BuOH) (analytical grade, 99.8% purity, Carlo Erba Farmitalia). BuOH was chosen for its low vapor volume. Standard solutions were in the range of 0.5–100 mmol/L for each compound. All solutions were prepared weekly, checked daily, and stored in the dark at 4°C. A set volume of 0.1 µL was injected using a 1-µL SGE syringe (Fisher Scientific, Elancourt, France) without dead volume to ensure good reproducibility. Injections were made in triplicate for each point of the calibration curves.

SPME

A manual SPME holder was used with five different fiber types, one for each type (gauge 24): 100 µm PDMS, 65 µm PDMS–Dvb, 75 µm PDMS–Carboxen (Car), 50 µm and 30 µm PDMS–Dvb–Car, and 65 µm Cwax–Dvb. All of these fibers were purchased from Supelco (Bellefonte, PA). SPME fibers were conditioned in the GC injector before use. Some physicochemical properties of the coatings, time, and temperature of desorption are shown in Tables I and II. All SPME

injections were done in triplicate.

Standard gas generating device

A standard gas generating device was constructed as shown in Figure 1. The connection of the different parts of the device was made with $^1/_4$-inch Teflon tubing and stainless steel seals from Swagelok (Lyon, France). Brooks mass flow meters were purchased from Serv' Instrumentations (Vitrolles, France), and the 2-L gas sampling bulb was supplied by Supelco.

A 500-µL Hamilton gas tight syringe (Fisher Scientific) was used with a Harvard syringe pump (Fisher Scientific) to deliver the VOCs mixture, which was evaporated with clean compressed air. By knowing the air (20 L/min) and mixture flow rates, analyte concentrations in the air streams could be easily deduced. Sampling in the passive mode was carried out by closing the two stopcocks of the gas sampling bulb. Overpressure in the gas sampling bulb was eliminated by briefly piercing the septum of the sampling port with a capillary tube.

Chromatography

A Hewlett-Packard 6890 Plus GC (Bios Analytique, Paris, France) equipped with a split/splitless injection port (operating in the splitless mode with a 0.75-mm-i.d. liner) and a flame ionization detector was used for GC analysis. Chromatographic separations were performed using an HP-1 column (100% PDMS, 50-m × 0.32-mm i.d, 1.05-µm film thickness) (Bios Analytique), and the oven temperature was programmed as follows: 40°C for 1 min, ramped at 15°C/min to 90°C, held for 4 min, and then ramped at 10°C/min to 120°C.

The carrier gas was helium with a flow rate of 2.5 mL/min. The temperature of the detector was 250°C and it was fed with 40 mL/min of hydrogen, 450 mL/min of reconstituted air, and 50 mL/min of helium (diluting gas). Signals were collected and recorded with HP 3398A software (Bios Analytique).

Results and Discussion

Determination of absolute amounts of VOCs extracted by SPME

This work was essentially based on the study of sorption kinetics, which was especially helpful with the determination of the VOCs' affinity with the different tested SPME coatings. With this aim in view, kinetics should be plotted by using absolute amounts of extracted analytes versus the time of extraction instead of peak areas that depend on the detector sensitivity for the compound. The absolute amount fixed on the fiber was determined through an external liquid calibration. The results are assumed to be accurate if liquid standard injections correlate well with SPME desorption (22). The procedure of liquid injection was therefore improved by selecting a relevant injection liner and a convenient injection temperature.

Liner diameter

In order to achieve sharp SPME injection bands, the transfer of the analytes from the injection port to the column must be as fast as possible, thus the thermal desorption step must be very efficient. Therefore, an inlet liner with a 0.75-mm i.d. should be used because it increases linear flow rates around the fiber in the injection port, which leads analytes to the column quickly. If this type of liner improves SPME injections, great care must be taken for liquid injections. The small liner diameter implies a small internal volume (i.e., 35 µL). Consequently, it is recommended that small volumes be injected in order to avoid an overpressure effect and discrimination at the purge vent valve (23). Using BuOH as a solvent and injecting 0.1 µL of the standard satisfied these requirements.

Injection-port temperature

This parameter is particularly important because this study deals with eleven VOCs, which represent molar weights from 32 to 116 g/mol and boiling points from 40°C to 138.3°C. Degradation of compounds can arise from too high of an injection temperature, or carryover problems can appear from incomplete vaporization of compounds with high boiling points (24). Also, the recommended desorption temperature is different according to the involved SPME fiber. Consequently, for liquid injections it was necessary to ensure that the injection-port temperature did not have a significant effect on peak areas. Under these conditions, it would be possible to perform only one calibration curve at a given temperature. Therefore, a middle-range standard solution (50 mmol/L) was injected at three injection-port temperatures (220°C, 270°C, and 320°C) in triplicate. Peak areas at each temperature and for each compound were compared using an F-test. The data at 220°C were statistically different from 320°C, but not from 270°C at the 95% confidence interval. Also, 320°C was not statistically different from 270°C (data not shown). Consequently, it was decided to calibrate the GC at 270°C. Five-point calibration curves were drawn for all compounds, with at least 0.991 as the correlation coefficients and less than 3% relative standard deviation for triplicates. These calibrations were used to estimate the absolute amount of each VOC extracted by SPME.

Comparison of fiber performances

The performances of the fibers were evaluated from the sorption kinetics determined with the equimolar VOCs' mixture (40 µmol/m^3) in static and dynamic mode. For these two modes, similar shaped curves were obtained, and only the kinetics related to the dynamic mode are reported in Figure 2.

