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Hervé Plaisance, Pierre Mocho, Alexandre Gross, Valérie Desauziers. Potential of static sampling using solid-phase microextraction for the assessment of formaldehyde sorption on building materials. *Atmospheric Environment*, 2019, 218, pp.117009. <10.1016/j.atmosenv.2019.117009>. <hal-02436496>

HAL Id: hal-02436496

<https://imt-mines-ales.hal.science/hal-02436496v1>

Submitted on 20 Feb 2020

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Potential of static sampling using solid-phase microextraction for the assessment of formaldehyde sorption on building materials

Herve Plaisance^{a,*}, Pierre Mocho^b, Alexandre Gross^c, Valerie Desauziers^a

^a IMT Mines Ales, C2MA, Hélioparc, 2 Av. P. Angot, 64000, Pau, France

^b Université de Pau et des Pays de L'Adour, Av. de L'Université, BP 576, 64012, Pau, France

^c Nobatek/INEF4, 67 Rue de Mirambeau, 64600, Anglet, France

A B S T R A C T

Formaldehyde is considered as a priority pollutant of indoor air due to its numerous indoor sources and health impact. Due to its physico-chemical properties, the interaction of gaseous formaldehyde with material surfaces is suspected to play an important role in the distribution and fate of this compound indoors. This paper proposes an experimental method providing several parameters characterizing the material/air exchanges for formaldehyde namely, the adsorption and desorption rate constants (k_{am} and k_{dm}) and the material/air equilibrium partition coefficient (K_e) and the initial gas-phase concentration in equilibrium with the material surface (C_{ieq0}). These parameters are assessed in a closed system (glass cell) containing the material and by a static sampling using solid-phase microextraction (SPME) fibers for measuring gaseous concentrations at the material surface during the emission and adsorption phases. Compared to the available methods of determining these parameters described in the literature, this method has the following advantages: (1) Taking into account of sorption on the inner walls of cell in the calculation of the material sorption parameters; (2) An analytical solution assessing the adsorption and desorption rate constants simultaneously from data of the adsorption phase; (3) An assessment of these sorption parameters under experimental conditions close to those encountered in indoor environments; (4) a satisfying reproducibility of the measured sorption parameters. The main performance of SPME sampling was assessed. The applicability of this method was proven to compare the sorption behavior of formaldehyde towards floor coverings.

Keywords:

Indoor air quality
Formaldehyde
Floor coverings
Partition coefficient
Sorption rate constants
SPME

H I G H L I G H T S

- Sorption parameters of formaldehyde on interior materials assessed by a new method.
- Checking the feasibility and reproducibility of this method from tests on floorings.
- Comparison of formaldehyde sorption behavior on five floorings.

1. Introduction

Formaldehyde has been of special concern as an indoor air pollutant because of its emissions from a wide range of products and the adverse health effects associated with the exposure to formaldehyde (Salt-hammer et al., 2010; Weschler, 2009). The indoor concentration of formaldehyde in homes, schools, and work offices are generally in the range of 10–90 $\mu\text{g m}^{-3}$ (Langer et al., 2016; Dassonville et al., 2014; Mandin et al., 2017). However, formaldehyde concentrations sometimes reach higher values when the emissions from the indoor sources are high

and the ventilation is deficient (Poulhet et al., 2014). Formaldehyde emissions from indoor materials have a major contribution to indoor contamination. However, some results showed that the sorptive interactions between this gaseous compound and material surfaces can play an important role in mass balance of formaldehyde indoors (Poulhet et al., 2014; Plaisance et al., 2013). Materials can act as formaldehyde sinks at first, then become emission sources for years when the environmental conditions are favourable to the re-emission. Some studies (Liu et al., 2009; Xu et al., 2012; Xu and Zhang, 2011) showed that the sink effect for formaldehyde on indoor materials

* Corresponding author.

E-mail address: herve.plaisance@mines-ales.fr (H. Plaisance).

(wallboards and carpets) increases slightly with the increase of humidity and its magnitude is higher compared to other compounds of nearby molecular weight (Plaisance et al., 2013). However, the mechanisms behind the sink effect for formaldehyde are not fully known (Xu et al., 2012; Ye et al., 2014). These interactions with indoor materials remote formaldehyde from the air at the rates that are of similar magnitude or greater than the rate at which this compound is removed by air exchange (Traynor et al., 1982; Plaisance et al., 2019).

The available methods to determine the sorption parameters are dynamic devices consisting of an emission chamber (Tichenor et al., 1991) or an emission cell (Rizk et al., 2016a) in which the material is exposed to airflow with pollutant (adsorption phase) and without pollutant (desorption phase) alternatively. Measured gas-phase concentrations were fit to equations developed from sorption models or sorption/diffusion models in the case of porous materials to obtain the key parameters characterizing the specific compound-material interactions (Xu et al., 2012; Xiong et al., 2011a).

These experiments require a measurement technique with high time resolution in order to describe the fast changes in gaseous concentration caused by the sorption processes.

Due to limited means for the near real-time measurements of formaldehyde, few data are available in the literature on the adsorption (k_{am}) and desorption (k_{dm}) rate coefficients for individual materials. Most studies on the sorption characteristics of formaldehyde were focused on the determination of the gas-material partition coefficient and the diffusion coefficient in the material (Xu et Zhang, 2011; Xiong et al., 2011b). Furthermore, the experimental conditions used were often far from those of indoor environments with higher formaldehyde concentration levels and higher airflow at the material surface. It has not been proven that these differences in conditions do not influence the results of adsorption and desorption rate coefficients. The direct injection mass spectrometry such as SIFT-MS (Selected Ion Flow Tube Mass Spectrometry) can be an interesting tool especially for assessing the sorption parameters of formaldehyde at low concentration levels typical of indoor environments (Thevenet et al., 2018). Another alternative is the using of Solid Phase Micro-Extraction (SPME) sampling performed in an airtight emission cell. Recent developments regarding the on-fiber derivatization allowed to expand the potential of SPME to measure gaseous formaldehyde at ppb level (Bourdin and Desauziers, 2014) and to combine it with emission cell to assess the gaseous concentration at the material surface (Desauziers et al., 2015). Fast changes in the concentration can be assessed by successive short samplings with solid-phase microextraction fibers. The equations of sorption model are to define in the specific case of a closed system and a static sampling by SPME. Furthermore, the sorption on the inner surface of cell is to consider in the model development for the assessment of formaldehyde sorption rate constants (k_{am} and k_{dm}) because its not taken into account was identified as a major source of error (Rizk et al., 2016b).

