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Indoor Environment Quality (User Comfort, Health and Behaviour)

Assessment of VOCs material/air exchanges of building products using the DOSEC®-SPME method

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Abstract

Using low emissive materials in building is an effective way to reduce indoor concentrations of pollutants such as VOCs. Material emissions are assessed by the ISO 16000-9 standard. This procedure is time-consuming and is not suitable for on-site measurements. This work aimed in assessing an alternative method, DOSEC®-SPME, for simple measurements. To validate it, emissions of 30 materials were characterized by both ISO 16000-9 and DOSEC®-SPME. A first correlation was found between the two methods for formaldehyde emissions of raw materials. This encouraging result allows considering the development of new decision making tools for the selection of healthy building materials.

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Keywords: formaldehyde; building materials; emission; DOSEC®-SPME; ISO 16000-9

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1. Introduction

Nowadays, indoor sources of air pollutants are known and are numerous: building materials and decoration (insulation, paint…), human activities such as cooking, consumer products (perfumes, incense ...), interior furniture, and external pollution as well. In France, indoor VOC concentrations were recorded from 5 to 7 times higher than the outdoor concentrations [1]. Since the recent thermal regulations in 2012, various constraints in the building appeared with the aim of reducing their energy consumption by limiting the air permeability or energy-efficient ventilation. This could cause adverse effect on indoor air quality (IAQ) by increasing the concentration levels of pollutants. New decision-making tools are hence needed to implement good practices in building construction or renovation phases. In this aim, the approach envisaged here involves a predictive model which helps in selecting low emission building and decoration materials. This model requires input data to operate such as material emissions. In France, the emissions of new products were assessed through a time-consuming procedure involving a 28-days emission test within an environmental chamber [2]. These test methods were based on an active sampling to transfer the VOCs emitted from the material to the sampling tubes to concentrate the compounds [3], [4]. These protocols, covered by EN ISO standards [5], [6], were suitable for laboratory testing for material labeling but were not able to evaluate the material behavior in real conditions of indoor environments. In the aim to determine the impact of materials, static sampling methods have been developed to obtain simpler and faster on-site sampling [7]–[9]. Our static sampling method consisted of coupling an homemade emission cell DOSEC® with solid-phase micro-extraction (SPME) [10]. This method allows a rapid sampling and a simple thermal desorption, directly performed in a gas chromatograph injector and allows a multi-pollutant analysis [11], [12]. It allows to measure the gas-phase concentrations at the material surface after reaching equilibrium inside the emission cell[13]–[15].

The objective of this work was to test the ability of the DOSEC®-SPME method to assess the gas-phase concentration at the material surface by comparison with emission chamber data (ISO 16000-9) on a large selection of building materials.

2. Material and method

2.1. VOCs and materials studied

The followed compounds were selected from the French labelling regulation list (decree n° 2013-321 of March 23, 2011). This list was completed by other VOCs mostly detected in the emissions of 20 representative construction materials. Finally, 16 pollutants were considered according to their health impact and/or their emission levels: formaldehyde, acetaldehyde, pentan-1-ol, propionaldehyde, hexanal, butyl acetate, α-pinene, camphene, ethyl-2-hexanol, toluene, ethylbenzene, xylene, styrene, 1,2,4-trimethylbenzene, 2-butoxyethanol, tetrachloroethylene and TVOC (Total Volatile organic Compounds) [16].

These VOCs emissions were characterized by both ISO 16000-9 and DOSEC®-SPME methods for 30 materials (Table 1). These materials include conventional products, materials which contain a fraction of natural components, and decontaminant materials which are advertised to reduce the formaldehyde concentration in indoor air.

2.2. Emission tests

Materials were purchased and stored according to EN ISO 16000-11. For the emission chamber method following the standard EN ISO 16000-9, materials were exposed in CLIMPAQ emission chambers (50.9 L or 225 L) under a clean air flow at 23±1 °C and 50±5 % relative humidity during 28-days. Two active samples using DNPH and TENAX® cartridges were taken at 3 and 28 days in order to determine the concentrations of aldehydes (by liquid chromatography) and VOCs (by gas chromatography – flame ionization detection) in the chamber with a detection limit of 0.3 $\mu g.m^{-3}$ and a repeatability of 14.0 % for formaldehyde [5], [16].

