Assessment of an experimental method for determining the three key parameters of VOC emissions from solid materials

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Abstract. The VOC emission processes from a solid material can be described by three key parameters: the partition coefficient (K), the initial emittable concentration (C₀) and, the diffusion coefficient (D). These emission key parameters need to be determined experimentally for a VOC-material pair. A new method from literature allows determining simultaneously the three emission key parameters. However, this method has been evaluated in a single experiment only for formaldehyde. Therefore, the purpose of this study is to assess the efficiency and the reproducibility of the experimental method from literature performing three tests in the same experimental conditions. This work permits to determine the three key parameters of eight main VOC emitted from a particleboard and to evaluate the accuracy of the experimental method. Successfully, experiments carried out using a 128 L well-mixed chamber containing a particleboard, and connected to an online gas analyzer (Selected Ion Flow Tube-Mass Spectrometry), allow the effective characterization of the source material. Results evidence that compared to other VOCs, formaldehyde shows a specific behaviour: the response of formaldehyde between airtight and ventilated regimes is highly contrasted with those of other emitted VOCs.

1. Introduction
Nowadays, Indoor Air Quality (IAQ) is a topic of interest in scientific research due to the time spent in indoor environments and the impacts on human health. Indeed, humans spend between 80 and 90 % of their lifetime in indoor environments. Indoor pollutants are known to be accountable for skin irritations, dizziness, and tiredness, as well as damages to pulmonary functions [1]. Among indoor pollutants, Volatile Organic Compounds (VOCs) are particularly studied given they are ubiquitous in indoor environments. Moreover, the emissions of VOC from solid materials are key contributors to indoor VOC concentrations. As IAQ prevention tools, numerical models are usually used to predict pollutant concentrations in indoor environments. However, the emission depletion and the impact of environmental factors are not embedded in current models. Models encompassing material emissions require input parameters describing the elementary processes related to VOC emissions. Three key parameters describing the VOC emission processes are required [2]: the partition coefficient (K), the initial emittable concentration in the solid material (C₀) and, the VOC diffusion coefficient within the solid material (D).

Several experimental methods from the literature allow determining the key parameters describing VOC emission. Among them, a large part of the existing methods proposes to measure independently each parameter such as multi flushing extraction method [3] or for simultaneous determination of two parameters such as two-chamber method [4]. However, these kinds of experimental method need to be combined with another in order to measure all emission key parameters. Currently, only two main experimental methods have been developed to simultaneously determine the three key emission parameters during a single experiment: (i) the C-history method [5]
and, (ii) the alternately airtight/ventilated emission method [6]. Both methods provide an equivalent accurately and efficiently determination of the three key parameters governing the VOC emission from solid material. Although the experiments are quickly carried out, the C-history method involves complex data processing. In contrast, the method proposed by Zhou et al. [6] is time consuming, but the data processing is easier than the C-history method. Therefore, Zhou’s method was chosen. Typical duration of experiments is lower than one week and remains acceptable. However, Zhou et al. have illustrated the method only for formaldehyde through a single test. The purpose of this work is to assess the applicability, the reproducibility and the accuracy of Zhou’s method through three tests under the same experimental conditions for the main VOCs emitted from a wood particleboard.

2. Materials and methods

2.1. Alternately airtight/ventilated emission method

The principle of the method proposed by Zhou et al. is based on the alternation of different emission states: (i) emission under airtight conditions and, (ii) emission under ventilated conditions [6]. In a first step, VOCs are emitted from a solid material, previously loaded in a clean experimental chamber under airtight conditions, until the equilibrium is reached regarding VOC concentrations. Then, clean air is introduced into the experimental chamber at a constant airflow rate that defines the beginning of VOC emission under ventilated conditions. When the VOC concentrations into the chamber reach new concentration equilibrium, the airtight emission is set again. The solid materials undergo five airtight emissions and four ventilated emissions. Then, K and C0 are retrieved from a linear fitting of multiple sets of experimental data following equation 1.

\[
\sum_{j=1}^{i-1} \frac{\Delta m_j}{V_m} = -(K + \beta)C_{eq,i} + C_0
\]

Where \(C_{eq,i}\) is the i equilibrium VOC concentration in an airtight chamber (mg.m\(^{-3}\)), \(\Delta m_j\) is the j exhaust VOC mass calculated by the trapezoidal quadrature formula (mg), \(V_m\) is the volume of the solid material (m\(^3\)) and \(\beta\) is the volumetric air/material phase ratio. The diffusion coefficient D is then calculated by non-linear fitting of the first experimental airtight emission curve using analytical resolution of the equation of gas-phase VOC concentrations in an airtight chamber with known K and C0 values [7]. More information is available in publication of Zhou et al. [6].