Extraction time

The equilibration time (see Table III) was defined as the time needed by the slowest compound to reach this state. For the PDMS and PDMS–Dvb fiber, this compound was AcBu. For Cwax–Dvb, PDMS–Car, and PDMS–Dvb–Car, it was pXyl.

The kinetics demonstrated that the equilibration time ranged from 5 min for the PDMS fiber to more than 150 min for the PDMS–Car fiber. This difference can be explained by sorption mechanisms. When using the PDMS fiber, sample extraction is governed by absorption mechanisms and is characterized by higher diffusion coefficients in the fiber phase than those for the adsorption mechanism. With an adsorbent such as Dvb or Car, diffusion into the pores may be responsible for the low diffusion kinetics as well as surface interaction or capillary condensation (25).

Equilibrium was achieved in 15 min for PDMS–Dvb and 10 min for the Cwax–Dvb fibers. Because these values were of the same order, it may be supposed that the equilibrium time for these two fibers was determined by Dvb and not PDMS or Cwax. Dvb is essentially composed of wide pores (meso- and macropores, Table II) that permit a short equilibration time (Table III), but is still longer than with the PDMS fiber. After 150 min, equilibrium was not achieved for VOCs adsorbed on the PDMS–Car fiber (Figure 2). Car is a carbon molecular sieve containing micropores (Table II). As a consequence, the equilibration time is longer than with Dvb. Using a PDMS–Dvb–Car SPME fiber, equilibrium appeared after 60 min of sampling. Analytes first entered into the Dvb pores and then into the Car pores, which explains the intermediate equilibrium time compared with that of the Dvb and Car-based SPME fibers.

This first comparison between fibers showed that PDMS was the most promising fiber in terms of extraction time. However, parameters such as competition for adsorption, selectivity of the coatings, sensitivity, or repeatability must be taken into account in order to obtain a good overview on the potential of SPME fibers for the analysis of trace VOCs in air.

Competition for adsorption

Adsorption kinetics with distinctive shapes were obtained when sampling with the PDMS–Dvb coating. The seven less-retained compounds presented an adsorption maximum at approximately 2 min followed by a decrease of the adsorbed quantity (Figure 2). The four other compounds reached a steady state without an adsorption maximum (data not shown on Figure 2). This clearly demonstrates the competitive adsorption process in which compounds with high affinity (AcBu, pXyl, EtBenz, and MIBK) displaced the compounds with low affinity. These displacement effects have already been shown for MEK and Ac in mixtures (15,26). Similar profiles were obtained with the Cwax–Dvb fiber, indicating that PDMS and Cwax had the same influence on VOC sorption, as previously stated.

The PDMS–Car fiber also showed competitive adsorption, but the release of compounds with low affinity was slower than that observed for PDMS–Dvb, because of the different distribution of pore sizes (Table II). After 150 min, seven compounds were displaced; one was stable between 120 and 150 min (Tol) and three had not reached an adsorption maximum in the experiments (AcBu, pXyl, and EtBenz). This situation was different from the one observed with the PDMS–Dvb fiber, with which an equilibrium was reached for all analytes, even though competitive adsorption occurred.

Using PDMS–Dvb–Car there were not any displacement effects, and equilibrium was reached probably because of the association of the two adsorbents. Nevertheless, this fact was difficult to explain because of the complexity of a multibed adsorption process.