The objectives of this study are to (1) develop an experiment method using an airtight emission cell coupled to SPME sampling and the associated model for the determination of parameters characterizing the material/air exchanges for formaldehyde including the adsorption and desorption rate constants (k_{am} and k_{dm}); (2) apply the method to five different floor coverings to check its feasibility and reproducibility.

2. Material and methods

2.1. Model principle and analytical solution

The method is based on mathematical equations using the Langmuir model and mass balance applied to a closed system (airtight cell, no airflow). The concentration of a pollutant i is assumed to be homogeneous in the cell air and the diffusion in the material is here not considered. The tested floorings are made of different types of polymers. The diffusion coefficients of formaldehyde in various polymer films were estimated from 10^{-12} to $10^{-15} \text{ m}^2 \text{ s}^{-1}$ (Ye et al., 2014). Basing on the

convective transfer coefficients in the materials calculated from data of Ye et al. (2014) (not shown here), the diffusion process in the material should be too low to play a significant role in sorption tests carried out in this study. The pollutant concentration change in the cell air is as a function of material emission and exchanges between air and the surfaces (material and inner walls of cell). The sorption on the walls of cell is taken into account by performing blank tests. The gas phase concentration change can be defined by the general equation:

$$\frac{dC_i}{dt} = R_s \frac{A_m}{V} + k_{dc} \frac{A_c}{V} C_{sc} - k_{ac} \frac{A_c}{V} C_i + k_{dm} \frac{A_m}{V} C_{sm} - k_{am} \frac{A_m}{V} C_i \quad (1)$$

with C_i the gas-phase concentration of compound in the cell ($\mu\text{g}\cdot\text{m}^{-3}$), R_s the material emission rate ($\mu\text{g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$), A_m the material surface (m^2), A_c inner surface of the cell (m^2), V the cell volume (m^3), k_{dc} the desorption rate constant for inner surface of cell (h^{-1}), k_{ac} the adsorption rate constant for inner surface of cell ($\text{m}\cdot\text{h}^{-1}$), k_{dm} the desorption rate constant for the material surface (h^{-1}), k_{am} the adsorption constant for the material surface ($\text{m}\cdot\text{h}^{-1}$), C_{sc} the compound concentration on inner surface of cell ($\mu\text{g}\cdot\text{m}^{-2}$), C_{sm} the compound material-phase concentration ($\mu\text{g}\cdot\text{m}^{-2}$).

Sorption experiment involves a 2-step protocol in order to determine the whole of parameters characterizing the material/air exchanges.

2.1.1. Emission phase

The material placed in a closed cell is exposed to humidified zero air. Early in this phase, the emission is the only term contributing to the gaseous concentration, that is:

$$\left(\frac{dC_i}{dt}\right)_{t=0} = R_s \frac{A_m}{V} \quad (2)$$

During this phase, the emission rate is gradually reduced until 0 and inversely, the gas-phase concentration is increased until a steady state is reached.

At the final stage, the value corresponds to the initial gas-phase concentration in the cell in equilibrium with the material surface, noted C_{ieq0} ($\mu\text{g}\cdot\text{m}^{-3}$). This parameter is an indicator of material emission.

2.1.2. Adsorption phase

For this phase, a humid air containing a high gaseous concentration of the compound i is fastly introduced in the cell, then this one is closed again. In these conditions, the emission term could be neglected and the variation of gaseous concentration in the cell then decreases as the only result of the sorption processes. The general equation is simplified as follows:

$$\frac{dC_i}{dt} = k_{dc} \frac{A_c}{V} C_{sc} - k_{ac} \frac{A_c}{V} C_i + k_{dm} \frac{A_m}{V} C_{sm} - k_{am} \frac{A_m}{V} C_i \quad (3)$$

To solve this equation (3), it requires to express C_{sc} and C_{sm} as a function of C_i . That is obtained from the mass balance carried out for two configurations during the adsorption phase: test with material and blank test (where the material is replaced by a disc of the same size and similar in nature to the cell).

In the case of test with material, the mass balance gives:

$$VdC_i + A_c dC_{sc} + A_m dC_{sm} = 0 \quad (4)$$

By integration and rearrangement of equation (4), we obtain:

$$C_{sm} = \frac{V}{A_m} (C_{i0} - C_i) + \frac{A_c}{A_m} (C_{sc0} - C_{sc}) + C_{sm0} \quad (5)$$

with C_{i0} is the gaseous concentration in the cell, C_{sc0} the concentration on inner surface of cell and C_{sm0} the material-phase concentration at the start of adsorption phase.

In the case of blank test (without material), the mass balance gives:

