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Dynamic versus static sampling for the quantitative analysis of volatile organic compounds in air with polydimethylsiloxane–Carboxen solid-phase microextraction fibers

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Abstract

Polydimethylsiloxane–Carboxen solid-phase microextraction fibers are now well known to be very efficient trapping media for the analysis of volatile organic compound (VOC) traces in air. However, competitive adsorption, due to the nature of the coating, considerably limits analyte quantitation. In this contribution, different experimental conditions are investigated to achieve quantitative analysis. Static and dynamic sampling were compared for the analysis of 11 VOCs in a standard gaseous mixture at different extraction times (1, 5, 15 and 45 min). The same experiments were performed with four isolated compounds. Adsorption results from gas mixture and isolated compounds were compared and a common linear range (i.e., where quantitative analysis is conceivable) was determined. When sampling was in the dynamic mode, compounds with lower affinity for the coating showed a very narrow linear range, meaning that competition for adsorption was quickly discriminative. The same experiments in static mode allowed one to obtain wider linear ranges for all compounds, especially for lower-affinity compounds: for a 1 min sampling time, acetone showed a linear adsorption range from 3 to 60 $\mu g\ m^{-3}$ in the dynamic mode which extended from 5 to 300 $\mu g\ m^{-3}$ in the static mode.

Keywords: Solid-phase extraction; Air analysis; Volatile organic compounds

1. Introduction

Volatile organic compounds (VOCs) are of environmental interest because they can be responsible for health hazards or malodorous atmospheres [1]. As a consequence, they must be determined at very low levels, in indoor air as well as outdoor air, which represents a challenging task. This can be achieved using conventional air sampling methods [2–4], i.e., sorbent tubes, canisters or cryogenic trapping. These techniques require the use of specific and expensive analytical equipment, and are time consuming.

Solid-phase microextraction (SPME) could become an alternative in the analysis of VOCs in air. It combines sampling and preconcentration in one step and is directly introduced into a heated gas chromatograph injection port for thermal desorption and transfer to the column. SPME has been extensively used in environmental applications (soils [5], water [6,7] plants [8]) and food analysis (beverages [9], meat [10]). However, this technique has been tested to a lesser extent in air analysis. The first experiments in this area were performed in the static mode [11,12] and dealt with sampling of volatile chlorinated hydrocarbons and aromatic compounds.

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The SPME fiber phase for these studies was polydimethylsiloxane (PDMS). Then dynamic sampling was performed by Namiesnik and co-workers. They particularly studied a PDMS SPME calibration procedure and applied their laboratory investigation to sample air from a student chemical laboratory [13], an indoor swimming pool [14] and a newly renovated flat [15]: the presence of benzene, toluene, ethylbenzene and xylenes (BTEXs), hydrocarbons, chlorinated hydrocarbons and chlorinated aromatic compounds was reported. Martos and co-workers [16,17] sampled a mixture of hydrocarbons and aromatic compounds with a PDMS SPME device and developed a calibration-free procedure for quantitative analysis.

Considering the nature of the SPME fiber for air sampling, it could be observed in the literature that the most commonly used coating is PDMS. This is because PDMS extracts analytes via absorption, and is not prone to competitive adsorption processes. The calibration procedure is simple, without any problems due to matrix effects. Nevertheless, for the most volatile molecules, PDMS suffers from low recoveries. A fiber coating comparative study [18] stated that PDMS–CAR (Carboxen) showed the highest recoveries among PDMS, PDMS–DVB (divinylbenzene), PDMS–DVB–CAR and CW (Carbowax)–DVB. But competitive adsorption and displacement effects limited the use of adsorptive SPME coatings. Gorecki et al. developed an equilibrium theory for the PDMS–DVB fiber [19] and Semenov et al. described a single compound adsorption kinetics onto this porous SPME fiber [20]. Then, air sampling was initiated and better apprehended.