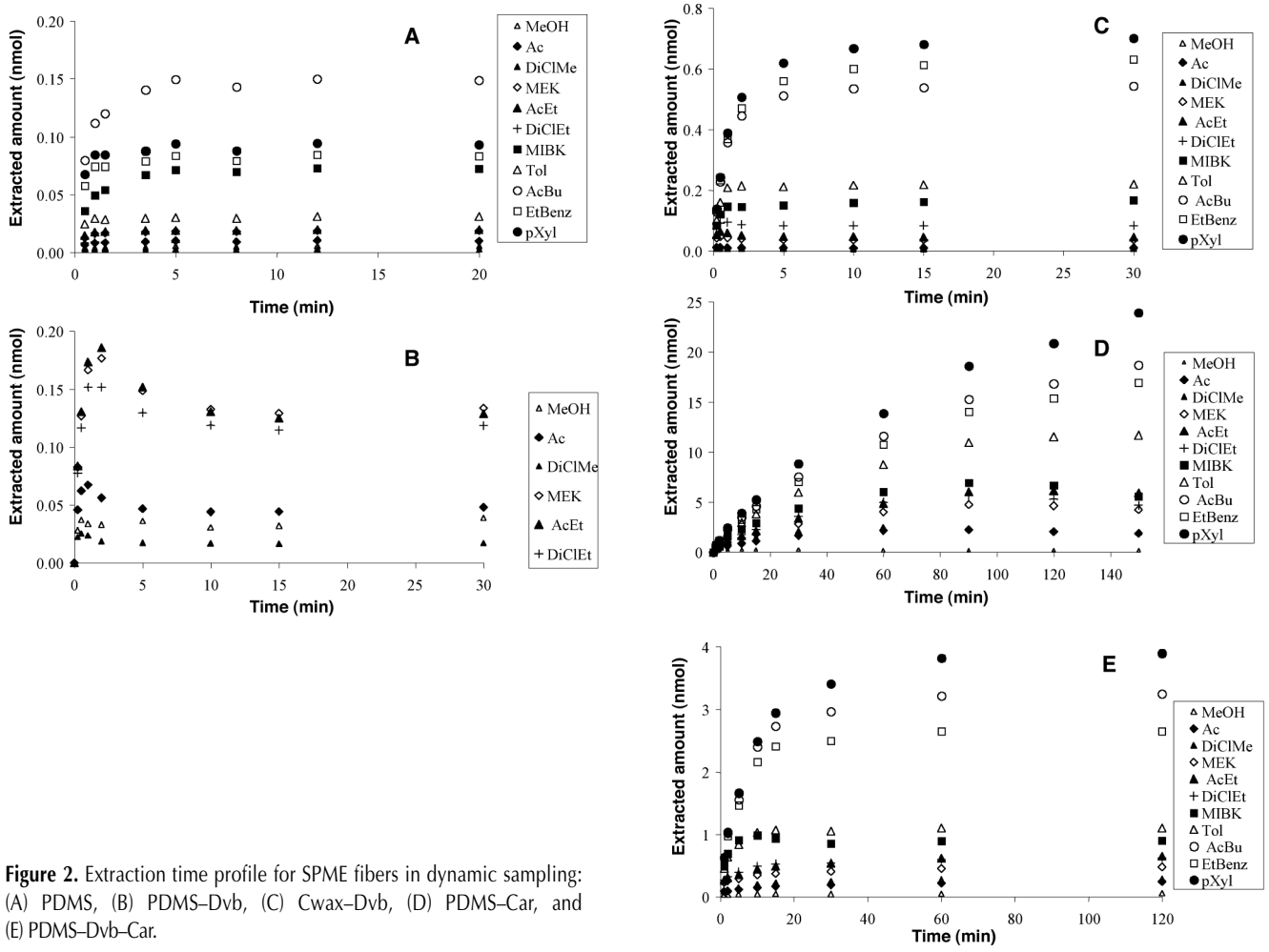

Figure 2. Extraction time profile for SPME fibers in dynamic sampling: (A) PDMS, (B) PDMS–Dvb, (C) Cwax–Dvb, (D) PDMS–Car, and (E) PDMS–Dvb–Car.

Sorption kinetics obtained with the PDMS fiber did not show any displacement effects, because of a noncompetitive absorption process of the analytes from the air sample.

For quantitative analysis, adsorbent-based fibers showed severe limitations (except PDMS–Dvb–Car). In a previous study (25), displacement effects have been observed relating competitive adsorption with underlying matrices effects.

Study of the affinity of the compounds with the different coatings

Three parameters representing physicochemical properties of the molecules were examined in order to explain the compound affinity with the different tested fibers at equilibrium (t = 90 min for PDMS–Car): (*a*) the vapor pressure commonly studied in case of adsorption, which is an exothermal phenomenon; (*b*) the liposolubility expressed as the octanol–water partition coefficient (log K_{ow}), which is recognized to fit the partition coefficient on the absorption-type fiber such as the PDMS (7,27,28); and (*c*) the molecular volume, which may be useful to explain adsorption on porous material. The molecular volumes were calculated at the Laboratory of Structural Chemistry (University of Pau, France) by using a software program that reviewed all of the possible conformations of a given molecule and determined the most cumbersome (29). Then, the barycenter distances between it and all other atoms of the molecule were calculated. These distances have been incremented with the Van der Walls radius value of each considered atom. The chosen radius of the molecule was the biggest (incremented) distance between the barycenter and atom. For each fiber type, the sorbed quantity of the VOCs was plotted versus these three parameters independently (Figures 3A, 3B, and 3C).

Table III. Equilibrium Time*

	Static mode	Dynamic mode
PDMS	5	5
PDMS–Dvb	> 30	15
Cwax–Dvb	10	10
PDMS–Car	> 150	> 150
PDMS–Dvb–Car	60	60

* In minutes, concentration = 40 µmol/m³ for each compound.

Table IV. Log K_{ow}, Vapor Pressure*, and Molecular Volume of the Compounds

Compounds	K_{ow}	Vapor pressure†	Molecular volume (Å³)
MeOH	–0.764	207.8	89
Ac	–0.268	220.4	168
DiClMe	1.249	432.6	175
MEK	0.261	110.7	260
AcEt	0.671	169.5	364
DiClEt	1.458	352.1	256
MIBK	1.189	8.7	418
Tol	1.729	22.3	352
AcBu	2.791	8.0	891
EtBenz	3.320	7.0	499
pXyl	3.440	6.1	424

* Reference 29.
† Millimeters of HG, 25°C.

PDMS and PDMS–Dvb fibers. The affinity order of the molecules was the same for these two fibers. Six compounds (MeOH, Ac, DiClMe, MEK, AcEt, and DiClEt) were not well retained. They corresponded with a combination of the most volatile, most polar, and smallest molecules. For the other compounds, the sorbed quantity classically increased with liposolubility and molecular volume and decreased with volatility (Figure 3A and 3B). However, MIBK was better sorbed than DiClEt even though it presented the same liposolubility. The same observation could be made for AcBu, which was better retained than pXyl and EtBenz. Therefore, at identical liposolubility it seemed that the sorption of compounds containing a linear carbon chain favored on these two organic polymers. In the case of PDMS–Dvb, this result