The VOC emission rate for the material is then calculated with the following equation:

$$\tau_{ij} = \frac{C_i \times V_C \times \lambda_C}{A_j} \tag{1}$$

where τ_{ij} was the formaldehyde emission rate of the material j (µg.m^{-2}.h^{-1}), C_i the formaldehyde concentration inside the CLIMPAQ (µg.m^{-3}), λ_C the air exchange rate inside the chamber (h^{-1}), V_C the volume of the test chamber (50 L) and A_j the j sample surface (m^2).

For the DOSEC®-SPME method, each material was conditioned before testing in an emission chamber under a clean air flow at 23±1 °C, 50±5 % relative humidity and an air exchange rate of 0.5 h^{-1} during 3 days. These conditions are similar to those of ISO 16000-9 in order to make comparable results obtained with the two methods after 3 days of conditioning. The DOSEC® emission cell was then placed on the material surface until reaching VOCs equilibrium between material and air. Then, a modified SPME fiber suitable for simultaneous VOCs and aldehydes sampling was introduced in the cell. The fiber was thermally desorbed and the sampled compounds are analyzed by gas chromatography coupled with dual detection – mass spectrometry – flame ionization detection (GC-MS/FID) with a detection limit of 3.1 µg.m^{-3} and a repeatability of 14.6 % for formaldehyde. After that equilibrium was reached inside the emission cell, the headspace concentration can be considered as the gas phase concentration at the material surface [13]–[15].

3. Results and discussion

3.1. Emissions results

The VOCs emissions of 30 materials were measured with the DOSEC®-SPME and the ISO 16000-9 methods after 3 days of conditioning. Among these 30 materials, only 19 materials were sources of formaldehyde. The Table 1 presents the formaldehyde and the TVOC concentration values measured for these 19 materials. TVOC is the sum of the VOCs eluting between n-hexane (C6) and n-hexadecane (C16). Concentrations are calculated as toluene equivalents.

Table 1: Formaldehyde and TVOC emissions quantified after 3 days conditioning by DOSEC®-SPME and ISO 16000-9 methods. (C=Conventional, N=Natural, D=Decontaminant) – each result is the mean of two replicates and the method's repeatability.

	DOSEC®-SPME method	ISO 16000-9 method		
Material	Formaldehyde surface concentration Cs_{ij} (µg.m^{-3})	Concentration of formaldehyde in CLIMPAQ C_i (µg.m^{-3})	Formaldehyde emission rate τ_{ij} (µg.m^{-2}.h^{-1})	TVOC emission rate (µg.m^{-2}.h^{-1})
Ceiling (C)	194.3 ± 29.1	135.0 ± 18.9	168.8 ± 23.6	92.5 ± 12.9
Plasterboard 1(C)	9.3 ± 1.4	15.0 ± 2.1	7.5 ± 1.1	17.5 ± 2.5
Plasterboard 2 (C)	14.2 ± 2.1	22.0 ± 3.1	11.0 ± 1.5	-
Conventional paint (C)	242.4 ± 36.4	5.0 ± 0.7	12.0 ± 1.7	141.6 ± 19.8
Natural paint 1 (N)	100.1 ± 15.0	2.5 ± 0.3	6.0 ± 0.8	<LD
Natural paint 2 (N)	100.2 ± 15.0	3.4 ± 0.5	8.2 ± 1.1	-
Decontaminant paint (D)	6.0 ± 0.9	0.7 ± 0.1	1.7 ± 0.2	<LD
Lime (N)	16.5 ± 2.5	1.4 ± 0.2	3.4 ± 0.5	-
Paneling (N)	29.2 ± 4.4	1.1 ± 0.2	0.6 ± 0.1	26.0 ± 3.6
OSB 1 (N)	69.4 ± 10.4	34.0 ± 4.8	17.0 ± 2.4	177.5 ± 24.9
OSB 2 (N)	11.3 ± 1.7	23.0 ± 3.2	11.5 ± 1.6	2,089.0 ± 292.5
Hardwood flooring (N)	10.6 ± 1.6	1.6 ± 0.2	1.9 ± 0.3	23.0 ±3.2
Multi layer parquet 1 (N)	342.4 ± 51.4	25.0 ± 3.5	31.3 ± 4.4	82.5 ± 11.6
Multi layer parquet 2 (N)	234.9 ± 35.2	5.6 ± 0.8	7.0 ± 1.0	96.3 ± 13.5
Wood wool (N)	6.8 ± 1.2	5.7 ± 0.8	2.9 ± 0.4	437.5 ± 61.3
Glass wool 1 (C)	3.0 ± 0.5	9.2 ± 1.3	4.6 ± 0.6	273.0 ± 38.2
Glass wool 2 (C)	6.2 ± 0.9	12.0 ± 1.7	6.0 ± 0.8	284.0 ± 39.8
Cellulose insulation (N)	14.1 ± 2.1	48.0 ± 6.7	54.2 ± 7.6	324.3 ± 45.4
Floor glue (C)	83.0 ± 12.4	13.0 ± 1.8	5.4 ± 0.8	-