Koziel et al. presented a diffusion-controlled extraction theory [21]. Very short sampling times and nonequilibrium conditions were used to avoid competitive adsorption. To support their theory, quantitative analysis of BTEXs in the air of a residential house, a chemical store or a vehicle shop [22–24] was performed. Good agreement was found between the SPME method and the validated reference National Institute for Occupational Safety and Health (NIOSH) 1501 method.

Even if air sampling with porous SPME fiber is expanding, there is still a lack in the investigated chemical families with adsorptive fibers. BTEX sampling has been performed, as well as derivatized formaldehyde, hydrocarbons or chlorinated hydrocarbons [22,23,25]. For other VOCs, and more especially solvents, a few references are available [26]. Moreover, for controlled atmospheres, like showcases in museum or clean rooms, where air pollutants levels are nearly constant, specific sampling conditions can be developed for routine control.

The aim of this work was therefore to widen the scope of air analysis with SPME, by studying different sampling strategies for a wide range of VOCs (methanol, esters, ketones, aromatic compounds, small chlorinated hydrocarbons). The PDMS–CAR fiber was used in static sampling as well as in dynamic sampling, in order to see if the previously reported differences in adsorption for these two modes [18] were exploitable. It was performed on a gaseous equimolar mixture and for isolated compounds. Calibration curves were plotted for various sampling times to find the best compromise limit of detection/linearity range. The differences between these two sampling modes, in terms of limit of detection, linearity range and adsorption preferences were stated.

2. Experimental

2.1. Chemicals and reagents

The studied VOCs were methanol (MeOH), acetone, dichloromethane (DCM), methyl ethyl ketone (MEK), ethyl acetate, (EtOAc), dichloroethane (DCE), methyl isobutyl ketone (MIBK), toluene (Tol), butyl acetate (BuOAc) purchased from Carlo Erba (Milan, Italy), and ethyl benzene (EtBenz), *p*-xylene (pXyl) supplied by Acros (Geel, Belgium). All these reagents were at least 99% purity. A liquid equimolar mixture was prepared with these 11 solvents. It was used in a syringe pump delivery system for generating the standard atmospheres. The standard gas generation system was previously described in a recent article [18].

Standard solutions for liquid calibration were prepared by dissolving different amounts of the VOC mixture in *n*-butanol (BuOH) of analytical grade (99.8% purity, Carlo Erba). *n*-Butanol was chosen for its low vapor volume [27]. Standard solutions

were in the range 0.5–100 mmol l^{-1} 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.

2.2. Instrumentation

2.2.1. Chromatography

A Hewlett-Packard (HP) 6890 Plus gas chromatograph (HP, Little Falls, DE, USA) equipped with a split/splitless injection port and a flame ionization detection (FID) system was used for GC analysis. The split/splitless injection port was equipped with a 0.75 mm I.D. liner and operated at 270 °C for liquid injections and 320 °C for SPME injections with the purge valve closed for 150 s. The carrier gas was helium with a flow-rate of 2.5 ml min^{-1}. Chromatographic separations were performed using a Hewlett-Packard HP-1 column (100% polydimethylsiloxane), 50 m×0.32 mm I.D., 1.05 μm film thickness, and the oven temperature was programmed as follows: 40 °C for 1 min, then ramped at 15 °C min^{-1} to 90 °C, held for 4 min, and ramped at 10 °C min^{-1} to 120 °C. The FID temperature was 250 °C. Signals were collected and recorded with HP 3398A software.