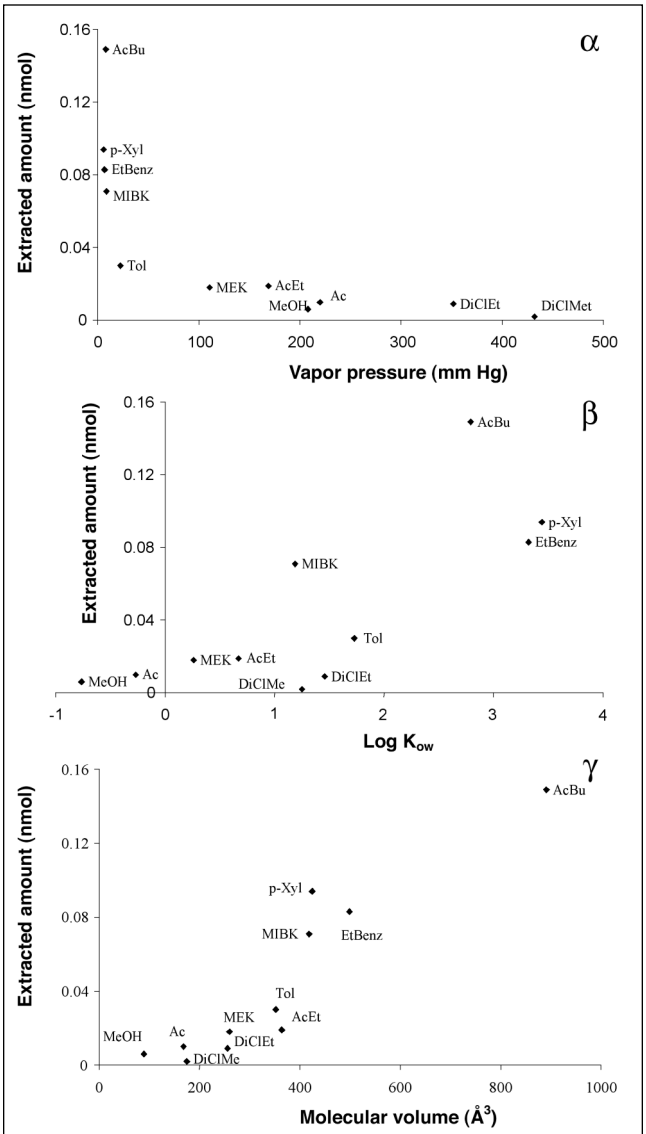

Figure 3A. Absolute extracted amounts with SPME fibers versus physicochemical "descriptors". (A) PDMS: vapor pressure (millimeters of Hg, 25°C), α; log K_{ow}, β; and molecular volume (Å³), γ.

could be surprising because it is generally understood that π–π interactions with the benzenic cycle of Dvb enhances the adsorption of molecules containing aromatic cycles. It can also be noted that the solid and porous nature of Dvb (Table II) had no influence on the compounds' sorption compared with the gel-type PDMS. The only difference was in the higher sorption capacity of Dvb, probably because of the higher surface available to adsorption.

PDMS–Car. The studied VOCs presented a different sorption behavior with this fiber. The six slightly sorbed molecules on the PDMS and PDMS–Dvb were significantly concentrated on the PDMS–Car, and linear relations were obtained for the sorbed quantity versus log K_{ow} (r^2 = 0.96 without chlorinated compounds) and the molecular volume (r^2 = 0.97 without aromatic compounds). Adsorption on the Car was therefore strongly related to these two physicochemical properties, which varied in the same way for the majority of the tested VOCs (Figure 3C, β and γ).

The chlorinated compounds were less adsorbed than expected when considering their relationship with log K_{ow} (Figure 3C, β). This could mean that in this case adsorption was not governed by liposolubility. On the contrary, DiClMe and DiClEt fit the linear relationship between the sorbed quantity and the molecular volume perfectly (Figure 3C, γ). For these compounds, the molecular size seemed to be the major parameter governing adsorption. This could be explained by the presence of micropores in Car.

However, the adsorption of aromatics on Car seemed essentially governed by liposolubility (Figure 3C, β). Indeed, for these compounds, the molecular volume was not significantly involved in adsorption. As an example, AcEt and Tol had the same molecular volume, but Tol was better adsorbed (Figure 3C, γ).

In conclusion, for all the sorbents studied the retention of the compounds can be explained by their volatility, liposolubility, and