TVOCs were spread over a wide range of concentrations. The OSB 2 (OSB PMDI) has the highest level (2,089 µg.m^{-3}) with hexanal (78 % in mass fraction) and α-pinene (15 %) as major compounds. Insulation is the category which emits the most TVOCs (more than 200 µg.m^{-3}) with hexanol-2-ethyl (between 10 to 50 %) as major compound.

As expected, the results show that formaldehyde is mostly emitted by wood-based materials which often contain urea-formaldehyde glue. The ceiling presents the highest formaldehyde concentration and is therefore the only material which is not classified A+ (low emissive materials) according to the French labeling regulation. For paints, the DOSEC-SPME method highlights that the natural products are two times less emissive than the conventional products. Moreover, the decontaminant paint shows a very low formaldehyde surface concentration compared to those of classical or natural paints. This demonstrates the ability of the DOSEC-SPME method to assess the depolluting activity of such products.

3.2. Emissions comparison between the DOSEC®-SPME and EN ISO 16000-9 methods

DOSEC®-SPME is seen as an interesting alternative for material emission measurements. Thus, the DOSEC®-SPME method should be validated, meaning that its ability to really measure surface concentration (C_{Sij}) should be demonstrated. For that, the DOSEC®-SPME measurements obtained for 19 materials were compared to those obtained by the standard method on the same samples (Table 1). In this paper, only formaldehyde was considered.

Under steady state conditions, the emission rate τ_{ij} (µg.m^{-2}.h^{-1}) of a VOC *i* for a material *j* can be related to its surface concentration C_{sij} (µg.m^{-3}) [14]:

$$\tau_{ij} = h_{ij}(C_{Sij} - C_i) \tag{2}$$

Considering CLIMPAQ test, C_i is the concentration inside the chamber (µg.m^{-3}) and h_{ij} is the convective mass transfer (m.h^{-1}). For formaldehyde, the chamber air concentrations C_i and the emission rates τ_{ij} are known (Table 1). Assuming that h_{ij} could be determined, it would be possible to calculate the surface concentration C_{sij} in the chamber and to compare them with the DOSEC®-SPME measurements. However, the convective mass transfer is difficult to assess. Indeed, it depends on the thickness of boundary layer itself related to the air velocity at the material surface. A previous work [14] gave a solution to evaluate the convective mass transfer for formaldehyde by experimental measurements in CLIMPAQ in combination with a modeling approach. An empirical relationship was deduced:

$$h_{ij} = 1.68 \times 10^{-3} \times U_m^{0.5} \tag{3}$$

Where U_m is the air flow velocity in the CLIMPAQ chamber (m.s^{-1}). In the present work, air velocities ranged between 0.1 and 0.3 m.s^{-1} according to the EN ISO 16000-9 standard method. In the Figure 1, a median air velocity was considered (U_m = 0.20 m.s^{-1}) leading to a h_{ij} value of 2.70 m.h^{-1}. The C_{sij} concentrations determined by DOSEC®-SPME versus C_{sij} calculated from the CLIMPAQ results is shown in Figure 1.

According to Figure 1a, which concerns all the 19 studied materials, no correlation between ISO 16000-9 and DOSEC®-SPME is evidenced. However, by considering raw materials only (Figure 1b), a linear relationship can be assumed. The slope (0.99) is close to 1 with the squared correlation of 0.95. This means that the DOSEC®-SPME method is able to really determine a surface concentration for raw materials. This result should be further consolidated by the analysis of other materials, especially in the 50 – 150 µg.m^{-3} concentration range.