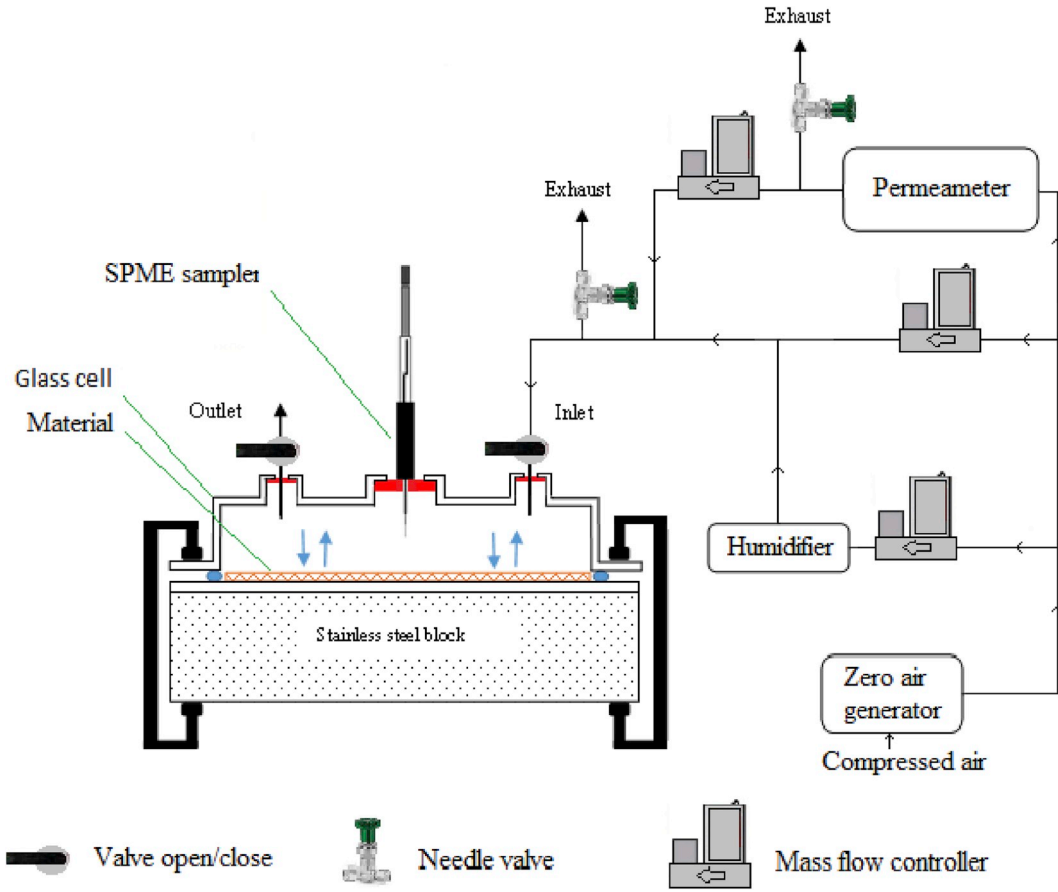


Fig. 1. Diagram of experimental setup for assessing the material/air exchanges parameters for formaldehyde.

$$VdC_i + (A_m + A_c)dC_{sc} = 0 \quad (6)$$

By integration and rearrangement of equation (6), we obtain:

$$C_{sc} = \frac{V}{(A_m + A_c)}(C_{i0} - C_i) + C_{sc0} \quad (7)$$

Replacing the expressions of C_{sm} (equation (5)) and C_{sc} (equation (7)) in the general equation (3) and after factorization, it leads to the following expression:

$$\begin{aligned} \frac{dC_i}{dt} + \left(k_{dm} - k_{dm} \frac{A_c}{(A_m + A_c)} + k_{ac} \frac{A_c}{V} + k_{am} \frac{A_m}{V} + k_{dc} \frac{A_c}{(A_m + A_c)} \right) C_i \\ = k_{dm} \left(C_{i0} + \frac{A_m}{V} C_{sm0} + \frac{A_c}{V} C_{sc0} \right) + \frac{A_c}{(A_m + A_c)} C_{i0} (k_{dc} - k_{dm}) \end{aligned} \quad (8)$$

This is a conventional first order differential equation of the form:

$$\frac{dC_i}{dt} + LC_i = P \quad (9)$$

$$\text{with } L = k_{dm} - k_{dm} \frac{A_c}{(A_m + A_c)} + k_{ac} \frac{A_c}{V} + k_{am} \frac{A_m}{V} + k_{dc} \frac{A_c}{(A_m + A_c)} \quad (10)$$

$$\text{and } P = k_{dm} \left(C_{i0} + \frac{A_m}{V} C_{sm0} + \frac{A_c}{V} C_{sc0} \right) + \frac{A_c}{(A_m + A_c)} C_{i0} (k_{dc} - k_{dm}) \quad (11)$$

By solving the differential equation (9) as well as the analysis at the limits leads to the following solution:

$$C_i = (C_{i0} - C_{ieq})e^{-Lt} + C_{ieq} \quad (12)$$

where C_{i0} is the initial concentration of the pollutant i in the air at the beginning of the adsorption phase and C_{ieq} is the concentration of the

pollutant i in the air at the end of the adsorption phase. By tracing $\ln \frac{C_i - C_{ieq}}{C_{i0} - C_{ieq}}$ as a function of t , the parameter L can be determined from the slope. Equation (12) can be derived as follows:

$$\frac{dC_i}{dt} = -L(C_{i0} - C_{ieq})e^{-Lt} \quad (13)$$

At the beginning of the adsorption phase, the desorption terms could be neglected compared to the adsorption terms. We can simplify equation (3) as follows:

$$\frac{dC_i}{dt} = -k_{ac} \frac{A_c}{V} C_i - k_{am} \frac{A_m}{V} C_i \quad (14)$$

Equality of equations (13) and (14) at the beginning of adsorption phase allows to obtain k_{am} .

$$k_{am} = \frac{LV}{A_m} \left(1 - \frac{C_{ieq}}{C_{i0}} \right) - k_{ac} A_m \frac{A_c}{A_m} \quad (15)$$

The desorption constant k_{dm} is obtain from equation (10):

$$k_{dm} = \frac{L - k_{am} \frac{A_m}{V} - k_{ac} \frac{A_c}{V} - k_{dc} \frac{A_c}{A_c + A_m}}{1 - \frac{A_c}{A_c + A_m}} \quad (16)$$

To obtain sorption constants for the material, it is necessary to assess in advance the sorption constants for the inner surface of cell (k_{dc} and k_{ac}). These constants are obtained from data of blank tests. In our experiments, a glass cell is used. For the blank tests, the material is replaced by a glass disc. The mathematical development (not shown here) is similar to material test considering only the exchanges between air and the glass disc and inner walls of cell. This leads to the following expressions of k_{dc} and k_{ac} :

$$k_{ac} = \frac{L'V}{A_c + A_m} \left(1 - \frac{C_{ieq}}{C_{i0}} \right) \quad (17)$$

$$k_{dc} = L' - k_{ac} \frac{A_c + A_m}{V} \quad (18)$$

with $L' = \ln \frac{C_{i0} - C_{ieq}}{C_i - C_{ieq}}$, term estimated from data of blank test (without material).

Note that the ratio of sorption rate constants $\frac{k_{dm}}{k_{dm}}$ is also the material/air equilibrium partition coefficient K_e (m) i.e. the ratio of the material-phase concentration on the gas-phase concentration adjacent to material surface when the system reaches a steady state: $K_e = \frac{C_{dm}}{C_{ieq}}$. The higher the K_e value, the greater the potential sink of material for the compound is, with the balance strongly shifted to material.