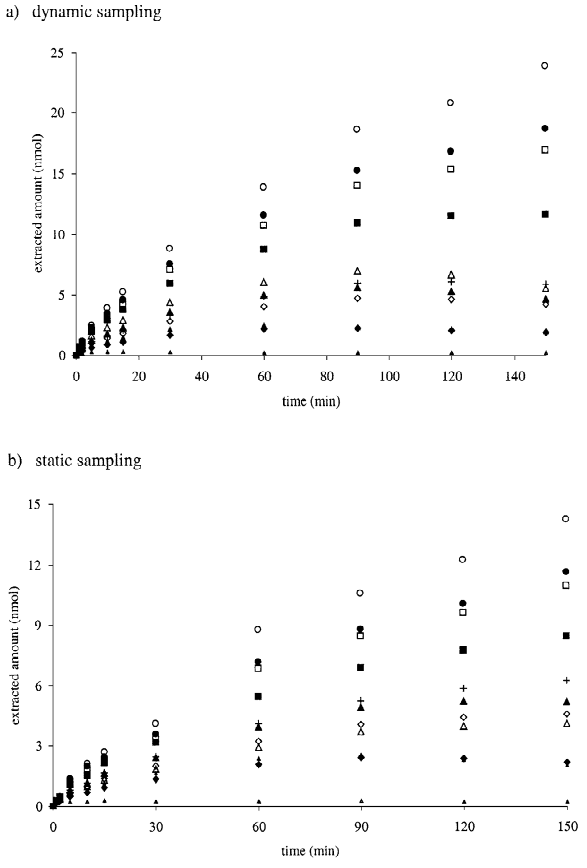

Fig. 1. Extraction time profile for PDMS–CAR SPME fibers. C = 40 μmol m^{-3} each compound. (a) Dynamic sampling, (b) static sampling. ▲=MeOH; ♦=acetone; ▲=DCM; ◇=MEK; +=EtOAc; ▲=DCE; △=MIBK; ■=Tol; ●=BuOAc; □=EtBenz; ○=pXyl.

2.2.2. Solid-phase microextraction

A manual SPME holder was used with a 75 μm PDMS–CAR fiber type purchased from Supelco (Bellefonte, PA, USA). The SPME fibers were conditioned in the GC injection port at 280 °C, for 5 h.

3. Results and discussion

3.1. Extraction time profile

Kinetics demonstrated that equilibrium was not reached after 150 min, for both sampling modes (Fig. 1). Carboxen is an adsorbent containing approximately 1/3 macropores, 1/3 mesopores and 1/3 micropores, which explained the slow mass transfer of analytes. The affinity order of the molecules for the fiber was identical in the two sampling modes: a first group, with butyl acetate, *p*-xylene and ethylbenzene, which are the most adsorbed molecules, followed by toluene, MIBK, ethyl acetate, dichloroethane and MEK, and the less extracted analytes, acetone, methylene chloride and methanol.

In the dynamic mode, the extracted amount of methanol reached a maximum after a 15 min exposure to the polluted atmosphere and then was desorbed from the fiber. Displacement effects were also noticed for six other compounds (acetone, methylene chloride, MEK, ethyl acetate, dichloroethane and MIBK), between 60 and 120 min. In static sampling, the adsorption profile was identical for methanol. For acetone and methylene chloride, displacement effects

occurred between 90 and 120 min. Other compounds from the mixture reached equilibrium (MIBK, MEK, dichloroethane, ethyl acetate) or were always adsorbing at 150 min (*p*-xylene, ethylbenzene, butyl acetate and toluene). Extracted amounts of analytes were lower for the static mode, affecting especially compounds having high affinity for the coating. A previous study of adsorption kinetics [18] showed that dynamic adsorption at 90 min was correlated to the molecular volume: the bigger the molecular volume, the better the adsorption. Static sampling could be a good alternative to favor adsorption of low-affinity compounds (i.e., small molecular volume) because they are less sensitive to air movement, leading to a better mass transfer from the sample to the outer surface of the PDMS–CAR fiber than the high-affinity compounds. These facts were related to a long sampling time, near the thermodynamic equilibrium. For short sampling times, discrimination is less likely to occur. SPME fiber is not saturated and molecular interactions are lessened. Then, combination of short sampling times and static sampling with PDMS–CAR could avoid discrimination of the small molecules. Fig. 2 supports this assumption. Ratios of extracted amounts, acetone (low-affinity compound)/pXyl (highest-affinity compound) and DCE (medium-affinity compound)/pXyl were plotted in dynamic and static modes for several sampling times. They were higher in the first 10 min period and then tended to be stable thereafter for both sampling modes. These ratios were nearer from the ideal value 1 [equal extracted amount (nmol) for each molecule] for the static sampling mode, which confirmed that the lowest-affinity compounds were less discriminated at short static sampling times. For example, at 1 min sampling time, the acetone/pXyl static ratio is up 70% on the dynamic ratio (40% for DCE).

