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Development of SPME on-fiber derivatization for the sampling of formaldehyde and other carbonyl compounds in indoor air

Delphine Bourdin · Valérie Desauziers

Abstract Solid-phase microextraction on-fiber derivatization applied to carbonyl compounds is known, but application to indoor air is poorly developed and the methods deserve to be complemented and optimized. In this work, two derivatization reagents, pentafluorophenylhydrazine and *o*-2,3,4,5,6-(pentafluorobenzyl)hydroxylamine (PFBHA), and three fiber coatings were tested in order to select the best combination. As Carboxen-based coatings were proven to induce the formation of by-products during the thermal desorption step, a polydimethylsiloxane–divinylbenzene fiber in association with PFBHA was finally chosen. The study of the derivatization kinetics showed that the reaction of PFBHA with carbonyl compounds was instantaneous, except for acetone. Analyses were performed by gas chromatography coupled with flame ionization detection and mass spectrometry. For 5 min fiber exposure, the limits of detection are below $0.5 \mu\text{g m}^{-3}$ in selected ion monitoring mode, the reproducibility was 15 % on average, and the linearity of the calibration curves was satisfactory. For on-site application, the influence of air humidity and the conditions in which the impregnated fibers were stored were studied. It is possible to store the fibers for 3 days before and for at least 2 days after sampling. The relative humidity of air was shown to have no influence on solid-phase microextraction sampling in the range from 0 to 70 %. For formaldehyde, the method was compared with sampling on 2,4-dinitrophenylhydrazine cartridges, and the

first results showed good agreement. Finally, the method was applied to three different indoor environments to check its feasibility.

Keywords Formaldehyde · Carbonyl compounds · Solid-phase microextraction · On-fiber derivatization · *o*-(2,3,4,5,6-Pentafluorobenzyl)hydroxylamine · Indoor air

Introduction

Indoor air quality has become a predominant topic in terms of public policy. In France, the “Indoor Air Quality Observatory” (OQAI) was created in 2002 and conducted many campaigns in dwellings and offices in order to have a first French indoor air overview. During the “dwellings campaign,” 20 compounds were identified as recurrent pollutants, such as formaldehyde, acetaldehyde, styrene, and benzene, toluene, ethylbenzene, and xylenes (BTEX). Of these pollutants, formaldehyde is of particular concern as it was recognized as “carcinogenic to humans” (class 1) by the International Agency for Research on Cancer and it is one of the OQAI’s ten priority substances. It is also found in almost every indoor atmosphere because of its numerous sources, such as furniture, human activity (tobacco), glues, and varnishes [1]. Even if its indoor air concentration tends to decrease with time, it usually reaches a stable level after a few years and remains significant [2–4]. A study in public places and houses in Strasbourg (France) revealed average concentrations between 3.1 and $217.1 \mu\text{g m}^{-3}$ [5]. In the USA, during a study realized in 2010 covering 200 houses, an average formaldehyde level of $21.2 \mu\text{g m}^{-3}$ was measured [3]. This pollutant is also present in specific indoor environments such as libraries, where it is the most concentrated aldehyde and where concentrations up to $105.9 \mu\text{g m}^{-3}$ were measured [6]. In France, the regulation concerning formaldehyde is evolving. The guide value for

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indoor air will be fixed at $10 \mu\text{g m}^{-3}$ for long-term exposure in 2023. Further, a decree requiring regular monitoring of indoor air quality will be applied from 2015. Among the other carbonyl compounds, acetaldehyde also belongs to the OQAI's ten priority substances and was defined as "potentially carcinogenic to humans" (class 2B) by the International Agency for Research on Cancer. Finally, hexanal is representative of wooden products and can also be found at relatively high concentrations in indoor environments (up to $106 \mu\text{g m}^{-3}$) according to the OQAI's dwelling campaign. Acetone is also one of the major contributors to the total carbonyl concentration in indoor air [7–9] and will be studied as a ketone representative compound.

A specific analytical method is necessary for formaldehyde as it has to be chemically derivatized prior to its chromatographic analysis. The standard methods involve active or passive sampling and use cartridges, badges, or tubes impregnated with 2,4-dinitrophenylhydrazine (DNPH) and a solvent extraction (NF ISO 16000-3, 2002) prior to analysis by high-pressure liquid chromatography (HPLC). This method requires pumps for on-site sampling in the case of active sampling and the use of a solvent for both extraction and HPLC. Solid-phase microextraction (SPME) could be an interesting alternative as it does not require any solvent, is easy to implement, and works like passive sampling [10]. Analytical methods based on SPME to quantify volatile organic compounds (VOCs) in air have already been developed [11, 12]. They consist, for instance, in filling a glass sampler of known volume with the air to be analyzed. The sampler is then closed and an SPME fiber is introduced into it for static extraction. SPME can then be done in either equilibrium or nonequilibrium mode [12], but the extraction times, which depend on the sample volume, can be long (3 h for a 1-L sample). These two methods were studied in our laboratory using a polydimethylsiloxane (PDMS)–Carboxen fiber and limits of detection below the microgram per cubic meter level were reached with both methods for indoor air VOCs [12].

For indoor air, these methods dedicated to screening VOCs should be complemented by the analysis of formaldehyde and other relevant carbonyl compounds. This can be performed by on-fiber derivatization [13]. The commonest reagents are *o*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) and pentafluorophenylhydrazine (PFPH) [14], and the derivatives are analyzed by gas chromatography (GC). This method has already been used for various applications, such as the analysis of aldehydes in aqueous solutions [15, 16], food industry products [17, 18], and cosmetics [19]. Some air applications were also developed for the control of workplace atmospheres [20] and exhaled breath [21], but few concerned indoor air [22]. Generally, a PDMS–divinylbenzene (DVB) SPME fiber impregnated with PFBHA is used. This SPME coating allows a lot of adsorption/desorption cycles and the desorption temperature is lower than for a PDMS–Carboxen fiber, thus

avoiding the peak tailing issue. With this method, a limit of detection of $1.23 \mu\text{g m}^{-3}$ was reached for 10 min sampling with flame ionization detection (FID). However, analysis of the SPME fiber had to be done less than 1 h after sampling. On the basis of the same principle, Pieraccini et al. [20] developed a new method to analyze indoor air glutaraldehyde by direct exposure of a PFBHA-loaded SPME fiber to ambient air. They also used a PDMS–DVB fiber coating and obtained a limit of detection of $80 \mu\text{g m}^{-3}$ with FID and $5.6 \mu\text{g m}^{-3}$ with electron capture detection for a 2-min fiber exposure. As SPME desorption is directly carried out in the injection port of the gas chromatograph, it can be easily used with a commercial portable gas GC/mass spectrometry (MS) system for on-site applications. For instance, Hook et al. [23] used SPME/GC/MS for the screening of contaminants in workplace air. Nevertheless, portable GC/MS systems are less sensitive and are not suitable for indoor air applications.