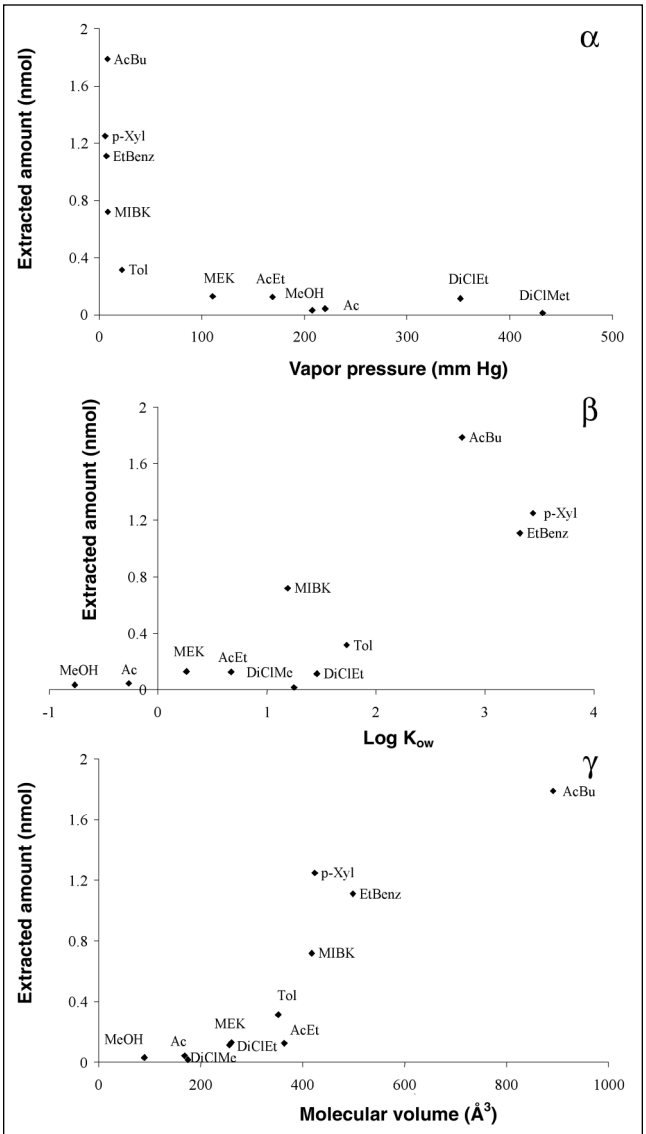

Figure 3B. Absolute extracted amounts with SPME fibers versus physicochemical "descriptors". (B) PDMS–Dvb: vapor pressure (millimeters of Hg, 25°C), α; log K_{ow}, β; and molecular volume (Å^3), γ.

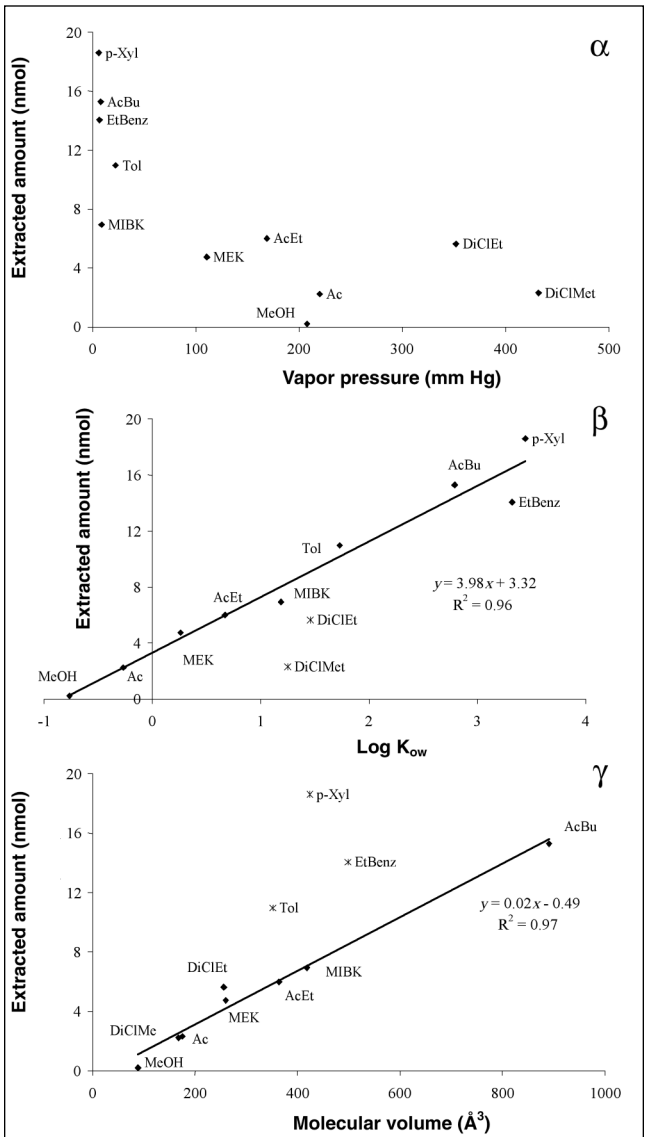

Figure 3C. Absolute extracted amounts with SPME fibers versus physicochemical "descriptors". (C) PDMS–Car: vapor pressure (millimeters of Hg, 25°C), α; log K_{ow} (chlorinated compounds are not included in the calculation of the regression line), β; and molecular volume (Å^3) (aromatics are not included in the calculation of the regression line), γ.

molecular volume. The sorption behavior in organic polymers is similar, whereas the microporosity of Car favors the adsorption of small polar molecules.

Comparison between static and dynamic sampling

For all the tested fibers except PDMS–Dvb, the time of equilibrium did not vary between the static and dynamic mode. No differences in the affinity order were observed between the two sampling modes as well. On the contrary, (as shown in Figure 4) the quantity of fiber-sorbed analytes changed from one mode to another.

With PDMS sampling, the absolute extracted amount in static mode (Q_{stat}) represented approximately 65% of the dynamic reference (Q_{dyn}), except for DiClMe, which rose to 85%. However, the quantity fixed on the fiber for DiClMe at this concentration was found to be near the limit of detection of the technique. Extraction was enhanced by air fanning, which may increase diffusion in the gel-type phase.

Using a PDMS–Dvb fiber, static and dynamic samplings were nearly similar for all analytes. For the large and less volatile analytes, the ratio was less than one, especially for AcBu. This compound was particularly sensitive to fanning, which shows that the kinetics of adsorption for compounds into porous polymer is partly because of external diffusion.

The Cwax–Dvb fiber presented the same equilibrium time in static and dynamic mode, but the distribution of compounds was different. For instance, with PDMS–Dvb, large compounds were less retained in static mode. Fanning did not favor them and a better sorption of small and polar compounds such as MeOH and Ac (Q_{stat}/Q_{dyn} ratio values between 1.2 and 1.5) was observed, though it was not the case with PDMS–Dvb (Q_{stat}/Q_{dyn} ratio values between 0.9 and 1.05). This indicates that in static mode, the polarity of the Cwax phase had a greater influence on sorption than in dynamic mode.