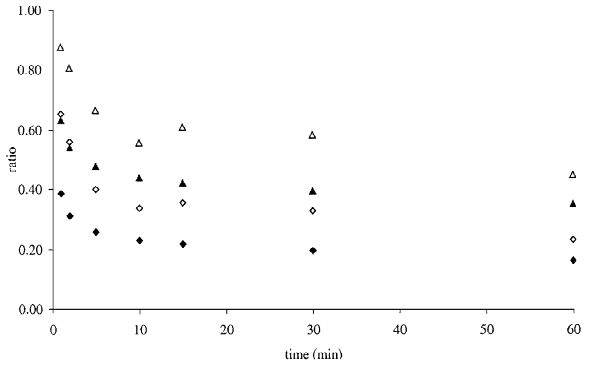

Fig. 2. Ratio of extracted amount, acetone/pXyl (♦ and ◇) and DCE/pXyl (▲ and △), for static (◇ and △) and dynamic (♦ and ▲) sampling at different sampling times in the equimolar gaseous mixture.

3.2. Calibration curves

Calibration curves were plotted for four sampling times, 1, 5, 15 and 45 min and for both sampling modes. The equimolar gaseous mixture was sampled, as well as four isolated compounds (acetone, dichloroethane, toluene and butyl acetate). The studied concentration range was 0.05–50 μmol m^{-3}, i.e., 0.0029–2.9 mg m^{-3}, 0.0049–4.9 mg m^{-3}, 0.0046–4.6 mg m^{-3} and 0.0058–5.8 mg m^{-3} for acetone, dichloroethane, toluene and butyl acetate, respectively. Ten concentrations were studied (0.05, 0.1, 0.25, 0.5, 1, 2.5, 5, 10, 25 and 50 μmol m^{-3}). The calibration curves corresponding to one compound in the two situations (mixture and isolated) were compared in order to detect matrix effects on linearity range and sensitivity (slope). They were called identical when they were fulfilling three conditions: acceptable correlation coefficients (r^2>0.95, no replicate), *y*-axis intercept close to 0 and similar slopes. This way, calibration curves obtained for isolated compounds could be used to quantify the specific standard gaseous mixture. By extension, quantitation of unknown air samples could be done using this single compound calibration curve, before matrix effects appeared. Table 1 sums up the results. The lower linear range limit is not representative of the limit of detection (LOD) but only of the lowest sampled concentrations. LODs will be determined later in this article.

3.2.1. Dynamic sampling

For long sampling times, i.e., 15 and 45 min, the common linear range was not exceeding 0.05–2.5 μmol m^{-3} for toluene and butyl acetate (or 4.6–230 and 5.8–290 μg m^{-3}, respectively). Even for these compounds with good affinity for the coating, the calibration line was quickly curving. This can be

