



# Impact of building material emissions on indoor air quality: simultaneous quantification of VOCs and formaldehyde in indoor air and at the air/material interface

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# VOCs and Formaldehyde in indoor air

## French Legislation

### Indoor air quality

- Decree n°2012-14: measurement of some indoor air pollutants in buildings open to the public (formaldehyde, benzene, CO<sub>2</sub>)
- Decree n°2011-1727: guide-values for formaldehyde (10 µg/m<sup>3</sup>) and benzene (2 µg/m<sup>3</sup>)

### Labeling of all building materials according to their VOCs emissions

- Decree n°2011-321: labeling of building products, flooring, wall covering, paints and varnishes on their volatile pollutants emissions (Formaldehyde, acetaldehyde, toluene, tetrachloroethylene, xylene, trimethylbenzene, dichlorobenzene, ethylbenzene, 2-butoxyethanol, styrene, TVOC)

Main source of indoor pollutants: building and decoration materials, furniture <sup>1</sup>



<sup>1</sup> Brown, Indoor Air 12 (2002) 55-63



Efficient tools to study both **indoor air** and **air/material interface** are needed

Indoor air diagnosis

Identification of materials responsible for VOC pollution

Modeling of Indoor air quality

Lyon, 26 septembre 2012



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# Analytical strategies

Indoor air

On-site material emissions



DNPH Cartridges



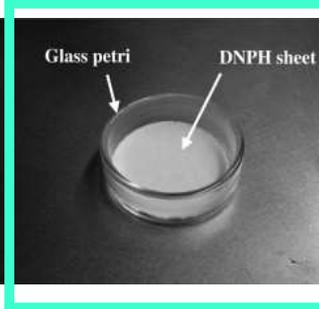
Adsorbent tubes



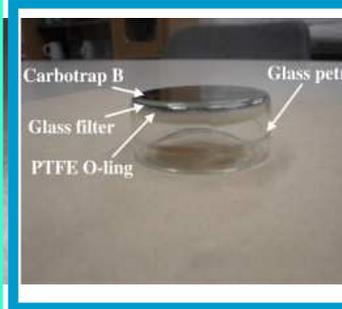
Radiello®



FLEC® (ISO 16000-10)



Glass petri DNPH sheet



Carbotrap B Glass filter PTFE O-ring Glass petri

Shinohara et al., 2009  
Blondel and Plaisance, 2010

VOCs (GC)

Aldehydes (HPLC)



Solid-Phase Micro Extraction (SPME)



Desorption directly in a GC injector

Development of an analytical method for the simultaneous quantification of VOCs and aldehydes

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# Analytical Performances

Indoor air

On-site material emissions



Instantaneous sampling

SPME fiber

Desauziers, Auguin,  
Techniques de  
l'ingénieur, 2012

✓ Mix of 9 compounds:

- Formaldehyde\*
- Acetaldehyde\*
- Toluene\*
- p-xylene\*
- Styrene\*
- Alpha-pinene°
- Dichlorobenzene\*
- Tetrachloroethylene\*
- Hexanal°

- \* Concerned by material labeling
- ° Wooden construction



SPME – emission cell coupling

Non-equilibrium → First Fick's law

$$n_f = U \cdot (C_i \cdot t)$$

$n_f$ : extracted amount on the fiber

$U$ : uptake rate

$C_i$ : concentration in air ( $\mu\text{g}\cdot\text{m}^{-3}$ )

$t$ : extraction time (min)

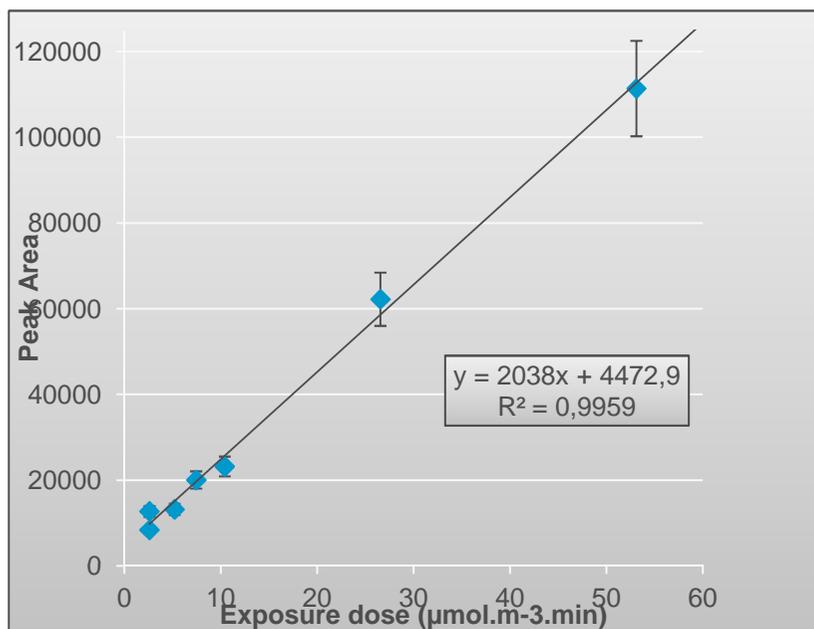


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# Analytical Performances: calibration curves (FID detection)