As stated above, most of the methods applied to air analysis involved PDMS–DVB fibers loaded with PFBHA, and indoor air applications are mainly focused on formaldehyde alone. Hence, the first objective of this work was to assess the efficiency of different fiber coatings and derivatization reagents to find the best compromise between analytical performances and easiness of implementation for four indoor air carbonyls: three aldehydes and one ketone. Particular attention was paid to the study of the chemical kinetics of acetone as its DNPH derivatization, which is used in the standard sampling methods, was shown to be not quantitative [24]. Then, the sampling procedure was developed on the basis of the nonequilibrium method is cited above and the performances in GC/FID and GC/MS were determined. With the aim of on-site application, the possibility to store the SPME fibers before and after extraction was studied. The influence of the relative humidity of air was also investigated, and the method was finally applied to the analysis of three different indoor environments and was compared with the standard DNPH sampling method.

Experimental

Reagents and materials

The derivatization reagents, PFBHA and PFPH, were supplied by Fluka (Buchs, Switzerland). Hexanal and acetone were purchased from Acros Organics (Morris Plains, NJ, USA) and VWR (Radnor, PA, USA), respectively. All these reagents were at least 99 % pure, except hexanal (96 %). Acetaldehyde and formaldehyde permeation tubes were provided by Metronics (Poulsbo, WA, USA). Acetonitrile (purity greater than 99.9 %) was supplied by Sigma-Aldrich (St. Louis, MO, USA).

Chromatographic analysis

GC/FID

A CP-3800 GC gas chromatograph (Varian, Les Ulis, France) equipped with a 1177 split/splitless injection port and a flame ionization detector was used. The split/splitless injection port was equipped with a 0.75 mm inner diameter liner. The injector was operated in splitless mode and the temperature was 250 °C for PDMS–DVB fibers and 320 °C for PDMS–Carboxen fibers. A 60 m×0.25 mm inner diameter Optima-5 Accent fused-silica column with 1- μ m film thickness (Macherey-Nagel, Düren, Germany) was used. The GC temperature was raised from 40 °C (4-min hold) to 90 °C at 15 °C min⁻¹ (4-min hold), then to 250 °C at 10 °C min⁻¹ (5-min hold). Helium was used as the carrier gas and the flow rate was 2 mL min⁻¹. The injector temperature was 250 °C and the injector was operated in splitless mode for the analysis of standard gases and with a ratio split of 100:1 for the analysis of pure derivatization reagents. The flame ionization detector was operated at 300 °C with gas flow rates for hydrogen, air, and helium of 30, 300, and 25 mL min⁻¹ respectively. Signals were collected and recorded with Varian Star Workstation (Varian, Les Ulis, France).

GC/MS

A Varian 3800 gas chromatograph coupled with a 1200Q quadrupole mass spectrometer (Varian, Les Ulis, France) was used for identification and quantification. The PTV 1079 injection port was equipped with a 0.75 mm inner diameter liner and was operated as for GC/FID. The carrier gas and oven temperature were the same as for the GC/FID analysis. The transfer line to the mass spectrometer was maintained at the same temperature as the final program temperature of the column. Acquisition in electron impact mode started 4 min after sample introduction. The mass range was 30–250 amu and the acquisition rate was half a scan per second. Acquisition was performed in full-scan mode or in selected ion monitoring (SIM) mode using the *m/z* 181 ion. Extracted ion chromatograms (EIC) from full-scan acquisitions were also used.

Standard gas generation device

Formaldehyde and acetaldehyde gases were generated by a permeation device designed by Calibrage (Saint Chamas, France). The permeation rates at 80 °C for formaldehyde and acetaldehyde were 649 and 678 ng min⁻¹, respectively. The permeation tubes were placed in a thermostated oven continuously swept with clean and dry air. Successive dry air dilutions of the concentrated gas were then applied to reach the desired concentrations. The system is able to generate atmospheres of formaldehyde and acetaldehyde from 0.01 to 954 μ g m⁻³ and from 0.01 to 995 μ g m⁻³ respectively.

Acetone and hexanal gases were generated with a device designed and supplied by Calibrage (Saint Chamas, France) and already described elsewhere [25]. The pure compounds were continuously injected with a syringe pump into a measured and controlled airflow. Successive dry air dilutions of this concentrated gas were then applied to reach the desired concentrations.

On-fiber derivatization

Solid-phase microextraction

SPME fused-silica fibers were used, and were coated with PDMS–DVB (65 μ m), PDMS–Carboxen (75 μ m), or PDMS–Carboxen–DVB (30/50 μ m) (Supelco, Bellefonte, PA, USA). Before use, fibers were conditioned in the injection port of the gas chromatograph at 260 °C (PDMS–DVB and PDMS–Carboxen–DVB) or 300 °C (PDMS–Carboxen) for 15 min.

Loading of fibers

Different processes were used to load the fibers with the derivatization reagents. The dry loading was performed by placing some pure reagent (5 mg of PFBHA or 3 mg of PFPH) in a 20-mL sealed headspace vial [21]. The vial was heated at 50 °C for 10 min. The SPME fibers were then exposed to the headspace vial at room temperature. The second process consisted of preparing 1 mL of an aqueous solution of PFBHA at 17 mg mL⁻¹ in a 4-mL vial [22]. The solution was stirred at 1,800 rpm for 2 min. The fibers were loaded by exposure to the headspace vial for 0.5–20 min.

Instantaneous air sampling followed by SPME

For air sampling, a 330-mL glass sampling bulb equipped with two Teflon stopcocks and a septum for fiber introduction was flushed with dry air for 10 min and then swept with the standard atmosphere or with indoor air. The bulb was then closed for SPME in static mode from 1 to 45 min. The concentrations of the different compounds ranged from 0.05 to 11.7 μ mol m⁻³. After sampling, the SPME fiber was desorbed directly into the injection port of the gas chromatograph at 250 °C (PDMS–DVB and PDMS–Carboxen–DVB) or 320 °C (PDMS–Carboxen) for 4 min.

Data analysis

The method developed is based on a nonequilibrium approach and relies, as other passive sampling techniques, on Fick's first law of diffusion (Eq. 1):

$$n_f = 2\pi D \times \frac{L}{\ln\left(b + \frac{\delta}{b}\right)} \int (C_a - C_{\text{sorb}}) dt, \quad (1)$$

where n_f is the amount of absorbed analyte on the sampler (μg), D is the diffusion coefficient of the analyte studied ($\text{cm}^2 \text{min}^{-1}$), L is the length of the fiber (cm), δ is the diffusion length (cm), b is the radius of the fiber (cm), C_a is the concentration of the analyte in air, C_{sorb} is its concentration at the air/fiber interface ($\mu\text{g cm}^{-3}$), and t the extraction time (min). At the beginning of the sampling process, C_{sorb} can be disregarded and it is assumed that the adsorbent acts as a perfect sink. Under these conditions, i.e., before equilibrium is reached, the following equation can be applied (Eq. 2):

$$n_f = UC_a t, \quad (2)$$

where $U = 2\pi D \times \frac{L}{\ln(b+\frac{\delta}{b})}$ is the uptake rate (mL min^{-1}).

This nonequilibrium approach is interesting as the extraction time can be adjusted according to the concentration expected using only a single calibration curve (Eq. 2).