Table 1
Linearity range for different sampling conditions

Compound	Calibration curve parameters	Matrix	Sampling conditions (time, mode)							
			1 min		5 min		15 min		45 min	
			Static	Dynamic	Static	Dynamic	Static	Dynamic	Static	Dynamic
Acetone	Linearity range (μmol m^{-3})	Isolated	0–50	0–5	0–50	0–2.5	0–25	0–0.25	0–5	0–0.5
		Mixture	0–5	0–1	0–2.5	0–1	0–2.5	0–0.25	0–1	0–0.25
	Equation	Isolated	$q=0.0056C+0.0011$	$q=0.0265C+0.0018$	$q=0.0216C+0.0023$	$q=0.0913C+0.0072$	$q=0.0486C+0.0044$	$q=0.2894C+0.0112$	$q=0.1303C+0.0012$	$q=0.5534C+0.0191$
		Mixture	$q=0.0062C+0.0033$	$q=0.0273C+0.0010$	$q=0.0200+0.0083$	$q=0.0937C+0.0052$	$q=0.0452C+0.0104$	$q=0.2753C+0.0047$	$q=0.1480C+0.0017$	$q=0.5446C+0.0051$
Dichloroethane	Linearity range (μmol m^{-3})	Isolated	0–50	0–10	0–50	0–5	0–10	0–5	0–10	0–0.5
		Mixture	0–10	0–2.5	0–10	0–2.5	0–5	0–2.5	0–5	0–0.25
	Equation	Isolated	$q=0.0062C+0.0004$	$q=0.0291C+0.0000$	$q=0.0261C+0.0037$	$q=0.1201C+0.0097$	$q=0.0716C-0.0015$	$q=0.2928C+0.0243$	$q=0.1666C+0.0027$	$q=0.9691C-0.0107$
		Mixture	$q=0.0063C+0.0019$	$q=0.0307C+0.001$	$q=0.0248C+0.0074$	$q=0.1212C+0.0086$	$q=0.0677C+0.0124$	$q=0.2753+0.0047$	$q=0.1483C+0.0025$	$q=1.0556C-0.0028$
Toluene	Linearity range (μmol m^{-3})	Isolated	0–50	0–10	0–50	0–10	0–25	0–5	0–25	0–2.5
		Mixture	0–10	0–2.5	0–5	0–2.5	0–5	0–2.5	0–5	0–1
	Equation	Isolated	$q=0.0073C-0.0008$	$q=0.0377C+0.0013$	$q=0.0351C+0.0057$	$q=0.1616C+0.0084$	$q=0.0859C-0.0097$	$q=0.4229C+0.0252$	$q=0.2131C-0.0052$	$q=1.1712C+0.0472$
		Mixture	$q=0.0063C+0.0020$	$q=0.0381C+0.0007$	$q=0.0295C+0.0070$	$q=0.1658C+0.0068$	$q=0.0784C+0.0199$	$q=0.4134C+0.0266$	$q=0.1988C+0.0435$	$q=1.1211C+0.0464$
Butyl acetate	Linearity range (μmol m^{-3})	Isolated	0–50	0–2.5	0–50	0–10	0–25	0–2.5	0–5	0–2.5
		Mixture	0–5	0–2.5	0–2.5	0–2.5	0–2.5	0–2.5	0–1	0–1
	Equation	Isolated	$q=0.0081C-0.0001$	$q=0.0342C+0.0016$	$q=0.0327C+0.0069$	$q=0.1795C+0.0080$	$q=0.0926C+0.0154$	$q=0.4832C+0.0084$	$q=0.3067C+0.0175$	$q=1.3404C+0.0174$
		Mixture	$q=0.0089C-0.0003$	$q=0.0381C+0.0009$	$q=0.0403C+0.0004$	$q=0.1813C+0.0109$	$q=0.1053C+0.0014$	$q=0.4562C+0.02$	$q=0.3414C+0.0075$	$q=1.3152C+0.0155$

q = extracted amount of compounds (nmol), C = gaseous concentration (μmol m^{-3}).

related to the Carboxen saturation because of the complex matrix, associated with long sampling times. For 1 and 5 min sampling times, the common linear range was not enhanced, even though the calibration curves for isolated compounds were straight lines for a wider range of concentrations (0.05–10 μmol m^{-3}, or 4.6–920 μg m^{-3} and 5.8–1160 μg m^{-3} for toluene and butyl acetate, respectively).

Acetone and dichloroethane showed a narrower linear range whatever the sampling time was. For acetone, the best compromise sensitivity/linear range was obtained with a sampling time of 5 min (identical linear range with 1 min sampling, 2.9–58 μg m^{-3}, better sensitivity). The calibration curve for dichloroethane was linear over the 4.9–245 μg m^{-3} range for the complex matrix at 5 min sampling time.

In conclusion, even for high-affinity compounds and short sampling times, the obtained common linear ranges were not wide, limiting the use of PDMS–CAR SPME fibers for quantitative analysis of VOC traces (sub-μg m^{-3} to mg m^{-3}) in air. Therefore, dynamic sampling is not suitable for sampling complex air matrices. Actually, a long preliminary development phase would be necessary to sufficiently characterize effluents before realizing quantitative analysis to ensure that measured concentrations are in the linear concentration range.