2.2. Experimental device

It consists of a glass emission cell of 504 mL (Fig. 1) and the implantation of a SPME sampling for monitoring gaseous formaldehyde which was developed by our laboratory and previously described (Bourdin and Desauziers, 2014; Bourdin et al., 2014). This cell is equipped with air inlet and outlet and a septum piercing needle for SPME fiber introduction. It is placed on the material covering an area of 206 cm². The tightness in the cell is ensured by an o-ring seal placed between the cell and a glass disk below the tested material and two seal clamps. Leak test is performed by circulating an airflow of 400 mL min⁻¹ in the cell. In these conditions, the air leakage is estimated at less than 1% and checked systematically before and after each experiment. The emission cell is supplied by a gas generation system producing two different gas mixtures. The first one is a humid clean air at the stable conditions of relative humidity and temperature (50 ± 3% at T = 23 ± 2 °C) produced by a dry zero air generator (Claind, Marcq en Baroeul, France) and a humidifier made of a water bubbler and mass flow controllers (Bronkhorst, Montigny-les-Cormeilles, France). The second one is an air loaded with formaldehyde produced by a permeameter (Calibrage, St Chamas, France) equipped by a para-formaldehyde permeation tube Dynacal® (VICI Metronics, Poulosbo, WA, United States) and diluted by the humid clean air to have a stable concentration about 350 µg m⁻³ and a relative humidity of 50%.

2.3. Emission-sorption protocol

Prior to the emission stage, the material was conditioned for 3 days under very low clean airflow (8 mL min⁻¹) at 50 ± 3% relative humidity and 23 ± 2 °C. Then, the cell was closed and the gaseous formaldehyde concentration pattern determined from successive measurements by SPME. This phase was extended until a steady concentration was reached in the cell and required from 5 to 9 SPME samplings of 10 min for at least 3 h.

Following the emission step, the adsorption phase was carried out. A high flow-rate (1.1 L min⁻¹) of humidified air (50% RH) containing 350 µg m⁻³ of formaldehyde was injected in the cell for 3 min. Then, the cell was closed and adsorption kinetics of formaldehyde was recorded. This phase required at least 9 SPME samplings during 6 h. To respect the quantification range of the method, the extraction time was gradually increased from 1 to 10 min during the adsorption phase.

2.4. SPME method

A PDMS-DVB (polydimethyl siloxane-divinylbenzene) SPME fibre (Sigma-Aldrich, Saint-Quentin Fallavier, France) loaded with O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) was used as sampling media because of its potential for GC analysis of formaldehyde by producing the corresponding oxime derivative (Bourdin and Desauziers, 2014; Plaisance et al., 2017). This modified fiber

Table 1
Information on the tested materials.

Material	Description	Size	Density (kg.m ⁻³)
PVC 1	. Commercial flexible PVC flooring packaged in roll. . Three-layer media	Disk of 206 cm ² with 0.2 cm thickness	1412
PVC 2	. Commercial flexible PVC flooring packaged in roll. . Two-layer media	Disk of 206 cm ² with 0.2 cm thickness	1502
Rubber 1	. Commercial flexible rubber flooring packaged in roll. . Single media	Disk of 206 cm ² with 0.2 cm thickness	1656
Rubber 2	. Commercial flexible rubber flooring packaged in roll. . Single media	Disk of 206 cm ² with 0.2 cm thickness	1383
Linoleum	. Commercial flexible linoleum flooring packaged in roll . Jute hessian upside down. . Two-layer media	Disk of 206 cm ² with 0.25 cm thickness	1108

was introduced into the emission cell for some minutes (from 1 to 10 min with respect to concentration levels) to trap and concentrate formaldehyde. Fibre was then directly desorbed into the injection port of a gas chromatograph (GC) coupled to mass spectrometry (MS) and flame ionization detector (FID) for analysis. For quantification, the analysis by FID was favored because of the greater calibration stability over time. Analytical conditions and the protocol for GC analysis of formaldehyde were given by Bourdin and Desauziers (2014).

As SPME is a passive sampling, the amount of compound adsorbed on the fibre is directly proportional to the product of its air concentration and the exposure time, product which is called "exposure dose" and expressed in µg.m⁻³.min (Tuduri et al., 2003; Larroque et al., 2006). To express the response of SPME method in concentration, a linear relationship was previously established between the peak area of formaldehyde oxime and the product of concentration, assessed by active DNPH method (reference value), and the exposure time. To this end, standard atmospheres at least two concentration levels and 50% relative humidity were generated in the cell and sampled by SPME in static mode (closed cell) with variable exposure time from 1 to 10 min. Active DNPH sampling was then performed to measure the concentrations of standard atmospheres. The DNPH cartridges were extracted and analyzed by HPLC according to the protocol described in a previous article (Vignau-Laulhere et al., 2015). Performance of SPME method under the conditions of use are given in section 3.1.

2.5. Test materials

Five different floor coverings (2 PVC, 2 rubbers and 1 linoleum) were tested as sorptive materials. Before the tests, the materials were stored in the laboratory away from light for over two months. The material sample was cut, placed in the cell and conditioned for 3 days under clean airflow (8 mL min⁻¹) at 50 ± 3% relative humidity and 23 ± 2 °C before the each emission-adsorption experiment. Descriptive information about the materials is given in Table 1.

3. Results and discussion

3.1. Performance characteristics of SPME method

In order to satisfy the measurement requirement for sorption experiments, a calibration on a wide range of exposure dose up to 400 µg m⁻³.min was required. To check its robustness, two calibration series with two different concentration levels (22 and 48 µg m⁻³) and several exposure times (from 1 to 10 min) were carried out before and after the sorption experiments (Fig. 2). A linear relationship between the method response (FID) and the product of concentration and the

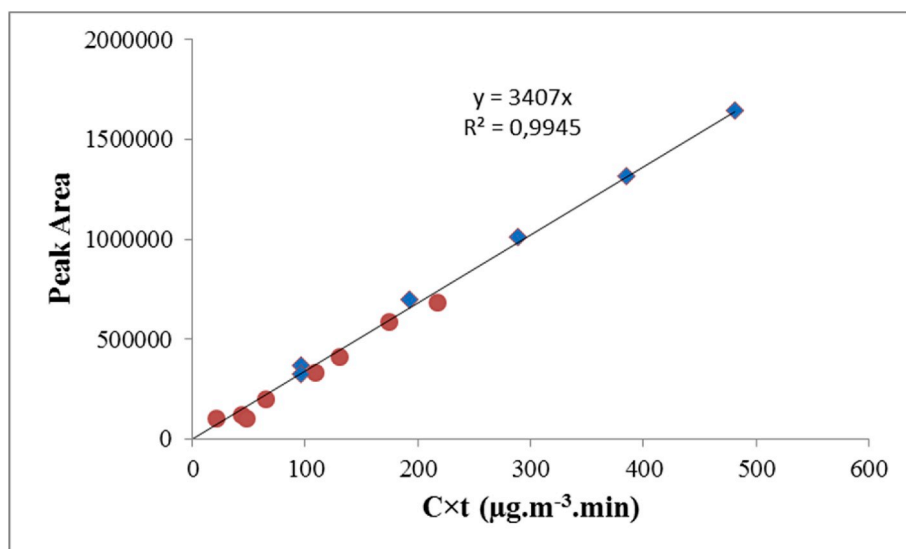


Fig. 2. Calibration curve obtained in GC-FID, $A = f(C \times t)$, for formaldehyde by combining the data of two calibration series before and after the sorption experiments (circles and diamonds, respectively).