Effect of air humidity on sampling

To study the influence of the relative humidity of air on SPME sampling, dry standard gases were enclosed in 250-mL glass sampling bulbs. Milli-Q water was then injected into the bulb with a 10- μL syringe, and the system was allowed to stabilize for 15 min before introduction of the fiber [12]. The injection of 1.4 μL , 2.4 μL , and 3.4 μL generated relative humidity of 30 %, 50 %, and 70 %, respectively.

Study of fiber storage

In accordance with to a method previously developed in our laboratory [26], SPME fibers were stored at room temperature (20 ± 3 °C) in Silcosteel-coated stainless tubes. A few milligrams of activated charcoal was placed inside the tubes to avoid fiber contamination.

Comparison with the DNPH standard method

This comparative study was conducted only for formaldehyde. The air samples were collected using low-volume personal pumps (SKC, USA) and 3-mL Lp-DNPH cartridges containing DNPH (Supelco, Bellefonte, PA, USA) at a flow rate of 500 mL min^{-1} . The sampling time was 3 h. The contents of the DNPH cartridges were then eluted with 5 mL of acetonitrile, and 25 μL of the solution obtained was analyzed by HPLC (Knauer, Berlin, Germany) with UV detection at 360 nm in a 10-mm cell (NF ISO 16000-3, 2002). The HPLC system was equipped with a C18-Zorbax 150 $\text{mm} \times 4.6 \text{ mm} \times 5 \mu\text{m}$ column. The mobile phase was composed of acetonitrile and water (45:55) and the flow rate was 1.3 mL min^{-1} . Quantification was done from a calibration curve obtained with standard DNPH-formaldehyde (Sigma-Aldrich, St. Louis, MO, USA).

Results and discussion

Influence of fiber's coating and desorption temperature

Three different coatings were tested: the PDMS–Carboxen fiber already used for analysis of indoor air VOCs [12], the PDMS–DVB fiber frequently used for on-fiber derivatization of aldehydes [20, 22], and the PDMS–Carboxen–DVB fiber involving a layer of DVB over a layer of Carboxen, which is supposed to combine the advantages of the two coatings. DVB and Carboxen have similar surface areas: 750 and 720 mg m^{-2} , respectively. The main difference between these two coatings is the much higher percentage of micropores in Carboxen than in DVB, which is primarily mesoporous. At first, the potential sensitivity that could be obtained with each fiber was estimated by comparing their capacities to load the two derivatization reagents. Each fiber was exposed for 1 and 30 min to a 20-mL headspace vial containing the derivatization reagent previously heated at 50 °C for 10 min [20]. We chose not to exceed 50 °C for the headspace generation because a higher temperature would prevent good adsorption of the reagents onto the fiber. This temperature is suitable for PFPH volatilization (melting point 75 °C), but is unfavorable for the generation of gaseous PFBHA (melting point 212 °C). The SPME fibers were then immediately desorbed and analyzed by GC/FID (Table 1). The quantification of the reagent adsorbed on the fibers was determined by external calibration using standard solutions in methanol.

The data in Table 1 confirm that the loading mode at 50 °C favored PFPH, which exhibited greater loaded quantities than PFBHA (from two to five times higher for PDMS–Carboxen–DVB and PDMS–DVB, respectively). For the PDMS–DVB fiber, the exposure time had no effect whatever reagent was used, suggesting that adsorption equilibrium was rapidly reached. This can be explained by the mesoporous/macroporous structure of DVB. In contrast, the rate of adsorption onto the Carboxen-containing fibers is slower, probably owing to the diffusion in micropores which would act as a limiting step.

Table 1 Quantity of derivatization reagents (nmol) loaded on different solid-phase microextraction (SPME) fibers for 1 and 30 min exposure (three replicates)

Stationary phase	PFPH		PFBHA	
	1 min	30 min	1 min	30 min
PDMS–CAR–DVB	205±45	322±42	81±8	138±62
PDMS–CAR	156±14	Not determined	40±7	91±13
PDMS–DVB	133±15	126±41	24±4	25±4

CAR Carboxen, *DVB* divinylbenzene, *PDMS* polydimethylsiloxane, *PFBHA* *o*-2,3,4,5,6-(pentafluorobenzyl)hydroxylamine, *PFPH* pentafluorophenylhydrazine

The PDMS–Carboxen–DVB fiber loaded with PFPH had the best potential sensitivity as at least 300 nmol could be loaded with this fiber and reagent combination. In comparison, DNPH cartridges are usually loaded with 1 mg of reactant (990 μmol). Thus, the cartridges are theoretically 3,300 times more sensitive than the PDMS–Carboxen–DVB fiber. Nevertheless, the use of DNPH cartridges involves a sample dilution induced by solvent elution (5 mL per cartridge). Further, only a small volume of the final extract is actually injected into the HPLC system (around 10 μL). With SPME, all the compounds sampled on the fiber are injected. Considering this, the SPME fiber is only 16 times less impregnated than the cartridge. This theoretical lack of sensitivity should therefore be balanced by the sensitivity of the detection, making the SPME method more sensitive than the cartridge method.

With SPME fibers loaded with PFPH, two supplementary peaks, identified by GC/MS, were observed in the chromatogram. They correspond to pentafluorobenzene and 2,3,4,5,6-pentafluorobenzamine (Fig. 1). Hence, the PFPH loading on a PDMS–Carboxen fiber for 30 min was not tested because of the high proportion of these by-products. For fibers loaded with PFBHA, one by product was identified: 2,3,4,5,6-pentafluorobenzyl alcohol.

This kind of artifact formation on Carboxen coatings was previously observed in the analysis of other thermolabile analytes such as reduced sulfurs and amines [27, 28]. This was related to both the nature of the coating and the desorption temperature of the fiber, as also observed here. To study the influence of the different parameters, the following ratio was used (Eq. 3):

$$r = \frac{n_{\text{by-product}}}{N} \times 100, \quad (3)$$

where $n_{\text{by-product}}$ is the quantity of by-product formed during the thermal desorption step and N is the amount of nonreacted reagent (mol) (Table 2).

For the same desorption temperature (250 $^{\circ}\text{C}$), the proportion of PFPH by-products was more than 40 times higher with the PDMS–Carboxen fiber than with the PDMS–DVB fiber and was ten times higher in the case of PFBHA by-products. Although the PDMS–Carboxen–DVB fiber also contains Carboxen, fewer by-products were formed than with a PDMS–Carboxen fiber, because the external coating exposed to analytes is DVB. The formation of these by-products could be due to the high temperature used during the thermal desorption step combined with the presence of iron and nickel on the Carboxen which could catalyze the degradation reaction [27]. Otherwise, even if the main factor for the formation of by-products seemed to be the nature of the stationary phase, the injector temperature should also be considered. For PFPH, the amount of 2,3,4,5,6-pentafluorobenzamine formed decreased with the temperature. This phenomenon was less preponderant for pentafluorobenzene. However, decreasing