3.2.2. Static sampling

The butyl acetate linear range was enhanced when sampled alone. It was quantifiable up to 2.9 mg m^{-3} at 45 min and 5.8 mg m^{-3} at 1 min. It was quantifiable in the complex mixture up to 0.56 mg m^{-3} (1 min).

Even if static sampling favored low-affinity compounds, Toluene also showed an enhanced common linear range at long sampling times (92–460 μg m^{-3}, 15 min sampling), because the fiber was less loaded. A fourfold gain in linearity range at the 1 min sampling time was achieved when compared to dynamic sampling (4.6–920 μg m^{-3} vs. 4.6–230 μg m^{-3}).

The common linear range was improved for dichloroethane for each sampling time. Alone, it was quantifiable up to 0.98 mg m^{-3} for sampling times from 15 to 45 min and up to 4.9 mg m^{-3} for shorter times (1 or 5 min). In the gaseous equimolar mixture, the common linear range raised to 0.98 mg m^{-3} (1, 5 min sampling time) a fourfold gain compared to dynamic sampling.

The linearity range for acetone was amplified for each sampling time and matrix in static sampling. If acetone was alone in air, it could be quantified up to 2.9 mg m^{-3} and up to 0.29 mg m^{-3} if other compounds were present (1 min sampling). The greatest increase (factor of 20) in linear range was obtained for the 5 min sampling time, with acetone alone.

3.2.3. Experimental limitations

The reported results suffered from experimental limitations. To be as accurate as possible in reporting the common linear range, one single fiber should be used for a set of experiments, because reproducibility of the fiber (10% in diameter, reported by Supelco) could affect comparison. If responses of sampled compounds need to be compared alone and in mixture, experiments must be done with the same fiber. In our case, it means that, in static sampling for example, 10 mixture concentrations were sampled at four different sampling times, leading to 40 sampling/thermal desorption cycles. Then four single compounds were also sampled, at four different sampling times and 10 concentrations, which means that 200 sampling/thermal desorption cycles were performed in static sampling. In general, less or more 100 cycles are recommended by the manufacturer as the upper limit of use, even if, to the best of our knowledge, nothing has been published to clarify SPME fiber capabilities. Then, reported results could be affected by variability in the PDMS–CAR adsorption capacities.

Because studies with one fiber are limited by the number of sampling/thermal desorption cycles, sampled concentrations have to be well defined. Here is reported an overview of PDMS–CAR applicability for VOC traces. These data should be used as a starting point to mark out the field of investigation in VOC traces analysis with a PDMS–CAR SPME fiber.

3.3. Repeatability

Repeatability, expressed as relative standard de-

Table 2
Repeatability of the sampling process and limits of detection

Compound	Sampling conditions (time, mode)							
	LOD ($\mu g\ m^{-3}$)				Repeatability (%)			
	1 min		45 min		1 min		45 min	
	Static	Dynamic	Static	Dynamic	Static	Dynamic	Static	Dynamic
MeOH					15.3	12.2	10.7	3.5
Acetone	4.7	3.3	1.7	0.4	8.4	6.7	5.4	2.1
DCM					8.3	9.2	7.9	2.2
MEK					4.1	6.9	5.0	3.4
EtOAc					4.6	7.4	6.5	4.5
DCE	5.0	5.7	0.6	0.3	5.0	8.1	6.8	3.4
MIBK					5.5	9.1	10.6	4.5
Tol	2.0	1.2	0.1	0.6	6.6	8.7	10.0	4.3
BuOAc	2.6	1.3	0.3	0.9	7.8	10.7	10.6	4.4
EtBenz					6.5	11.1	11.0	3.9
pXyl					6.3	11.7	11.2	4.4