Formaldehyde

- ✓ Good linearity for the 9 compounds
- ✓ Should be possible to analyse higher concentrations for other applications...

| Compound            | R <sup>2</sup> | Linearity range for a 5 minute SPME extraction ( $\mu\text{g.m}^{-3}$ ) |
|---------------------|----------------|---|
| Acetaldehyde        | 0.9178         | 528   |
| Formaldehyde        | 0.9959         | 480   |
| Toluene             | 0.9720         | 920   |
| Tetrachloroethylene | 0.9688         | 1660  |
| P-xylene            | 0.9858         | 1480  |
| Styrene             | 0.9746         | 1460  |
| Alpha-pinene        | 0.9653         | 1900  |
| hexanal             | 0.9699         | 1500  |
| 1,2-dichlorobenzene | 0.9616         | 2040  |
| <b>AVERAGE</b>      |                | <b>1328</b>   |



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# Analytical Performances: Limits of detection (LOD), limits of quantification (LOQ) and reproducibility

SPME: 20 minute exposure

Concentration of each compound in the standard gas:  $2.4 \mu\text{mol.m}^{-3}$

Results in  $\mu\text{g/m}^3$

| Compounds           | GC/FID           |            |             | GC/MS – SIM mode |                   |
|---------------------|------------------|------------|-------------|------------------|-------------------|
|                     | % RSD<br>(n = 6) | LOD        | LOQ         | LOD<br>(S/N = 3) | LOQ<br>(S/N = 10) |
| Toluene             | 17%              | 3.6        | 11.8        | 0.012            | 0.042             |
| Tetrachloroethylene | 14%              | 4.7        | 15.8        | 0.014            | 0.048             |
| P-xylene            | 8%               | 2.1        | 6.8         | 0.027            | 0.091             |
| Styrene             | 5%               | 1.4        | 4.7         | 0.013            | 0.043             |
| Alpha-pinene        | 11%              | 3.3        | 10.9        | 0.049            | 0.164             |
| 1,2-dichlorobenzene | 9%               | 2.8        | 9.5         | 0.011            | 0.037             |
| Formaldehyde        | 16%              | 4.2        | 14.0        | 0.005            | 0.016             |
| Acetaldehyde        | 22%              | 11.3       | 37.8        | 0.051            | 0.170             |
| Hexanal             | 13%              | 3.7        | 12.3        | 0.124            | 0.414             |
| <b>AVERAGE</b>      |                  | <b>4.1</b> | <b>13.7</b> | <b>0.034</b>     | <b>0.113</b>      |

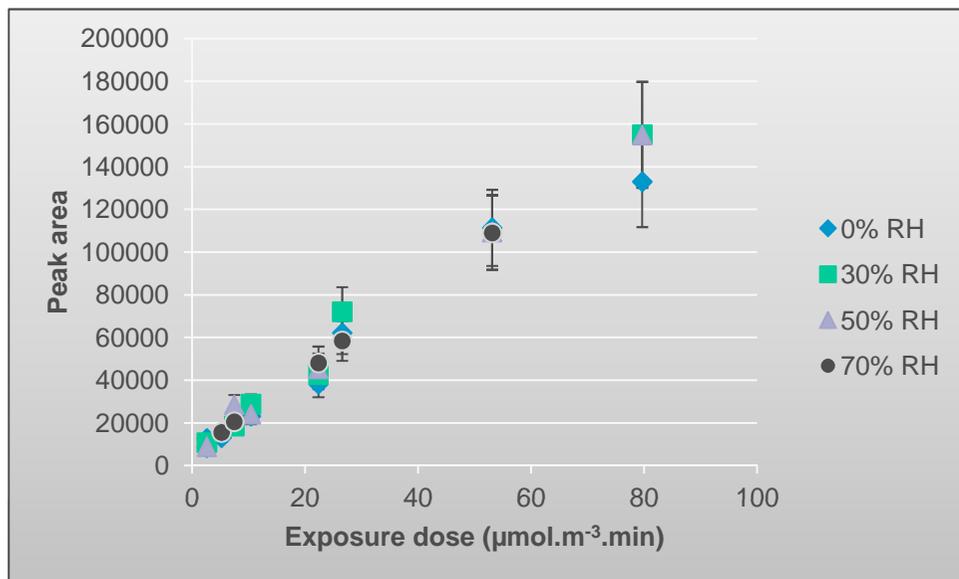


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# Influence of air relative humidity