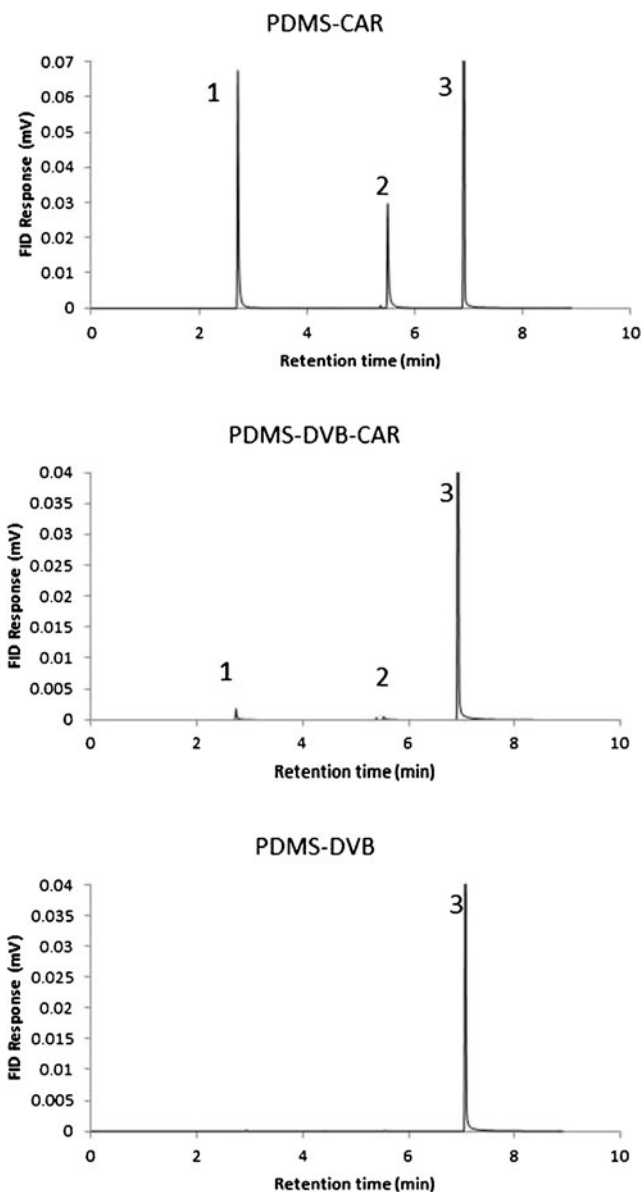


Fig. 1 Typical gas chromatography (GC)/flame ionization detection (FID) chromatograms of solid-phase microextraction (SPME) fibers impregnated with pentafluorophenylhydrazine (PFPH). These chromatographic separations were made on a 30-m column. (VF-5, 30 m \times 0.25-mm inner diameter, 0.25 μm , Varian, Les Ulis, France). 1 pentafluorobenzene 2 2,3,4,5,6-pentafluorobenzamine, 3 PFPH, CAR Carboxen, DVB divinylbenzene, PDMS polydimethylsiloxane

the injector temperature could lead to memory effects owing to incomplete desorption of the analytes. PFBHA was finally chosen as the derivatization reagent as only one by-product was formed with this compound. Considering the proportion of by-product formed, the PDMS–DVB SPME fiber was selected, and no memory effect was observed at 250 $^{\circ}\text{C}$.

Optimization of the PFBHA loading

Two different processes were tested to impregnate PDMS–DVB fibers with PFBHA. The most often used involves an

Table 2 Ratio *r* of by-products and derivatization reagent for different coatings and desorption temperatures

Stationary phase	Injector temperature (°C)	PFBHA	
		2,3,4,5,6-Pentafluorobenzyl alcohol (%)	PFPH Pentafluorobenzene (%) 2,3,4,5,6-Pentafluorobenzamine (%)
PDMS-CAR-DVB	270	4	3
PMDS-CAR	320	28	49
	280	21	37
	250	21	45
PDMS-DVB	250	2	< 1

aqueous solution of PFBHA (the solubility of PFBHA in water is 5 %), and the other one, which is easier to implement for on-site measurements, consists in loading the fiber from pure reagent (5 mg of pure reagent was placed in a 20-mL headspace vial). For the dry process, equilibrium was reached after 5 min, confirming the results in Table 1, and 75 nmol of derivatization reagent was loaded (Fig. 2). The relative standard deviation from one loading to another on the same SPME fiber was 18 % ($n=3$).

When the loading was performed from aqueous solution, equilibrium was reached after 20 min, and up to 400 nmol could be loaded on the SPME fiber (Fig. 2). In this case, the relative standard deviation from one fiber to another was 0.8 % ($n=3$). Because of its better reproducibility and the highest amount of derivatization reagent loaded on the fiber, the later process was finally chosen.

Kinetics of reaction: difference between aldehydes and acetone

Three SPME fibers were exposed to gaseous hexanal at $510 \mu\text{g m}^{-3}$ for 15 min: a PDMS-Carboxen fiber, a PDMS-DVB fiber and a PDMS-DVB fiber loaded with PFBHA. When the SPME fiber loaded with PFBHA was exposed to gaseous hexanal, only the two peaks corresponding to the derivatives appeared in the chromatogram, showing a quantitative reaction (Fig. 3). The response obtained with PDMS-DVB was better than the response obtained with PDMS-Carboxen.

Acetone did not react in the same way: the reaction with PFBHA was not instantaneous. When an SPME fiber loaded with some PFBHA was exposed to gaseous acetone ($160 \mu\text{g m}^{-3}$) both peaks of acetone and PFBHA-acetone could be seen in the chromatogram. At the beginning of the extraction, there was thus no linear relationship between the amount of PFBHA-acetone formed on the fiber and the extraction time as Fick's first law of diffusion predicts. Hence, in that case, on-fiber reaction cannot be neglected in comparison with diffusion in the gaseous phase (Fig. 4).

When the exposure time of the SPME fiber increased, the quantity of free acetone decreased, whereas at the same time the

amount of PFBHA-acetone increased. After 25 min all the acetone had been derivatized (see Figs. S1 and S2 for more details).

According to these results, quantification of acetone through the formation of its oxime with PFBHA did not seem to be relevant. Indeed, it took 25 min for a quantitative reaction between acetone and PFBHA, and the oxime gave a weaker FID signal than the underivatized acetone. Further, analysis of acetone on Carboxen SPME fibers gives good results with limits of detection below the microgram per cubic meter level [12]. The PFBHA on-fiber derivatization, therefore, seems only suitable for the analysis of aldehyde compounds.