RSDs: Based on triplicates, performed on the equimolar mixture ($C = 40\ \mu mol\ m^{-3}$ each compound). $LOD = 3.3\sigma/s$ ($\mu g\ m^{-3}$), where: σ is the standard deviation of the response near the limit of detection (=1 min static: 0.1 $\mu mol\ m^{-3}$; 1 min dynamic: 0.05 $\mu mol\ m^{-3}$; 45 min, static and dynamic: 0.01 $\mu mol\ m^{-3}$) and s is the slope of the calibration curve near the limit of detection.

viation (RSD) was determined for each sampling time and each compound of the mixture (Table 2). For clarity, data resulting from 5 and 15 min sampling times are not included in Table 2 (available on request). For 5, 15, 45 min sampling times, RSDs were better for dynamic sampling for all involved compound. For 1 min, results were slightly better for the static mode, excepted methanol, acetone and methylene chloride. It is pointed out that, even for 1 min sampling time, when analyte uptake rates are maximum (adsorption kinetics rise rapidly), RSDs were still satisfactory.

Globally, RSDs were all reasonably low enough to develop quantitative analysis methods.

3.4. Limit of detection

The chosen determination method for the LOD was advised by the International Conference on Harmonization (ICH) [28]. The definition is:

$$LOD = 3.3\sigma/s \quad (1)$$

where σ is the standard deviation of the response near the limit of detection (six replicates) (1 min static: 0.1 $\mu mol\ m^{-3}$; 1 min dynamic: 0.05 $\mu mol\ m^{-3}$; 45 min, static and dynamic: 0.01 $\mu mol\ m^{-3}$) and s is the slope of the calibration curve near the limit of detection.

Among all possible determinations, this one was selected because the slope of the calibration curve was present in the definition. Then, the LOD, and consequently the limit of quantification (LOQ = 3LOD) value was connected to the SPME calibration process, a key parameter for quantitative analysis. Obtained values could be then theoretically realistic. One possible drawback was to generate sufficiently low VOC concentrations to determine the LOD. As the generated concentrations were not small enough, the standard deviation increased, leading to overestimation of the LOD. Limits of detection (1 and 45 min) are reported in Table 2.

Acetone presented a limit of detection around the $\mu g\ m^{-3}$ level, with an obvious difference for 45 min sampling between static and dynamic sampling. 0.4 $\mu g\ m^{-3}$ could be detected in the dynamic mode. For 1 min sampling, the LOD was similar. Dichloroethane showed a better LOD at 45 min sampling than acetone and a worse one at 1 min, for both sampling modes, meaning that acetone was less discriminated for the 1 min sampling time.

Overestimation of the LOD appeared for butyl acetate and toluene in dynamic sampling at 45 min sampling. The laboratory-made standard gas generat-

ing device was not able to produce rigorously sufficiently low concentrations, i.e., 0.002 μmol m^{-3} (or 0.180 and 0.230 μg m^{-3} for toluene and butyl acetate, respectively). Then, the reported value was biased by a factor of 7–8. Nevertheless, hundreds of ng m^{-3} could be easily detected at 45 min and a few μg m^{-3} at 1 min. The loss in sensitivity between static and dynamic sampling for 1 min was poor for the high-affinity compounds, meaning that favoring low-affinity compounds was not overpenalizing high-affinity compounds.

4. Conclusion

Because of the displacement effect due to competitive adsorption, quantitative analysis with a PDMS–CAR SPME fiber is a challenging task. In this work, different air sampling conditions have been studied with this kind of SPME fiber, in order to avoid discrimination for adsorption between low- and high-affinity compounds. Static and dynamic sampling were studied at different times, on isolated compounds and mixtures. For each sampling conditions, a linear adsorption range was defined, where quantitative analysis was achievable. Short sampling times were beneficial to all compounds. Combined with static sampling, the low-affinity compounds were favored, i.e., the calibration curves were linear on a wider range. Dichloroethane presented a linear calibration curve between 5 and 980 μg m^{-3}, acetone between 4.7 and 300 μg m^{-3} for 1 min in static sampling. Even for these short sampling times, RSDs were good enough, and limit of detections were around the μg m^{-3} level. This work could widen the scope of air sampling with SPME, because limitations due to competitive adsorption are shown and the range of compounds of interest is expanded.

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