2.2. Assessment of method accuracy

The accuracy and the robustness of Zhou’s method were assessed by performing three experiments under the same environmental conditions. Because of the principle of this method is based on the depletion of the material that is a finite source of VOCs, one material plate is used per experiment. Before the assessment of Zhou’s method, there is a need to evaluate the material variability. This is performed by testing three different material plates under identical ventilated conditions.

2.3. Experimental well-mixed chamber

In this work, all experiments were carried out using a 128 L ventilated experimental chamber with dimensions 0.8x0.4x0.4 m (Figure 1), at a temperature of 22.5 ± 2.5 °C and a relative humidity of 50 ± 5 %. Temperature and relative humidity conditions were continuously monitored using a probe placed inside the chamber.

![Figure 1. Schematic representation of the experimental bench encompassing a 128 L well-mixed experimental chamber.](image-url)
The inlet and the outlet ports of the chamber present circular sections with a diameter of 0.04 m and are located on opposite faces of the chamber. The main axes of the inlet and outlet ports are located 0.055 m from the top and 0.055 m from the bottom of the experimental chamber respectively. During the ventilated emission state, the clean air flow introduced into the chamber is set by mass flow controllers and allows a constant air exchange rate of 2.35 h⁻¹. Conservation flows between the inlet and the outlet is ensured by a system composed of mass flow controller and a vacuum pump. The use of mass flow controllers provides a control on the air exchange rate, while a mixing fan is continuously used to regulate the air mixing inside the chamber, which can be regarded as a well-mixed reactor. The mixing fan is fixed to the ceiling of the chamber and positioned directly in the axis of the inlet flow at a distance of 0.1 m from the inlet port.

2.4. Selected material
This paper focuses on a wood particleboard with a waterproof coating. The wood panel of 0.795x0.395 m with a thickness of 0.015 m is placed inside the experimental chamber with only one face of the panel exposed.

2.5. Analytical methods
Volatile Organic Compounds emitted from the wood particleboard are monitored using an online Selected Ion Flow Tube - Mass Spectrometer (SIFT-MS). The analytical device continuously samples an airflow rate of 25 mL/min from the center of the experimental chamber. Along measurements, the sampled volume is negligible compared to the volume of the chamber. However, this analytical device only allows the monitoring of specific ions that have been defined in the analytical method prior to the experiment. Complementarily, air samplings have been performed from chamber onto sorbent cartridges to screen the diversity of C6-C16 VOCs and carbonyl compounds emitted by the selected material. Chromatographic analyses allow addressing the main VOCs emitted from the wood particleboard, namely acetone, acetaldehyde, formaldehyde, propanal, butanal, pentanal, hexanal, pinene, limonene, carene, camphene and phellandrene. Since the principle of mass spectrometry is to separate compounds according to their mass, the mass resolution of the SIFT-MS device does not allow the discrimination of the different terpenes emitted from the wood panel. In the following section, terpene is used to designate the sum of emitted terpenoid VOCs.

3. Results and discussion
3.1. Material variability
The material variability has been evaluated by testing three different particleboards under the same experimental ventilated conditions. From the same batch of wood panels, the variability in the use of different panels is lower than 8 % except for terpenes with 21.3 %.

3.2. Data correction with respect to temperature
It appears that temperature of the experimental chamber varied between 20 and 25 °C following night and day cycles during experiments. This observation can be explained by the temperature variations of the laboratory according to exposure to sunlight affecting significantly the temperature of the chamber. Therefore, a data correction has been applied on concentration profiles using the following equations:

\[ C_{corr} = C_{exp} + \alpha C_{exp} (T_{ref} - T_{exp}) \]  \hspace{1cm} (2)

\[ \alpha = \frac{C_\infty(T_{max})-C_\infty(T_{min})}{(T_{max} - T_{min})C_\infty(T_{ref})} \]  \hspace{1cm} (3)

Where \( C_{corr} \) is the corrected concentration, \( C_{exp} \) is the experimental concentration, \( T_{ref} \) is the reference temperature set at 21 °C, \( T_{exp} \) is the experimental temperature and \( \alpha \) is the relative change of concentration when temperature increases of one-Celsius degree. This latter parameter is calculated according to the experimental assessment of the impact of temperature on the steady state VOC concentration previously carried out under ventilated conditions following equation 3, where \( C_\infty \) is the steady state concentration, \( T_{max} = 25^\circ C \) and \( T_{min} = 20^\circ C \).
3.3. Summary of results

Table 1. Average values of parameters obtained for 8 VOCs.