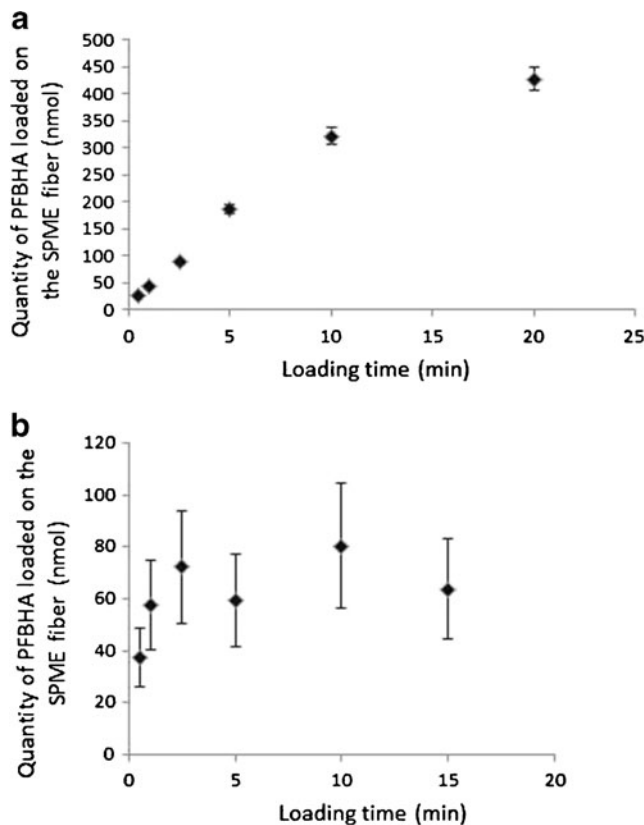


Fig. 2 Kinetics of *o*-2,3,4,5,6-(pentafluorobenzyl)hydroxylamine (PFBHA) loading from an aqueous solution (a) and from pure product (b) on a PDMS-DVB SPME fiber

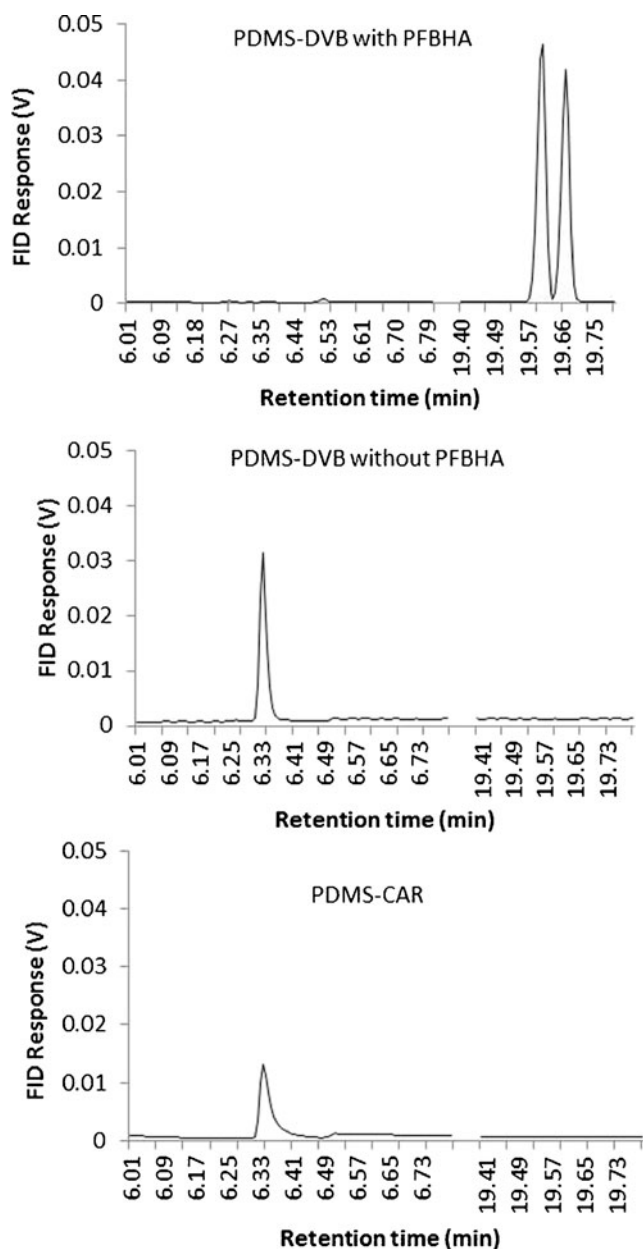


Fig. 3 Typical GC/FID chromatograms of PDMS–DVB SPME fibers, impregnated or not impregnated with PFBHA and exposed to gaseous hexanal. 1 hexanal, 2 Z isomer of PFBHA–hexanal, 2c E isomer of PFBHA–hexanal

Formaldehyde extraction yield

The formaldehyde extraction yield was determined by successive 7-min exposures of a PFBHA-impregnated PDMS–DVB fiber to the same standard atmosphere ($20 \mu\text{g m}^{-3}$). After four consecutive extractions, the amount of formaldehyde still present in the standard gas was below the limit of quantification. It was below the limit of detection from the sixth exposure. Further, the amount of derivative formed during the first five exposures was equal to the amount of formaldehyde initially present in the 330-mL sampling bulb (0.220 nmol),

assuming quantitative extraction. This was confirmed by a 45-min single exposure of the fiber (Fig. 5).

Following these results, two ways for the quantification of formaldehyde could be considered. With short extraction times (in nonequilibrium conditions), Fick's first law of diffusion can be applied to determine the concentration of formaldehyde in air via calibration curves obtained from standard gases. Another way is to use the fiber's ability to quantitatively extract the formaldehyde present in the sampling bulb. Thereby, with a long enough extraction time (45 min for the 330-mL glass bulb), the concentration in the air sample could be deduced from the amount of PFBHA oxime formed on the fiber, which would be simply determined by calibration with oxime standard solutions. In this case, the calibration would not require a gas generator. In this study, the calibration was performed using standard gases.

Analytical performances

The calibration curves (Eq. 2) for formaldehyde, acetaldehyde, and hexanal were plotted from GC/FID analyses (Fig. 6).

For acetaldehyde and hexanal, the sum of the two peaks corresponding to the two isomeric derivatives was used to plot the calibration curves for better sensitivity. Good linearity was obtained for the three aldehydes. Concentrations higher than the microgram per cubic meter level were not tested here as they are not relevant for indoor air quality issues. However, the analysis of higher concentrations in other applications can be expected.

With GC/FID, limits of detection, limits of quantification, and reproducibility (Tables 3, 4) were determined from six consecutive analyses with the same SPME fiber. The concentration in standard gas was $0.15 \mu\text{mol m}^{-3}$ and the extraction time was 15 min. The limit of detection was then determined according to the following equation [28]:

$$LOD = \frac{3.3 \delta_b}{a}, \quad (4)$$

where δ_b is the standard deviation of the peak area for the six consecutive analyses and a is the slope of the calibration curve.

From Eq. 4, the limit of quantification could be determined directly with Eq. 5:

$$LOQ = \frac{10\delta_b}{a}. \quad (5)$$

The limit of detection and the limit of quantification were calculated in micromoles per cubic meter minute. The values were then converted to micrograms per cubic meter considering a 5-min or a 20-min extraction time (Table 5).