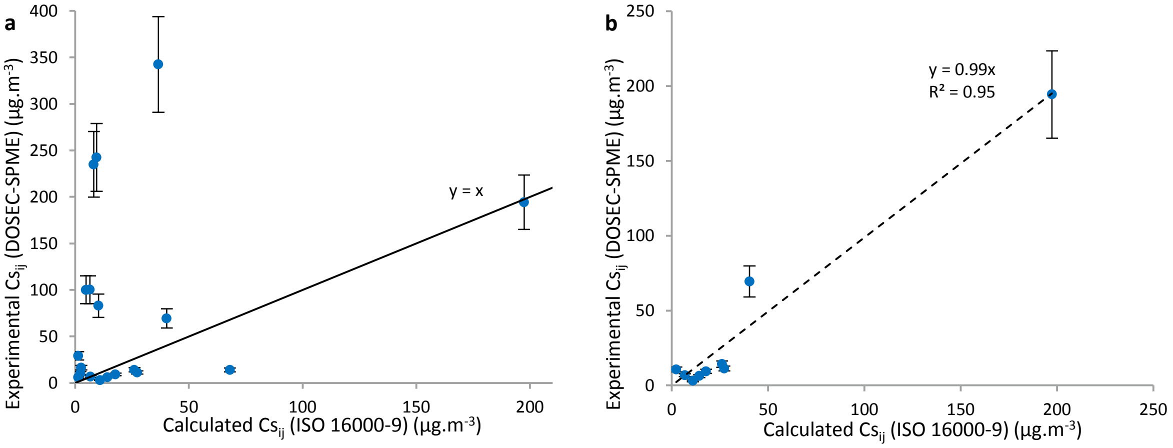

Figure 1: Calculated surface concentration for an air velocity of 0.20 m.s^{-1} from the emission chamber results versus surface concentration measured by DOSEC®-SPME method (a) all 19 materials (b) raw materials.

For the other materials which do not follow this correlation, different assumptions can be proposed. Cellulose insulation has a higher calculated surface concentration than the C_{sij} measured. This result can be explained by the contribution of edges that could not be removed for EN ISO 16000-9 test, in opposite to the DOSEC®-SPME method which strictly measures a surface concentration.

For the three coated materials studied (oiled multi-layer parquet, varnished multi-layer parquet and paneling), the DOSEC® method gives higher C_{sij} compared to those of the chamber test. This may be due to a barrier effect of the coatings which slows down the diffusion of formaldehyde from the raw material to its surface. In the CLIMPAQ, the steady state is not reached for these coated materials. The emission is then controlled by the diffusion in the material which becomes hence the limiting process instead of the diffusion in gas phase. This result is a low surface concentration in the CLIMPAQ test, due to the air exchange. In DOSEC®, measurements are made at equilibrium in a closed system: C_{sij} seems to finally reach the value which would be obtained for the raw material without its coating. This result highlights the importance of air flow conditions near the material for the estimation of the impact of its emission on IAQ.

For the 6 liquid materials (mainly paints), the measurement uncertainty is high due to the difficulty in controlling film thickness and the drying process for different samples. Measurements carried out on the same sample by both methods (DOSEC®-SPME and ISO 16000-9) will help to reduce these uncertainties and to understand the difference of results between the two methods.

4. Conclusion

The VOCs emissions of 30 different materials were analyzed according to two methods: the ISO 16000-9 and the DOSEC®-SPME with 19 formaldehyde sources. The comparison shows that it is possible to qualify the new DOSEC®-SPME method against the standard ones in the case of formaldehyde emissions from raw materials. However, for other samples (liquid or coated materials), it was difficult to establish a correlation between the two methods in the current state of the results. Further studies are needed.

In the future, the correlation between the two methods will be studied for the 15 other selected VOCs. In addition, DOSEC®-SPME will also be applied to deepen the study of material/air exchanges by determining adsorption/desorption constants of VOCs. The influence of material assemblies (constituting building walls, for example) on indoor air quality is also envisaged at laboratory and at real scale in test modules. Finally, all of these results will allow creating a new material database and a new IAQ predictive model. The resulting decision making tool will help in finding the best compromise between energy saving and IAQ for building conception and renovation.

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