Table 2

Blank values and limits of detection (LOD) and quantification (LOQ) obtained from the analysis of 25 blanks (non-exposed fibers).

Formaldehyde	Extraction time			
	1 min	2 min	5 min	10 min
Concentration equivalent to mean of blank values ($\mu\text{g}\cdot\text{m}^{-3}$)	37	18	7.4	3.7
LOD ($\mu\text{g}\cdot\text{m}^{-3}$)	21	10	4.2	2.1
LOQ ($\mu\text{g}\cdot\text{m}^{-3}$)	70	35	14	7

Table 3

Reproducibility (RSD) obtained by analysis of standard atmospheres with a single SPME fiber and multiple SPME fibers for various concentration levels and extraction times. The experimental conditions were maintained at $50 \pm 3\%$ relative humidity and $23 \pm 2^\circ\text{C}$.

	Extraction time	Concentration ($\mu\text{g}\cdot\text{m}^{-3}$) Mean \pm standard deviation	RSD (%)
Series of measures with a single fiber (n = 6)	5 min	19.1 ± 0.6	3.1
Series of measures with multiple fibers (n = 7)	5 min	26.3 ± 3.9	15
Series of measures with multiple fibers (n = 7)	2 min	124.8 ± 3.6	2.9

n: number of replicates.

exposure time was obtained with a squared correlation coefficient greater than 0.99. None deviation was observed between the two calibrations.

The limits of detection (LOD) and Quantification (LOQ) were calculated as three times and ten times the standard deviation of the blank (non-exposed fiber), respectively (Table 2). The blank level is high with this SPME method since it accounts up to $37 \mu\text{g}\cdot\text{m}^{-3}$ for the short extraction time of 1 min. Accordingly, a value measured with this SPME method was systematically subtracted from the blank value. The limit of detection varies from $21 \mu\text{g}\cdot\text{m}^{-3}$ for 1min extraction (lowest time) to $2.1 \mu\text{g}\cdot\text{m}^{-3}$ for 10 min extraction (highest time). This sensibility is sufficient towards the concentrations which were measured in the experiments.

Reproducibility was investigated at three concentration levels and

Table 4

Average \pm standard deviation of equilibrium gas-phase concentration at the emission phase and sorption coefficients for the glass cell without material-Results of Langmuir isotherm model.

	Emission phase		Adsorption phase		R^2
	$C_{\text{ieq}} (\mu\text{g}\cdot\text{m}^{-3})$	$k_{\text{ac}} (\text{m}\cdot\text{h}^{-1})$	$k_{\text{dc}} (\text{h}^{-1})$	$K_e (\text{m})$	
Glass cell + Glass disk (n = 5)	6.1 ± 0.4	0.032 ± 0.007	0.325 ± 0.03	0.10 ± 0.02	0.98

n: number of replicates.

two extraction times (2 and 5 min) using a single SPME fiber and seven different SPME fibers (Table 3). The relative standard deviations (RSD) ranged from 2.9 to 15%. A trend of increasing RSD % was observed when multiple fibers were used for measuring a low concentration. The fast decay in concentration during the adsorption phase requires the use of seven different SPME fibers. The measurements were multiplied at the end of the adsorption phase in order to improve the accuracy in this final part of concentration pattern.

Note that the SPME fibers were subjected to preliminary tests to verify their sampling efficiency from the sampling of standard atmospheres. About 20% of the SPME fibers were discarded for sampling defects (most often an underestimated response). Without this selection, the inter-fiber reproducibility would have been increased to a RSD from 20 to 25%.

3.2. Formaldehyde sorption on glass cell (blank test)

As the cell is composed of glass, it is important to assess the sorption parameters of glass by testing without material. To this end, the cell was placed directly on a glass disk. In this configuration, all inner surfaces in contact with air are made of glass. Five blank tests were performed. The results are presented in Table 4 and one example of gaseous formaldehyde concentration patterns and the sorption model curve are shown in Fig. 3.

A sorption effect on the inner glass walls of cell was observed. The glass cell itself acts as an exchange surface of formaldehyde and its effect tends to decrease the gaseous concentration from 318 to $62 \mu\text{g}\cdot\text{m}^{-3}$

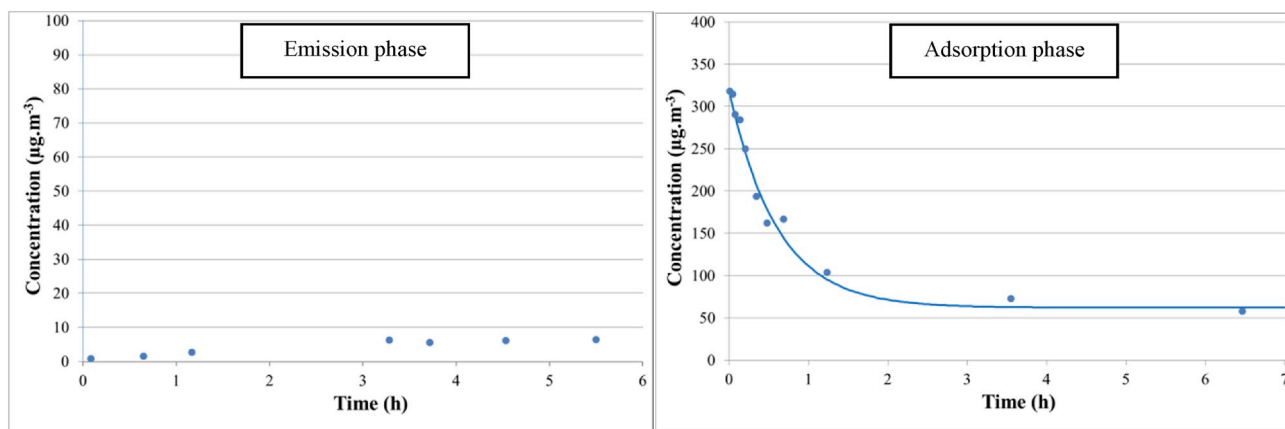


Fig. 3. Gaseous formaldehyde concentration patterns and the sorption model curve for a blank test (without material).