|        | Formaldehyde | Acetone | Acetaldehyde | Propanal | Butanal | Pentanal | Hexanal | Terpenes |
|--------|--------------|---------|--------------|----------|---------|----------|---------|----------|
| K      | 3989         | 216     | 186          | 222      | 341     | 298      | 305     | 111      |
| C₀ (mg.m⁻³) | 1510       | 3220    | 117          | 24       | 14      | 39       | 2381    | 392      |
| D (m².s⁻¹) | 2.7x10⁻⁸    | 2.5x10⁻⁹| 3.7x10⁻⁹    | 2.2x10⁻⁹| 1.2x10⁻⁹| 1.3x10⁻⁹| 2.3x10⁻⁹| 4.4x10⁻⁹|

After reviewing the literature data, the emission key parameters depend mainly on the kind of solid material and the nature of VOC. Since formaldehyde is widely studied in the literature, it will be used as a reference to assess our results. According to references [5], [6], our initial emittable concentration C₀ values are in the range of literature data, which is very large, showing an average initial VOC concentration in building materials of 17 g.m⁻³ for formaldehyde, with a standard deviation of 100 %. Then, the value of the partition coefficient can vary from one hundred to several thousand [6], [8]. Nevertheless, partition coefficient values of formaldehyde from our results are very close to results from literature [5], [6], [8]. Finally, the diffusion coefficient depends on the porosity of the material and the considered VOC, which results in different values ranging from 10⁻¹⁰ to 10⁻⁶ m².s⁻¹ [5], [8]. Regarding formaldehyde, the method provides values around 2.7x10⁻⁸ m².s⁻¹ that are in agreement with those in literature [9].

3.4. Evaluation of the method reproducibility

In order to determine K and C₀, a linear fitting of experimental data has been performed according to Zhou et al. [6]. Determined coefficients are gathered and reported in the table 2 and 3 respectively for the partition coefficient and the initial emittable concentration. Uncertainties correspond to the standard deviation (SD) calculated from the values obtained after performing the three distinct experiments under the same experimental conditions.

Table 2. Partition coefficient of the eight VOCs monitored for the three replicas.

|        | Formaldehyde | Acetone | Acetaldehyde | Propanal | Butanal | Pentanal | Hexanal | Terpenes |
|--------|--------------|---------|--------------|----------|---------|----------|---------|----------|
| Test 1 | 4380         | 211     | 180          | 193      | 312     | 273      | 313     | 113      |
| Test 2 | 4404         | 212     | 180          | 206      | 355     | 317      | 316     | 109      |
| Test 3 | 3184         | 225     | 198          | 267      | 357     | 305      | 287     | 110      |
| SD (%) | 17.5         | 3.7     | 5.6          | 17.8     | 7.5     | 5.5      | 3.2     | 2.1      |

According to table 2, all VOCs present partition coefficients within the same order of magnitude except formaldehyde, which shows the highest partition coefficient. The partition coefficient reflects the mutual ability to transfer between the adsorbed and the gas phases. Most VOCs present acceptable uncertainties relative to partition coefficient below 7.5%. Formaldehyde and propanal are the most sensitive compounds with respectively uncertainties of 17.5 and 17.8 % but remain reasonable.

Table 3. Initial emittable concentration of the eight VOCs monitored for the three replicas (mg.m⁻³).

|        | Formaldehyde | Acetone | Acetaldehyde | Propanal | Butanal | Pentanal | Hexanal | Terpenes |
|--------|--------------|---------|--------------|----------|---------|----------|---------|----------|
| Test 1 | 1545         | 2484    | 105          | 22.6     | 12.4    | 33.7     | 2261    | 354      |
| Test 2 | 1729         | 3188    | 127          | 28.2     | 15.9    | 43.6     | 2611    | 409      |
| Test 3 | 1257         | 3988    | 119          | 21.1     | 14.7    | 40.5     | 2270    | 411      |
| SD (%) | 15.7         | 23.4    | 9.3          | 15.6     | 12.3    | 12.8     | 8.4     | 8.3      |

Formaldehyde, acetone and hexanal are characterized by the highest initial emittable concentration (> 1200 mg.m⁻³), while other VOCs have initial emittable concentrations lower than 45 mg.m⁻³, such as propanal, butanal and pentanal (Table 3). Uncertainties of initial emittable concentration are also acceptable with values below 23.4 %. Overall, the experimental method is reproducible for three distinct experiments under the same conditions and is sufficiently efficient for determining the partition coefficient and the initial emittable coefficient given the widely reasonable uncertainties.
After the determination of $K$ and $C_0$, the diffusion coefficient $D$ is calculated by solving the analytical equations of gas-phase VOC concentrations in the airtight mode [7]. Although the analytical equation is solved in an airtight chamber, the convective mass transfer coefficient through the boundary layer $h_m$ appears in the equation because the airflow inside the chamber is convective due to the mixing fan. However, some difficulties in the determination of $D$ were encountered due to an unrealistic convective mass transfer coefficient. This parameter does not allow a satisfying correlation between the experimental curve and the solution of the analytical equation. According to Axley [10], the convective mass transfer coefficient $h_m$ can be calculated using theoretical equations. These theoretical equations are based on ideal cases and mainly depend on two unreliable parameters: the mean fluid velocity in the vicinity of the material surface ($U$) and the length of the surface in the direction of the flow ($L$). $U$ and $L$ parameters can greatly vary from one case to another. Therefore, the convective mass transfer coefficients require being calculated again using $U$ and $L$ parameters with a better agreement with all VOCs. In this paper, $h_m$ only depends on the molecular diffusivity of VOCs in air.