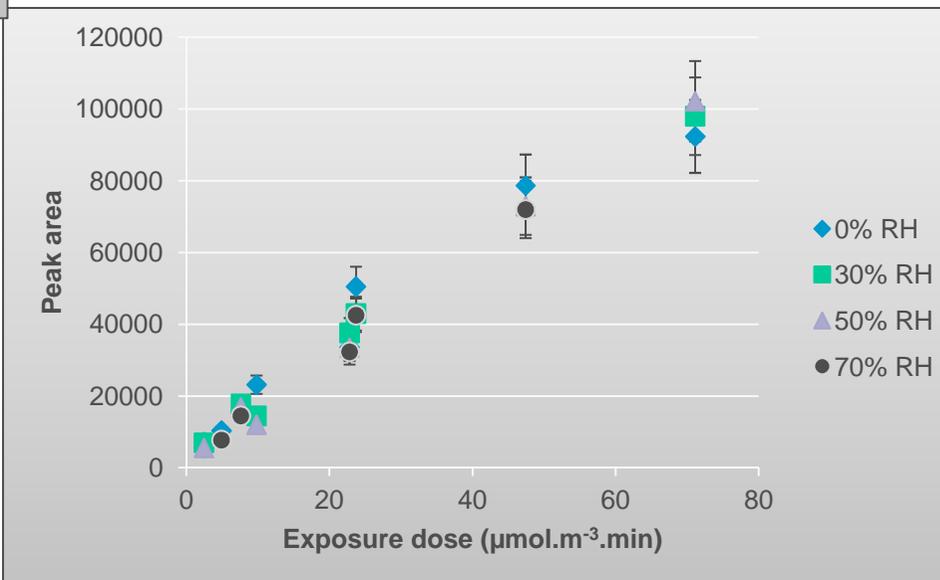
Formaldehyde



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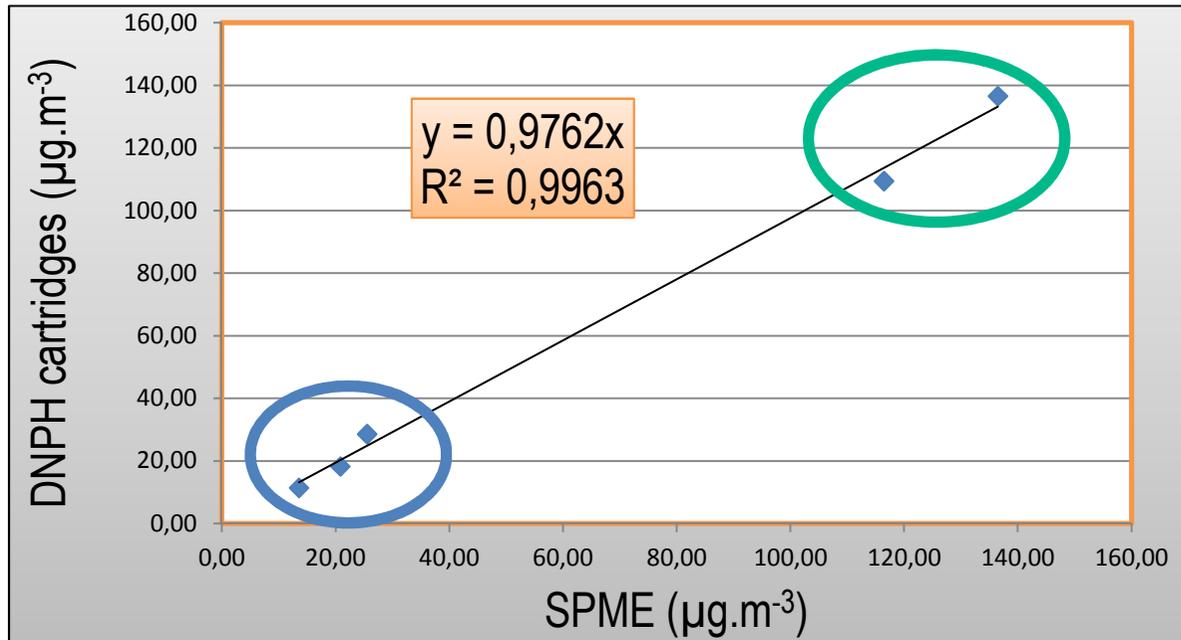
Alpha-pinene