Table 5

Average and range of equilibrium gas-phase concentration at the emission phase and sorption coefficients for stainless steel test - Results of Langmuir isotherm model.

	Emission phase		Adsorption phase		
	C_{ieq0} ($\mu\text{g}\cdot\text{m}^{-3}$)	k_{am} ($\text{m}\cdot\text{h}^{-1}$)	k_{dm} (h^{-1})	K_e (m)	R^2
Glass cell + Stainless steel disk (n = 3)	9.2 [6.3_12.5]	0.063 [0.045_0.076]	0.79 [0.65_1.0]	0.08 [0.07_0.1]	0.96

n: number of replicates. Minimum and maximum are enclosed in brackets.

during the adsorption phase. This effect cannot be neglected in the tests on materials. Therefore, the adsorption and desorption constants of the glass cell were considered in the calculation of material constants (Eqs.

(15) and (16)). The geometry of the cell has a high ratio of the material area on the glass surface (=0.6) which is an asset for the determination of the sorption parameters of material. However, the adsorption rate constant of glass should be sufficiently low compared to that of material does not mask the sorption effect of material.

3.3. Formaldehyde sorption on stainless steel

As an alternative to glass, the cell may be made of stainless steel. To check this option, a series of three sorption tests was carried out to access the sorption parameters of stainless steel. To this end, the cell was directly placed on a flat stainless steel surface. The protocol with the emission and adsorption phases was performed. The results are presented in Table 5 and the gaseous formaldehyde concentration pattern is compared with that of a blank test (sorption on glass only) in Fig. 4.

According to these results, the stainless steel has a sorption effect greater than the glass. The adsorption rate constant is almost twice as

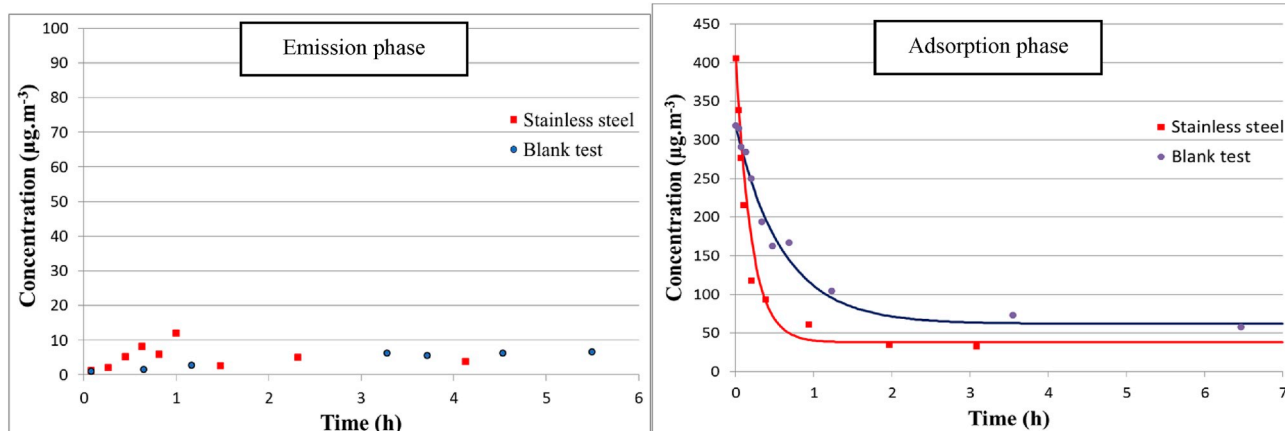


Fig. 4. Gaseous formaldehyde concentration patterns and the sorption model curves for the test with stainless steel disk and blank test (without material).

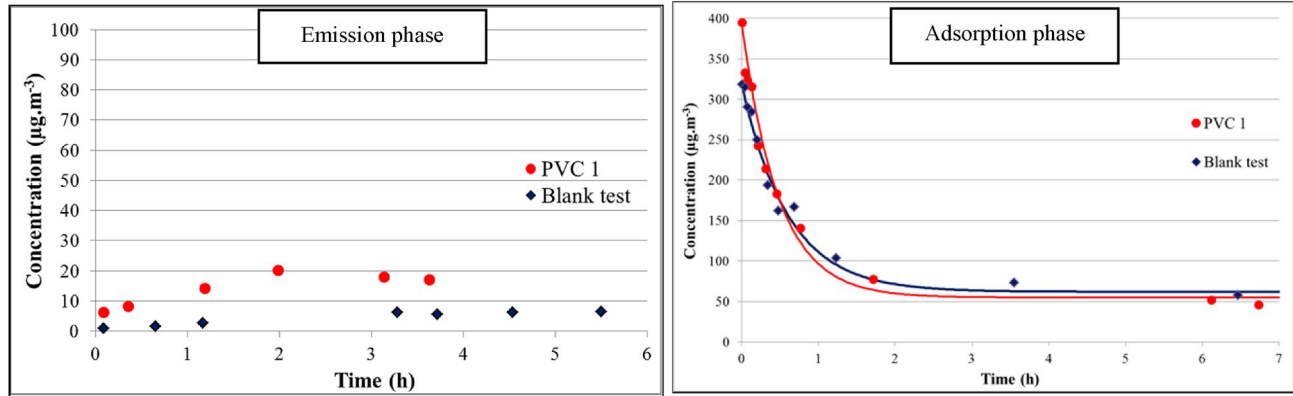
Table 6

Average and range of equilibrium gas-phase concentration at the emission phase and sorption coefficients for material tests – Results of Langmuir isotherm model.

	Emission phase		Adsorption phase		
	C_{ieq0} ($\mu\text{g}\cdot\text{m}^{-3}$)	k_{am} ($\text{m}\cdot\text{h}^{-1}$)	k_{dm} (h^{-1})	K_e (m)	R^2
PVC 1 (n = 2)	23 [19_27]	0.003 [0_0.007]	0.51 [0.24_0.78]	0.005 [0_0.01]	0.98
PVC 2 (n = 2)	19.3 [17_22]	0.06 [0.057_0.065]	0.41 [0.33_0.49]	0.15 [0.13_0.17]	0.97
Rubber 1 (n = 2)	7.3 [5.2_9.5]	0.075 [0.073_0.077]	0.019 [0.017_0.021]	3.9 [3.4_4.5]	0.98
Rubber 2 (n = 2)	16.5 [9_24]	0.063 [0.050_0.076]	0.24 [0.23_0.24]	0.26 [0.21_0.31]	0.97
Linoleum (n = 2)	22.9 [21_24]	0.059 [0.057_0.06]	0.9 [0.88_0.93]	0.065 [0.061_0.068]	0.98

n: number of replicates. Minimum and maximum are enclosed in brackets.