Data for the PDMS–Car fiber showed that large and less volatile compounds were affected by the sampling mode. AcBu, pXyl, and EtBenz were retained in the static mode at approximately half of what it was before. Other compounds showed the same effect but to a lesser extent. Only Ac and DiClMe presented the same affinities with the fiber. After 150 min of sampling, four compounds were released, three were stable (between 120 and 150 min), and four were always adsorbing. This is the same process that occurs in the dynamic mode, even though fewer compounds with good affinities for the coating are present on the fiber. Consequently, it

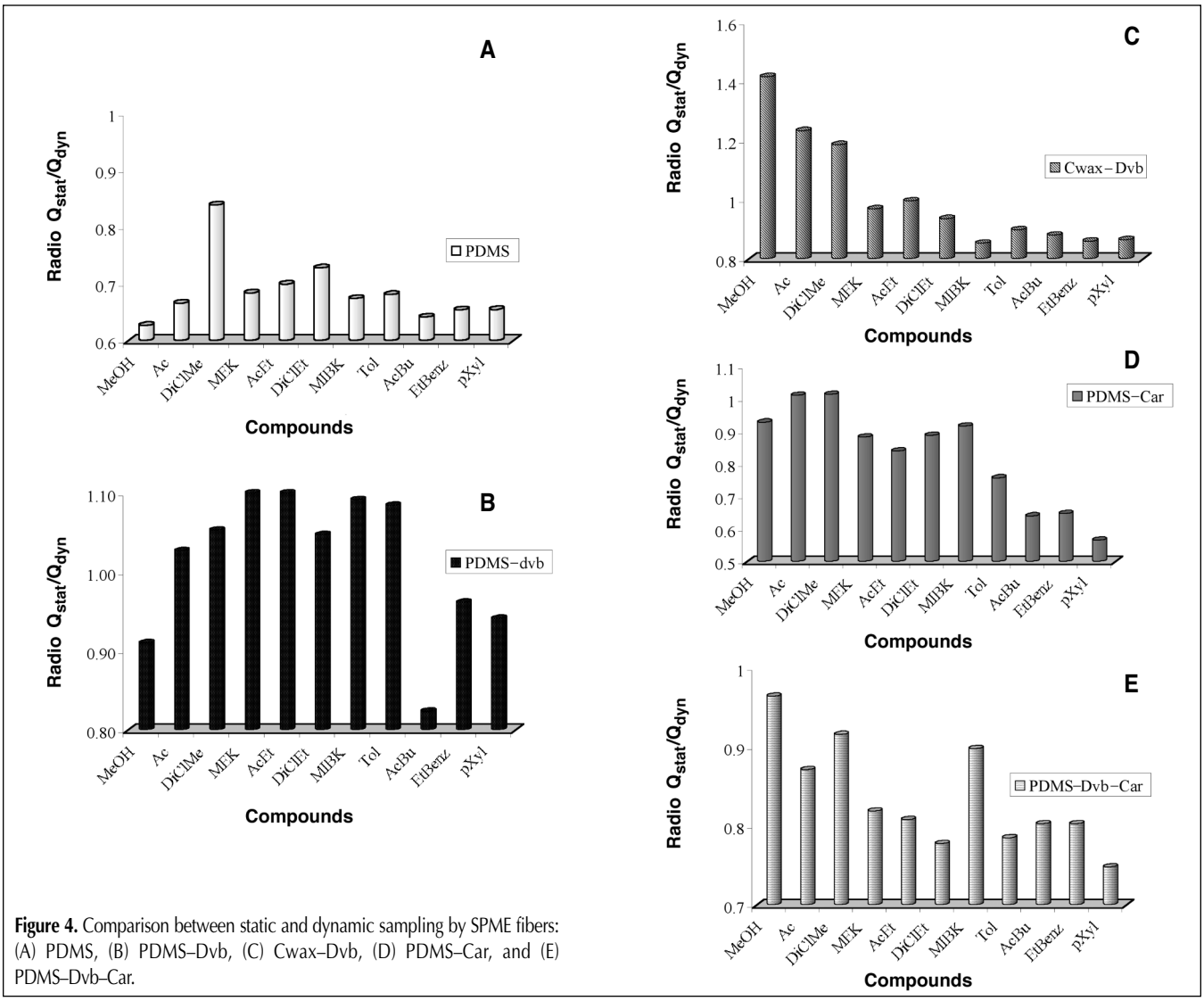

Figure 4. Comparison between static and dynamic sampling by SPME fibers: (A) PDMS, (B) PDMS–Dvb, (C) Cwax–Dvb, (D) PDMS–Car, and (E) PDMS–Dvb–Car.

is assumed that displacement effects are not only the result of competitive adsorption (limited number of adsorption sites) but also of molecular interactions.

The same study with the PDMS–Dvb–Car fiber allowed one to divide the compounds into two classes. The first one presented the Q_{stat}–Q_{dyn} ratio at approximately 0.8 and less, and the other one had the ratio at approximately 0.9 and more (MeOH, Ac, DiClMe, and MIBK). This fact is difficult to interpret or quantitatively correlate with physicochemical properties because of the heterogeneity of the involved compounds. Additionally, the diffusion through two cylindrical layers of different adsorbents is a complex process.

For all of the investigated fibers, it was observed that two calibration modes were necessary, because the response of each analyte greatly varied between the static and dynamic sampling.