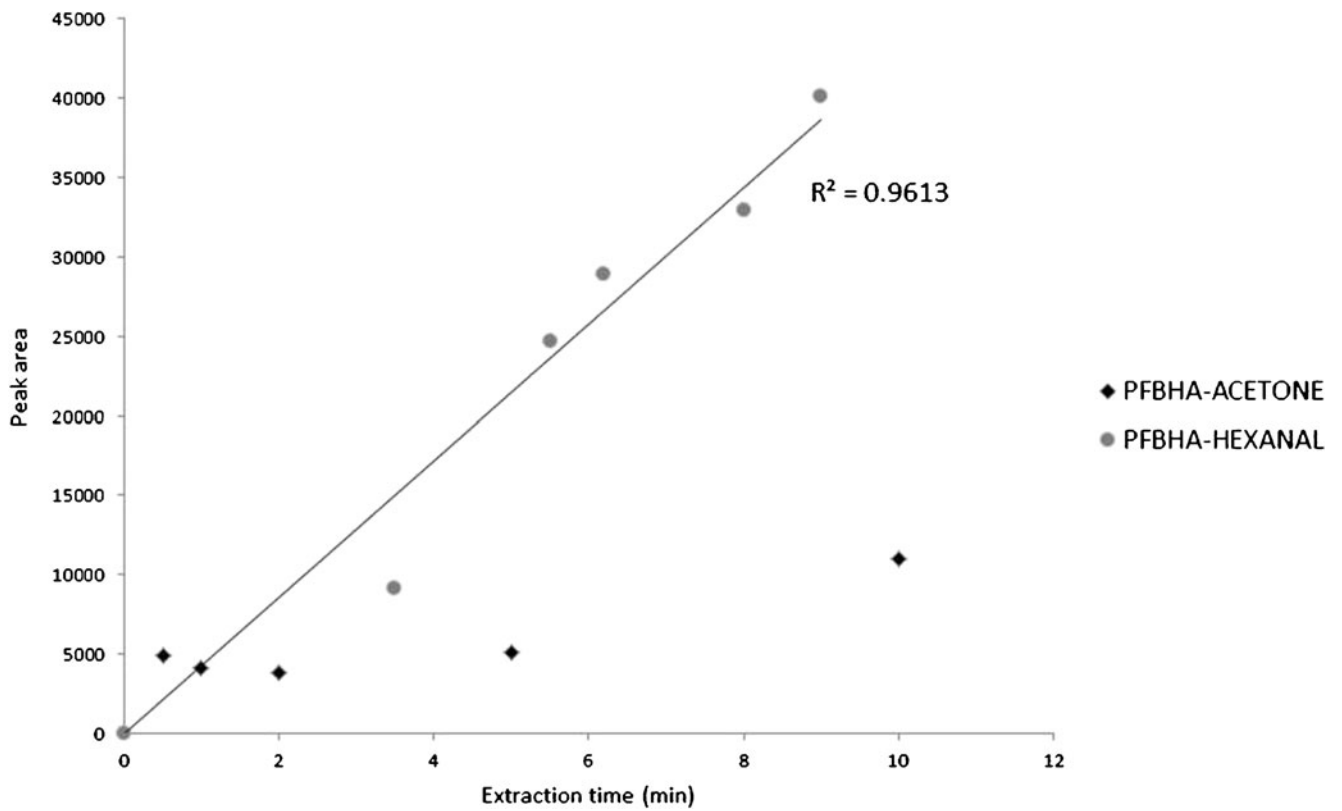


Fig. 4 Formation kinetics of PFBHA–acetone ($2.7 \mu\text{mol m}^{-3}$) and PFBHA–hexanal ($2.0 \mu\text{mol m}^{-3}$) on a PDMS–DVB SPME fiber in a 330-mL glass bulb. The chromatographic analyses were made with a 30-m column

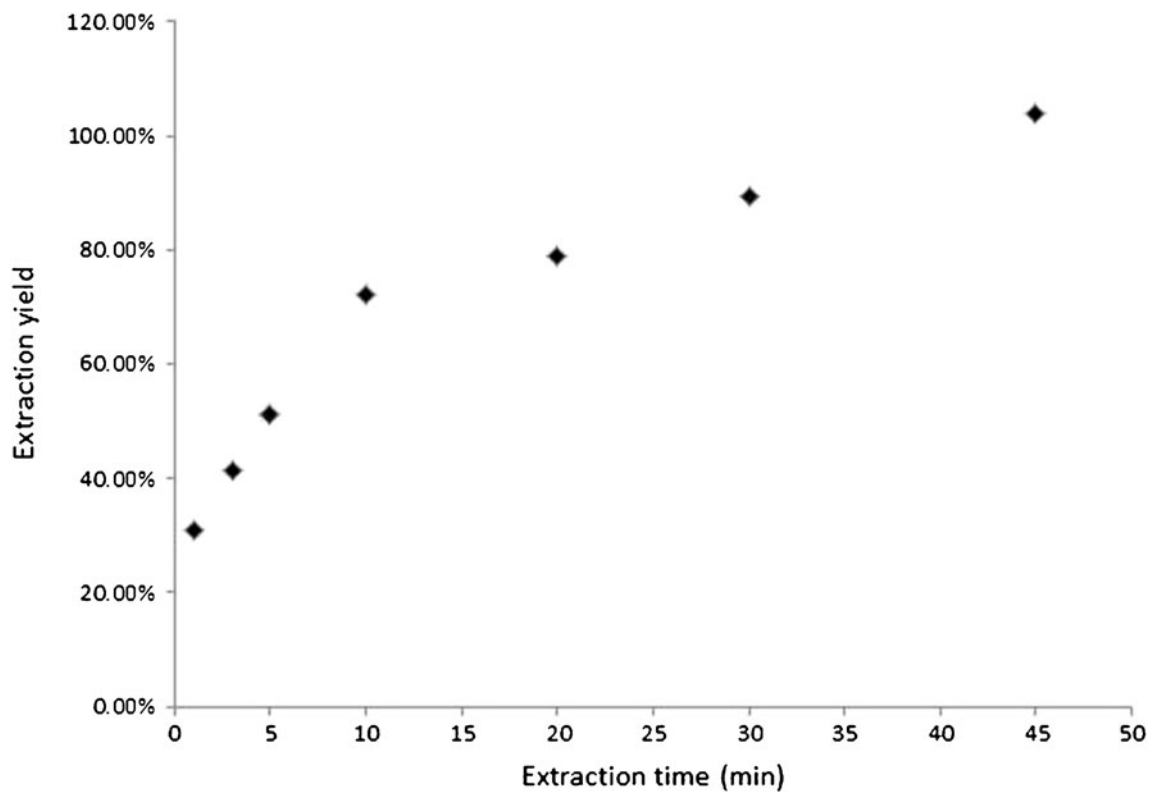


Fig. 5 Extraction yield of gaseous formaldehyde at $10 \mu\text{g m}^{-3}$ on a PDMS–DVB fiber in a 330-mL glass bulb