PVC1:



Rubber 1:

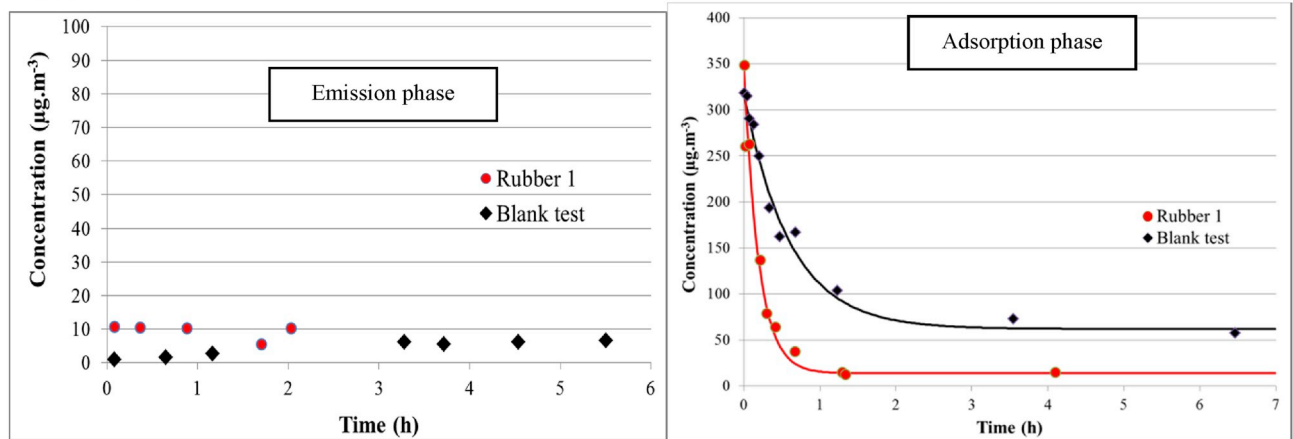


Fig. 5. Gaseous formaldehyde concentration patterns and the sorption model curves for the tests of two floorings (PVC1 and Rubber 1) in comparison with those of blank test (without material).

high for stainless steel as for glass. The use of a stainless steel cell would not reduce the sorption due to the inner walls of the cell. The glass cell appears as the best solution for formaldehyde sorption tests.

3.4. Formaldehyde sorption on floor coverings

Five floor coverings (2 PVC, 2 rubbers and 1 linoleum) were analyzed twice according to the emission-sorption protocol described in section 2.3. All results are detailed in Table 6.

Two concentration patterns showing contrasted sorption behaviours are shown in comparison with that of blank test (Fig. 5).

According to equilibrium gas-phase concentrations at the emission phase from 5 to 27 $\mu\text{g m}^{-3}$, the five materials have low formaldehyde emission levels. In consequence, the contribution of material emission can be considered as negligible in the adsorption phase.

A satisfying reproducibility of the measured sorption parameters was obtained with deviation from the mean of less than 20%, except for PVC1 where no sorption effect was found (k_{am} close to 0).

The sorption behavior of formaldehyde is different depending on the flooring. The capability of a sink material to adsorb indoor air pollutants is represented by K_e ; the higher the K_e value, the greater the mass adsorbed on the sink is (i.e., the stronger the sink).

For PVC1, the gaseous formaldehyde concentration pattern during the adsorption phase is almost confounded with that of blank test (Fig. 5). The adsorption rate constant (k_{am}) as well as the K_e value are close to 0. Formaldehyde is not adsorbed on the surface of this material.

For the four other materials, the k_{am} values were fairly consistent comprised between 0.05 and 0.08 m h^{-1} . However, large differences were recorded in the desorption rates. With a K_e value exceeding 3 m, Rubber 1 represents a sink due to its very low desorption constant close to 0. A low concentration of 14 $\mu\text{g m}^{-3}$ is reached at the end of adsorption phase for this material showing its stronger adsorbent character (Fig. 5). This high K_e value for Rubber 1 is comparable to those of carpets identified by Won et al. (2000) as adsorptive reservoirs for volatile organic compounds.

PVC2, Rubber2 and linoleum have intermediate sorption characteristics to those of PVC1 (no sorption) and Rubber 1 (a sink). Note that the sorption does not seem to depend on the type of materials but rather on characteristics specific to material. Indeed, the sorption characteristics of the two PVCs on the one hand and the two rubbers on the other hand are not similar. For this reason, it is difficult to compare these data with literature. Furthermore, there is few data on sorption coefficients for formaldehyde available in the literature. Table 7 gathers the sorption coefficients for several indoor materials exposed to formaldehyde assessed by different experimental devices (dynamic chambers, dual-chamber system and dynamic system using a FLEC cell). Marked discrepancies are noted between these published data and those of our study. In these experiments in dynamic chambers, the sorption on the internal walls of device was rarely taken into account in the calculation of material sorption coefficients which can lead to a significant bias on the results as shown in sections 3.2 and 3.3. Rizk et al. (2016b) also showed large differences of several orders of magnitude in the

Table 7Comparison of k_{am} , k_{dm} and K_e values available in the literature for several indoor materials with results of this study.