Table V. Concentration Factor (F) of Different Fibers and Compounds*

F	250 µL gas	PDMS	PDMS–Dvb	PDMS–Car	PDMS–Dvb–Car	Cwax–Dvb
Ac	1	1.0	4.4	223	22	1.0
DiClMe	1	0.2	1.6	230	28	1.2
MEK	1	1.8	1.3	473	45	3.6
AcEt	1	1.9	13	599	61	4.5
DiClEt	1	0.9	11	553	60	8.3
MIBK	1	7.9	72	694	89	17
Tol	1	3.0	31	1098	110	22
AcBu	1	14.9	179	1521	321	54
EtBenz	1	8.3	111	1405	265	63
pXyl	1	9.4	125	1861	381	70
Mean chlorinated	1	0.6	6.5	391	44	4.8
Mean ketones	1	3.6	26	463	52	7.1
Mean esters	1	8.4	96	1059	191	29
Mean aromatics	1	6.9	89	1454	252	52
Mean	1	5	50	789	126	22

* $F = Q_f / Q_a$.

Table VI. SPME Fiber Repeatability* and the Dynamic and Static Modes

	PDMS (*t* = 5 min)		PDMS–Dvb (*t* = 15 min)		Cwax–Dvb (*t* = 15 min)		PDMS–Car (*t* = 90 min)		PDMS–Dvb–Car (*t* = 60 min)	
Analysis	**Static**	**Dynamic**	**Static**	**Dynamic**	**Static**	**Dynamic**	**Static**	**Dynamic**	**Static**	**Dynamic**
MeOH	5.7	33.3	12.5	16.6	9.8	7.0	13	20.4	10.7	8.4
Ac	10.0	14.4	1.7	7.5	5.0	11.4	4.7	4.1	4.3	2.5
DiClMe	13.5	1.1	8.6	9.0	4.2	13.3	6	7.3	4.0	1.4
MEK	12.4	2.2	1.6	4.3	4.6	7.4	4.8	3.7	2.1	3.1
AcEt	11.9	1.0	3.0	4.0	4.4	6.8	4.8	4.0	2.2	3.2
DiClEt	8.0	2.1	3.6	4.2	5.9	7.2	5.4	3.3	1.9	3.0
MIBK	9.0	0.8	1.4	1.8	3.9	4.4	7.5	2.2	2.9	2.2
Tol	7.7	2.3	3.4	1.7	4.2	4.9	5.3	2.1	0.9	2.5
AcBu	8.3	0.5	5.7	3.3	4.2	4.1	8.8	2.9	5.9	2.5
EtBenz	5.8	3.5	3.5	1.3	4.6	4.5	8.8	2.6	5.1	2.2
pXyl	5.8	5.4	4.2	2.2	4.7	4.5	9.7	2.9	6.4	2.2
Mean	8.9	6.1	4.5	5.1	5.1	6.9	7.1	5.0	4.2	3.0

* $n = 3$, concentration = 40 µmol/m^3.

Fibers concentration factor

The ability of each fiber to concentrate trace VOCs was evaluated at the equilibrium time (90 min for PDMS–Car) for dynamic sampling. It should be noted that for PDMS–Dvb, Cwax–Dvb, and PDMS–Car, the equilibrium time does not correspond to the maximum sensitivity of all the compounds, because of competitive adsorption.

The concentration factor (F) corresponding to each couple fiber/compound was calculated. F is the ratio between the quantity of analytes fixed onto a fiber exposed to the equimolar gas mixture (Q_f) and the theoretical quantity of analytes in 250 µL of the same air injected with a gas sampling valve in a GC (Q_a) (all of the values are presented in Table V). Overall, the PDMS–Car fiber presented the highest concentration factors, followed by PDMS–Dvb–Car, PDMS–Dvb, Cwax–Dvb, and PDMS. F shows that the PDMS fiber does not concentrate DiClMe and DiClEt (MeOH was not considered because of an interfering peak present on the chromatogram).

The static mode (as demonstrated in Figure 4) will exhibit concentration factors very close to those for dynamic sampling. The greatest difference was noticed for pXyl when sampling with PDMS–Car (F = 1042 instead of 1861 for dynamic sampling). In terms of the limits of detection, the same order of magnitude will be reached for these two modes.

Repeatability

Relative standard deviations were determined at equilibrium (90 min for the PDMS–Car fiber) for both sampling modes (results are shown in Table VI). They were satisfactory in dynamic sampling as well as in static sampling. Differences between the RSDs for these two sampling modes were not obvious, except for PDMS and PDMS–Car fibers, which performed better in dynamic mode. Ac and methylene chloride both individually presented the biggest RSDs. An interfering peak was detected at the retention time of MeOH (2.7 min) during the SPME injections, which explains the high RSDs for this compound. The RSDs were considered to be low enough to consider an analytical development of this sampling method. The average RSD was always less than 9% (most were less than 5%).

Conclusion

The potential of SPME fibers for sampling VOCs in air were confirmed. The sampling time varied from 5 min with the PDMS fiber to more than 120 min with PDMS–Car. SPME fibers could sample a wide range of concentrations and compounds, because of the variety of available coatings. PDMS presented the poorest concentration factor, whereas PDMS–Car was the most efficient. Generally, the adsorbent-based SPME fiber was found to be more sensitive than PDMS, but competitive adsorption occurred, which limited the possibility of quantitative analysis. The first approximation of the limits of detection in the dynamic mode could range from 1–3 ng/m^3 to 1–3

mg/m^3, depending on the compound and fiber used. Dynamic and static sampling (representative of different field sampling conditions) gave different concentration factors for a given compound, meaning that several SPME calibration procedures were necessary.

These facts are general guidelines that have to be completed in order to provide an accurate measurement method for trace VOCs in air.