### Table 4. Calculated convective mass transfer coefficient $h_m$ (m.s$^{-1}$).

|         | Formaldehyde | Acetone | Acetaldehyde | Propanal | Butanal | Pentanal | Hexanal | Terpenes |
|---------|--------------|---------|--------------|----------|---------|----------|---------|----------|
| $h_m$   | 1.61x10$^{-4}$ | 1.26x10$^{-4}$ | 1.26x10$^{-4}$ | 1.12x10$^{-4}$ | 1.01x10$^{-4}$ | 9.4x10$^{-5}$ | 8.8x10$^{-5}$ | 7.7x10$^{-5}$ |

Then, VOC diffusion coefficients within the solid material were determined by fitting first experimental concentration curve under airtight conditions and the results of the analytical resolution using known $K$ and $C_0$. Diffusion coefficients obtained for each VOC are reported in table 5.

### Table 5. Diffusion coefficient of the eight VOCs monitored for the three replicas (m$^2$.s$^{-1}$).

|         | Formaldehyde | Acetone | Acetaldehyde | Propanal | Butanal | Pentanal | Hexanal | Terpenes |
|---------|--------------|---------|--------------|----------|---------|----------|---------|----------|
| **Test 1** | 2.5x10$^{-8}$ | 3.0x10$^{-9}$ | 5.0x10$^{-9}$ | 2.0x10$^{-9}$ | 1.5x10$^{-9}$ | 1.5x10$^{-9}$ | 3.0x10$^{-9}$ | 8.0x10$^{-8}$ |
| **Test 2** | 2.5x10$^{-8}$ | 3.0x10$^{-9}$ | 4.0x10$^{-9}$ | 3.0x10$^{-9}$ | 1.0x10$^{-9}$ | 1.5x10$^{-9}$ | 3.0x10$^{-9}$ | 5.0x10$^{-8}$ |
| **Test 3** | 3.0x10$^{-8}$ | 1.5x10$^{-9}$ | 2.0x10$^{-9}$ | 1.5x10$^{-9}$ | 1.0x10$^{-9}$ | 1.0x10$^{-9}$ | 1.0x10$^{-9}$ | 2.0x10$^{-9}$ |

During the three tests, a low gap between diffusion coefficient values is noticed for all VOCs except terpenes that present contrasted diffusion coefficient values. Results of terpenes could be explained by a higher material variability of terpenes emissions compared to other VOCs as reported in section 3.1. This variability could affect the first experimental concentration profile under airtight conditions required to determine $D$. Furthermore, formaldehyde presents the highest diffusion coefficients with an order of magnitude of 10$^{-8}$ m$^2$.s$^{-1}$, while those of other VOCs are comprised between 1.0x10$^{-9}$ and 5.0x10$^{-9}$ m$^2$.s$^{-1}$. The high diffusion coefficient values of formaldehyde seem to corroborate the quick establishment of equilibrium concentration observed during experiments.

### 3.5. Singular behaviour of formaldehyde

The figure 2 represents time series of formaldehyde and terpenes concentrations after performing the alternately airtight/ventilated emission method [6]. When switching from airtight to ventilated conditions occurs, a high decrease of terpenes concentration is observed with an average concentration drop of 83.9 % between both regimes according to figure 2. In contrast, the concentration gap of formaldehyde between airtight and ventilated regimes is lower than terpenes with an average concentration drop of 44.9 %. Formaldehyde maintains a high concentration of about 175 ppb under ventilated conditions while terpenes concentration is less than 80 ppb. In addition, the steady state concentrations of formaldehyde under airtight conditions remain constant while the steady state concentrations of terpenes decrease from 485 to 90 ppb after five cycles (figure 2). These findings suggest that formaldehyde emission could be controlled by different mechanism than other emitted VOC.
4. Conclusion
The determination of the partition coefficient and the initial emittable concentration by linear fitting provides an acceptable accuracy for all VOCs and is reproducible from one test to another. Moreover, the resolution of analytical equations for determining the diffusion coefficient is reproducible for 7 out of 8 VOCs. The use of the experimental method for determining the VOC emission key parameters highlights the singular behaviour of formaldehyde compared to other VOCs. The low concentration gap observed for the formaldehyde under ventilated and airtight conditions suggests that formaldehyde emission could be controlled by different mechanisms than other monitored VOCs.

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