	Method and experimental conditions	k_{am} (m.h ⁻¹)	k_{dm} (h ⁻¹)	K_e (m)	Refs.
Painted gypsum wallboard (porous media)	Dynamic chamber, AER = 1 h ⁻¹ , C ₀ = 3000 µg m ⁻³ , 24 °C, 45–47% RH	From 0.42 to 0.51	From 0.03 to 0.04	From 10.9 to 14.7	Liu et al. (2009)
Painted gypsum wallboard (porous media)	Dual-chamber system, AER = 1.6 h ⁻¹ , C ₀ = 4080 µg m ⁻³ , 23 °C, 50% RH	ND	ND	From 5.8 to 6.2 ^a	Xu et al. (2012)
Calcium silicate (porous media)	Dual-chamber system, AER = 3.6 h ⁻¹ , C ₀ = 372 µg m ⁻³ , 23 °C, 50% RH	ND	ND	From 25.7 to 37.8 ^a	Xu and Zhang (2011)
Gypsum board (porous media)	Dynamic system using a FLEC cell, AER = 857 h ⁻¹ , C ₀ = 120–600 µg m ⁻³ , 23 °C, 50% RH	ND	ND	40.4	Thevenet et al. (2018)
Plastic flooring	Dynamic chamber, AER undisclosed, C ₀ = 174 µg m ⁻³ , 19 °C, 8% RH	17.6	1.19	14.8	Tiffonnet et al. (2018)
Floorings	Static Method using a closed cell, No AER, C ₀ = 350 µg m ⁻³ , 23 °C, 50% RH	From 0.003 to 0.077	From 0.017 to 0.93	From 0 to 4.5	This work
MDF (high emission material)	Alternately airtight/ventilated emission method, 25 °C, 50% RH	ND	ND	3.6 ^a	Huang et al. (2013)
MDF, PB and BB (high emission materials)	C-history method in a closed chamber during the emission phase, No AER, 23–33 °C, 50% RH	ND	ND	From 4.1 to 68 ^a	Xiong et al. (2011b)
MDF and PB (high emission materials)	Alternately airtight/ventilated emission method, 28 °C, 45% RH	ND	ND	From 7.7 to 79 ^a	Zhou et al. (2018)

ND: not determined.

AER: air exchange rate.

C₀: Formaldehyde concentration in the air inflow.

MDF: Medium density fiberboard; PB: Particle board; BB: Block board.

^a Estimated from the dimensionless partition coefficient (K) and material thickness.

determination of sorption coefficients for a same material between FLEC and chamber methods. Moreover, the airflow at the material surface and concentration are very different depending on the methods and often far from those of indoor environments. The influence of airflow on the results of the sorption coefficients was not specifically studied. There is a need to better know the influencing experimental factors in order to seek convergence of methods to estimate these sorption parameters. Despite these uncertainties on the influence of experimental conditions, the K_e values reported in these studies are among the highest found for VOCs under comparable experimental conditions indicating a strong tendency to sorption of formaldehyde on interior surfaces (Tichenor et al., 1991; Thevenet et al., 2018; Won et al., 2000, 2001; An et al., 1999). Note also that low-emitting materials as the floorings and gypsum board have the K_e values comparable with those of the wood-based materials having high formaldehyde emission levels assessed by other recent methods (Huang et al., 2013; Xiong et al., 2011b; Zhou et al., 2018).

Basing on the results of this study, we support the view that the assessment of sorption coefficients in static conditions with taking into account of the sorption on the internal walls of cell can be considered as representative from material/air exchanges occurring in real indoor environments. Further works will be carried out by field experiments at room scale completed by modeling in order to check the applicability of sorption coefficients obtained in laboratory. Further investigations will also focus on the mechanisms that can explain differences in sorption behavior of materials.

3.5. Limitations of the study

An emission phase was included before the adsorption phase to obtain the initial gas-phase concentration adjacent to material surface

C_{eq0} and to have a material sample in equilibrium with air before the adsorption phase and therefore to meet reproducible conditions for the experiments. A formaldehyde amount released by the material during the emission phase can be partially adsorbed on the inner glass walls of cell and be found during the adsorption phase. This sorbed part could influence the results on the k_a and k_d values. With the initial gas-phase concentrations adjacent to material surface at the end of emission phase (C_{eq0}) comprised between 7 and 23 µg m⁻³, the five floorings can be considered as low-emitting materials for formaldehyde. The gas-concentrations into the cell during the adsorption phase have always been higher than C_{eq0} (from 15 to 50 times at the beginning of adsorption phase and from 2 to 3 times at the end of adsorption phase). Therefore, it is not realistic for this sorbed fraction to be shifted from the glass walls to gas-phase considering the gas concentration gradients into the cell.

In the cases of materials having high formaldehyde emission levels, the two phases (emission and adsorption) should be conducted separately. The cell will have to be cleaned between the two phases to remove the formaldehyde amount sorbed on the inner glass walls of cell during the emission phase.

The SPME fiber extracts a formaldehyde amount at each sampling whose result would be to underestimate the measured gas-phase concentrations in the cell and could affect the results on the k_a , k_d and K_e values. The uptake rate of formaldehyde on the SPME fiber was assessed to 0.009 ng/(µg.m⁻³.min) in our previous work (Bourdin and Desauziers, 2014). Considering this uptake rate value, the cell volume, the extraction time and the measured gas-phase concentrations during the adsorption stage, the extracted amounts and the reduction of concentrations caused by the successive samplings can be calculated. For the tests carried out, this reduction accounts for 1 and 4% of the measured

concentration for the first six samplings with the short extraction times of 1–2 min and between 3 and 11% for the following samplings with longer extraction times of 3–6 min. This reduction is low and slightly modifies the concentrations at the end of adsorption phase. Considering the concentrations corrected to sampling amounts, the k_a values remain unchanged while variations up to a range of 20% are found in k_d and k_e values of sorption tests. This deviation due to sampling is considered as acceptable for the kind of experiments.

4. Conclusions

In this study, a method to assess material sorption coefficients for formaldehyde was developed. Its originality is to determine the sorption parameters in a closed cell (static condition) using solid-phase microextraction fibers for measuring gaseous concentrations at the material surface during the adsorption phase. An analytical solution assessing the adsorption and desorption rate constants was found basing on the equations of Langmuir model and mass balance. The results highlighted a significant formaldehyde sorption on the inner walls of cell, a component that was essential to take into account in the calculation of the material sorption parameters. The gaseous concentration patterns during the adsorption phase were correctly described by Langmuir model and a satisfying reproducibility of the measured sorption parameters was obtained. The applicability of this method was proven to compare the sorption behavior of formaldehyde on different types of floor coverings. Contrasted sorption behaviors were obtained depending on the specific characteristics of material ranging from a material having no sorption to a material having a significant capacity of sorption for formaldehyde. The lack of data on formaldehyde sorption in the literature and the specific character of formaldehyde sorption on materials limit the comparison with our results. A better knowledge of influencing experimental factors in these sorption tests would be necessary to explain the discrepancies of results between the studies.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

The authors acknowledge the French Agency ADEME in the framework of SAFEMATER project for their financial support through the CORTEA program (N° grant: 1762c0007).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.atmosenv.2019.117009>.

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