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References

1. P. Le Cloirec. *Les Composés Organiques Volatils dans l'Environnement*, 1st ed. Lavoisier Tec & Doc, Paris, France, 1998, pp. 10–11.
2. T. Sebo and N. Onda. Analysis of VOCs in air by automated tube sampling and thermal desorption GC–MS. *Anal. Sci.* **13:** 437–42 (1997).
3. J.L. Wang, S.W. Chen, and C. Chew. Automated GC with cryogenic/sorbent trap for the measurement of volatile organic compounds in the atmosphere. *J. Chromatogr. A* **863:** 183–93 (1999).
4. J. Pawliszyn. *Solid Phase MicroExtraction: Theory and Practice*, 1st ed. Wiley-VCH, New York, NY, 1997, pp. 1–247.
5. I. Valor, C. Cortada, and J.C. Molto. Direct solid phase microextraction for the determination of BTEX in water and wastewater. *J. High Resolut. Chromatogr.* **19:** 472–74 (1996).
6. K.D. Buchholz and J. Pawliszyn. Optimization of solid phase microextraction conditions for determination of phenols. *Anal. Chem.* **66:** 160–67 (1994).
7. M. Chai, C.L. Arthur, and J. Pawliszyn. Determination of volatile chlorinated hydrocarbons in air and water with solid phase microextraction. *Analyst* **118:** 1501–1505 (1993).
8. A.A. Boyd-Boland, S. Magdic, and J. Pawliszyn. Simultaneous determination of 60 pesticides in water using solid phase microextraction and gas chromatography–mass spectrometry. *Analyst* **121:** 929–38 (1996).
9. R.E. Shirey. Rapid analysis of environmental samples using solid phase microextraction (SPME) and narrow bore capillary columns. *J. High Resolut. Chromatogr.* **18:** 495–99 (1995).
10. F.J. Sanlos, M.N. Sarrion, and M.T. Galceran. Analysis of chlorobenzenes in soils by headspace solid phase microextraction and gas chromatography–mass spectrometry. *J. Chromatogr. A* **771:** 181–89 (1997).
11. Y. Yang, S.B. Hawthorne, D.J. Miller, Y. Liu, and M.L. Lee. Adsorption versus absorption of polychlorinated biphenyls onto solid phase microextraction. *Anal. Chem.* **70:** 1866–69 (1998).
12. M. Mestres, O. Busto, and J. Guasch. Headspace solid phase microextraction analysis of volatile sulphides and disulphides in wine aroma. *J. Chromatogr. A* **808:** 211–18 (1998).
13. M. Chai and J. Pawliszyn. Analysis of environmental air samples by solid phase microextraction and gas chromatography/ion trap mass spectrometry. *Environ. Sci. Technol.* **29:** 693–701 (1995).
14. C.L. Arthur, L.M. Killam, K.D. Buchholz, J. Pawliszyn, and J.R. Berg. Automation and optimization of solid phase microextraction. *Anal. Chem.* **64:** 1960–66 (1992).
15. C. Grote and J. Pawliszyn. Solid phase microextraction for the analysis of human breath. *Anal. Chem.* **69:** 587–96 (1997).
16. F. Mangani and R. Cenciarini. Solid phase microextraction using fused silica fibers coated with graphitized carbon black. *Chromatographia* **41:** 678–84 (1995).
17. J. Namiesnik, D. Gorlo, L. Wolska, and B. Zygmunt. Analysis of selected gaseous organic micro-pollutants in air by means of solid phase microextraction–gas chromatography–mass spectrometry. Calibration problems. *Analusis* **26:** 170–74 (1998).
18. D.P. Lucero. Performances characteristics of permeation tubes. *Anal. Chem.* **43:** 1744–49 (1971).
19. A.E. O'Keefe and G.C. Ortman. Primary standards for trace gas analysis. *Anal. Chem.* **38:** 760–63 (1966).
20. P.A. Martos and J. Pawliszyn. Calibration of solid phase microextraction for air analyses based on physical chemical properties of the coating. *Anal. Chem.* **69:** 206–15 (1997).
21. P.A. Martos and J. Pawliszyn. Time-weighted average sampling with solid phase microextraction device: implications for enhanced personal exposure monitoring to airborne pollutants. *Anal. Chem.* **71:** 1513–20 (1999).
22. L. Tuduri, V. Desauziers, and J.L. Fanlo. Determination of absolute amount extracted by SPME: different approaches under examination. *J. Microcol. Sep.* **12:** 550–57 (2000).
23. J.V. Hinshaw. The effects of inlet liner configuration and septum purge flow rate on discrimination in splitless injection. *J. High Resolut. Chromatogr.* **16:** 247–53 (1993).
24. A. Kaufmann. Maximum transfer condition for splitless injection. *J. High Resolut. Chromatogr.* **20:** 193–200 (1997).
25. T. Górecki, X. Yu, and J. Pawliszyn. Theory of analyte extraction by selected porous polymer SPME fibres. *Analyst* **124:** 643–49 (1999).
26. T. Górecki, P. Martos, and J. Pawliszyn. Strategies for the analysis of polar solvents in liquid matrices. *Anal. Chem.* **70:** 19–27 (1998).
27. C.L. Arthur, L.M. Killam, S. Motlagh, M. Lim, D.W. Potter, and J. Pawliszyn. Analysis of substituted benzene compounds in groundwater using solid-phase microextraction. *Environ. Sci Technol.* **26:** 979–83 (1992).
28. J.R. Dean, W.R. Tomlinson, V. Makovskaya, R. Cumming, M. Hetheridge, and M. Comber. Solid-phase microextraction as a method for estimating the octanol–water partition coefficient. *Anal. Chem.* **68:** 130–33 (1996).
29. Molecular Analysis Pro and the solvent database software, Version 2.32. Available at http://www.windowchem.com.

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