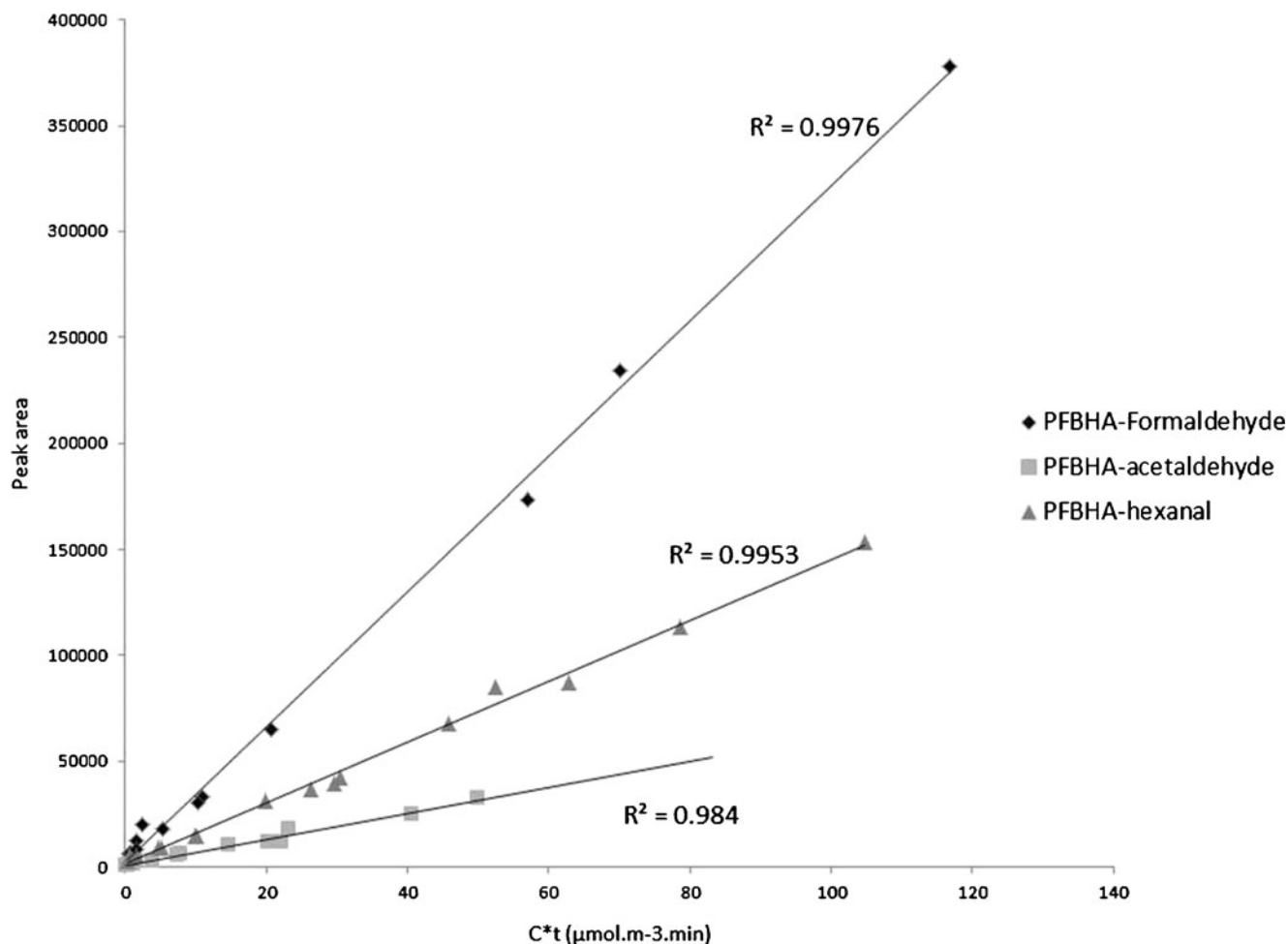


Fig. 6 Calibration curves, $A=f(Ct)$, for formaldehyde, acetaldehyde, and hexanal in GC/FID

For formaldehyde, the limit of detection in GC/FID was comparable with the limit of detection previously obtained by Martos et al. [13] with a 1-L gas sampling bulb and with a 5-min extraction ($5.66 \mu\text{g m}^{-3}$). The limits of quantification for hexanal and acetaldehyde were too high to consider indoor air analysis. The performances were thus also determined with GC/MS detection, first in full-scan mode [total ion chromatogram (TIC) and EIC] and then in SIM mode using m/z 181 (Tables 4, 5). The limits of detection were calculated for a signal-to-noise ratio of 3, for short (5-min) and long (20-min) extraction times. For acetaldehyde, the signal-to-noise ratio of the second oxime peak, which is less affected by the PFBHA

signal, was used. For hexanal, the two oxime peaks were not totally resolved, and the signal-to-noise ratio of the first maximum value of the peak was used.

For formaldehyde and hexanal, the reproducibility (relative standard deviation) was below 20 % in all cases. With GC/MS detection, it was the same for TIC and EIC plots. In SIM mode, the reproducibility was better for formaldehyde and acetaldehyde. For acetaldehyde, oxime peaks were not totally resolved from the PFBHA peak. That would explain why the

Table 3 Reproducibility (relative standard deviation, *RSD*) obtained for gas chromatography (GC)/flame ionization detection (FID) analysis for a 20-min SPME

	Formaldehyde	Acetaldehyde	Hexanal
Concentration ($\mu\text{g m}^{-3}$)	1.7	1.8	4.9
RSD (%)	20.3	58.0	10.9

Table 4 Reproducibility (RSD) obtained for GC/mass spectrometry (MS) analysis in full-scan and selected ion monitoring (SIM) modes for a 15-min SPME

	Formaldehyde	Acetaldehyde	Hexanal
Concentration ($\mu\text{g m}^{-3}$)	3.1	3.3	10.1
RSD (%)			
TIC	12.3	17.9	16.8
EIC	12.0	30.8	15.3
SIM	8.9	14.9	25.3

EIC extracted ion chromatogram, TIC total ion chromatogram

Table 5 Limits of detection (*LOD*) and limits of quantification (*LOQ*) obtained for GC/FID and GC/MS analyses in full-scan and SIM modes for different detection times

		Formaldehyde		Acetaldehyde		Hexanal	
		5 min	20 min	5 min	20 min	5 min	20 min
LOD ($\mu\text{g m}^{-3}$)	GC/FID	8.5	2.1	63.6	15.9	20.4	5.1
	GC/MS (TIC)	0.27	0.07	3.81	0.95	4.62	1.15
	GC/MS (EIC)	0.07	0.02	1.95	0.49	1.53	0.38
	GC/MS (SIM)	0.008	0.002	0.126	0.032	0.087	0.022
LOQ ($\mu\text{g m}^{-3}$)	GC/FID	25.6	6.4	191.2	47.8	61.2	15.3
	GC/MS (TIC)	0.89	0.22	12.70	3.17	15.39	3.85
	GC/MS (EIC)	0.22	0.06	6.50	1.62	5.10	1.28
	GC/MS (SIM)	0.027	0.006	0.420	0.107	0.290	0.073

results obtained in terms of the limits of detection and reproducibility were not as good as for formaldehyde or hexanal. The EIC plot did not improve the resolution probably because the *m/z* 181 ion used was also very intense for PFBHA. The limits of detection obtained here for both the TIC mode and the SIM mode for a 20-min exposure were ten times lower than those determined with a PDMS–Carboxen fiber for underivatized acetaldehyde and a 4-h exposure [12]. Obviously, in all cases, the limits of detection obtained in SIM mode were at least ten times lower than those obtained for EIC plots. The limits of detection and limits of quantification obtained for all aldehydes are low enough to consider studying indoor air quality with GC/MS, either in full-scan mode with the EIC signal for carbonyl screening or in SIM mode for quantification.

Effect of relative humidity of air

Previous studies conducted on PDMS–Carboxen fibers showed competitive adsorption with water under certain operating conditions [12]. Even if the fiber and the sorption mode are different here, one should verify that water does not interfere during the carbonyl sampling. The effect of relative humidity was investigated in 250-mL glass sampling bulbs. The calibration curves for formaldehyde, acetaldehyde, and hexanal were plotted for a PMDS–DVB SPME fiber previously impregnated with PFBHA (see Fig. S3).

The relative humidity of air did not seem to have any influence on on-fiber derivatization. As the process used here to load the fiber occurred in the headspace of an aqueous solution, there is a great probability that some water would already be adsorbed onto the fiber. The water present in the air would thus not influence adsorption of aldehydes. Moreover, the solubility of formaldehyde in water may favor its sorption onto the impregnated fiber. Another assumption is that the derivatives, having high molecular weights, have higher affinity for the sorbent than small molecules (e.g., H_2O) and are thus less sensitive to competitive adsorption.

Fiber conservation

The conservation of the fiber before on-site sampling was studied just after the PFBHA loading. The storage after sampling was evaluated by exposing an impregnated fiber to a gaseous atmosphere of formaldehyde at $19.8 \mu\text{g m}^{-3}$ for 10 min. Once the SPME fiber had been saturated with PFBHA, $84 \pm 4 \%$ ($n=3$) of the initial amount was still adsorbed on the fiber after 2 days at room temperature. This conservation yield decreased to $77 \pm 6 \%$ ($n=6$) after storage for 3 days. However, these results were better than those obtained in a previous study, where the conservation yield was 85 % after only one night [13].

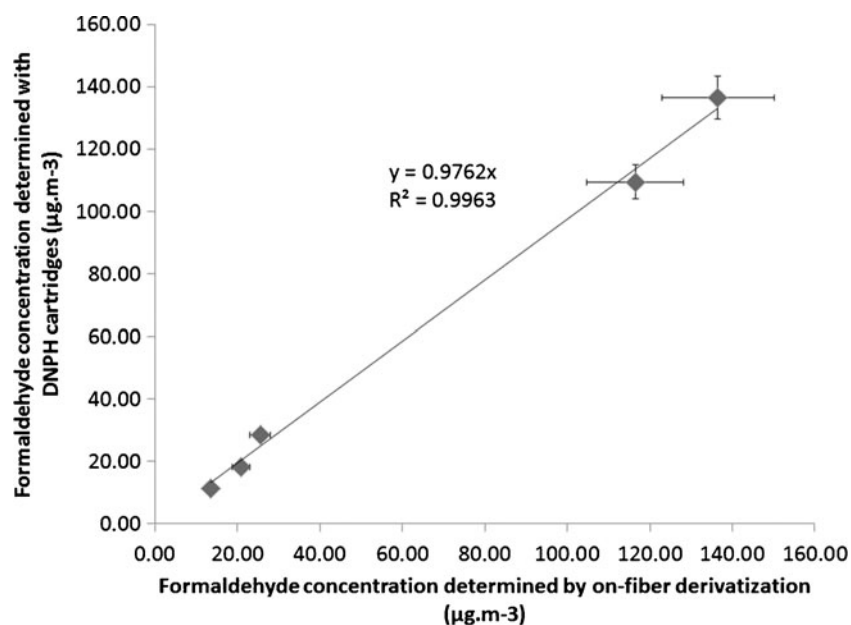
After formaldehyde sampling, the storage yield of the derivative adsorbed on the fiber was $102 \pm 9 \%$ ($n=3$) after 3 days at room temperature. Therefore, it is possible to consider on-site application as the fiber can be stored for several days before and after sampling.

Comparison with the DNPH standard method

Before checking the applicability of the method developed in indoor environments, we evaluated the consistency of the results obtained in comparison with those obtained with a standard method. The standard method applied was active sampling on DNPH cartridges and is described in “Experimental.” The comparison was made for two different kinds of atmosphere: typical indoor air for low concentrations and air of an emission chamber containing particle board materials (oriented strand board and medium-density fiberboard panels), which are known to be strong formaldehyde emitters, for high concentrations. The locations studied for typical indoor air were the same as the those described in the following section. The instantaneous air sampling in glass bulbs was performed during DNPH active sampling. The results are presented in Fig. 7.

The results obtained during this comparison showed there was no significant difference between the two methods. This

Fig. 7 Comparison of quantification of indoor air formaldehyde with 2,4-dinitrophenylhydrazine (DNPH) cartridges and on-fiber derivatization



also indicates that the air samples were homogeneous, owing to the sampling durations, which were very different for the two methods: a few seconds for filling the sampling bulb (SPME method) and 3 h for the standard method. Nevertheless, the complete validation of the SPME analytical method would require more experiments, especially for concentrations in the range from 40 to 120 $\mu\text{g m}^{-3}$.

Application to indoor air analysis

The method developed was applied to analyze three different rooms of a 40-year-old office building: a copy room, a closed storage area, and a meeting room. The storage area is a small room (12.6 m^2) where a lot of samples, including oriented strand board panels were kept. The meeting room is a 13- m^2 room, used only for meetings. It is furnished with just one table and five chairs. The copy room is a 5.2- m^2 room dedicated to the use of two printers and a computer. The extraction on the SPME fiber lasted 15 min for this practical case. The formaldehyde concentrations determined in the meeting room, the copy room, and the storage area were 13.5, 20.8, and 25.5 $\mu\text{g m}^{-3}$, respectively. For both hexanal and acetaldehyde, the concentrations were below the limit of quantification for this extraction time. For the storage area, it was not surprising to find the highest formaldehyde concentration as oriented strand board panels, which are well known as formaldehyde emitters [29], had been kept in this area for several months. The meeting room had the lowest formaldehyde concentration of the three environments investigated, which was consistent with the fact that it is the least occupied and the least furnished room. The formaldehyde concentration in these rooms was

also low enough to meet the upcoming French regulation for buildings open to the public.

Conclusion

A simple, fast, and sensitive method for the analysis of trace carbonyls based on on-fiber derivatization and GC analysis was developed. Different SPME fibers and two derivatization reagents were compared to find the best compromise between analytical performances and easiness of implementation for indoor air application. Carboxen-based coatings exhibited the best reagent loading capacities, but the formation of artifacts during the desorption step prevented their use. PDMS–DVB fiber and PFBHA as a reagent, which have already been used in other applications, were thus selected. The fiber loading was then optimized and the study of the reaction kinetics for acetone showed that this method is not suitable for ketone quantification. Good analytical performances were obtained in GC/MS. The limits of detection in SIM mode were below 0.5 $\mu\text{g m}^{-3}$ for only 5 min of fiber exposure. An average reproducibility of 16 % was determined. The influence of relative humidity on the calibration curves was also evaluated in the range typically experienced in indoor environments. No significant difference was noticed compared with dry air conditions. The storage of the fibers in hermetically closed Inox tubes was shown to be possible for at least 2 days before and after sampling. Finally, the first comparison with the DNPH standard method was encouraging even though complete validation is still to be conducted, and application to indoor air samples was demonstrated.

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