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# Comparison with the standard method

|          | NF ISO 16000-3 (2002)<br>DNPH Cartridges                              | SPME  |
|----------|---|---|
| Sampling | 3.5 hours for indoor atmospheres<br>15 minutes for material emissions | Instantaneous sampling<br>15 minute SPME extraction |
| Analyses | HPLC/UV   | GC/FID  |



Material emissions in environmental chamber



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Indoor air



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# Case Study



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Office building located in Mont-de-Marsan (40)  
Occupied since one year  
Built in a HQE approach

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# Case Study



- ✓ Meeting room of 40 m<sup>2</sup>
- ✓ Study of indoor air by vacuum vial
- ✓ Study of surface's concentration by emission cell
  - Floor
  - Tables
  - Chairs
  - Doors
  - Ceiling
  - Roller blind



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➔ Identification of terpenes, aldehydes and alkanes

➔ 4 compounds belonging to our model compounds were quantified:  
alpha-pinene, formaldehyde, acetaldehyde and hexanal

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# Formaldehyde

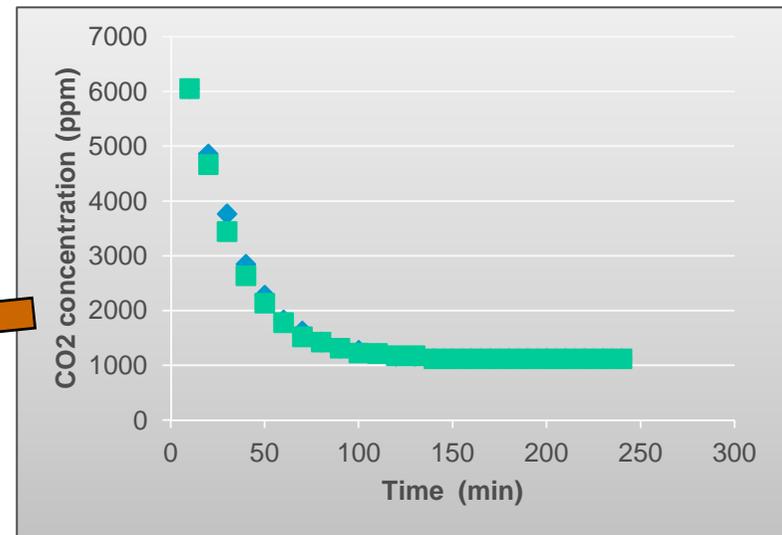
## Material emissions

| Surface                    | Air interface concentration ( $\mu\text{g.m}^{-3}$ ) |
|----------------------------|--|
| Table                      | 42.8   |
| Floor                      | 15.3   |
| Chair                      | 6.7  |
| Ceiling (painted part)     | 7.7  |
| Wall (paint)               | 10.1   |
| Door                       | 16.5   |
| Ceiling (ventilation area) | 11.8   |
| Roller blind               | 10.2   |

Indoor concentration ( $\mu\text{g.m}^{-3}$ )

7.0

Measurement of air exchange rates by  $\text{CO}_2$  injection



Indoor air quality modeling



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# Indoor Air Modeling

## Mass Balance

$$\frac{dC_i}{dt} = \sum_{j=1}^m Q_{ji} + \lambda_{air} f C_{ext} - \lambda_{air} C_i - U_{dep} \left(\frac{A}{V}\right) C_i$$

Indoor Concentration

Material Input

Outdoor Concentration

Room Ventilation

Sink Effect

$C_i$ : indoor air concentration (ppb)

$t$ : time (s)

$Q_{ji}$ : emission rate (ppb.s<sup>-1</sup>)

$\lambda_{air}$ : air exchange rate (s<sup>-1</sup>)

$C_{ext}$ : outdoor concentration (ppb)

$U_{dep}$ : deposit velocity (m.s<sup>-1</sup>)

$A$ : surface (m<sup>2</sup>)

$V$ : room volume (m<sup>3</sup>)

$f$ : penetration rate (0 < f < 1)

$$C_i(t) = C_0 e^{-(U_{dep} \frac{A}{V} + \lambda_{air})t} + \frac{\sum_{j=1}^m Q_{ji} + \lambda_{air} C_{ext}}{U_{dep} \frac{A}{V} + \lambda_{air}} \left(1 - e^{-(U_{dep} \frac{A}{V} + \lambda_{air})t}\right)$$



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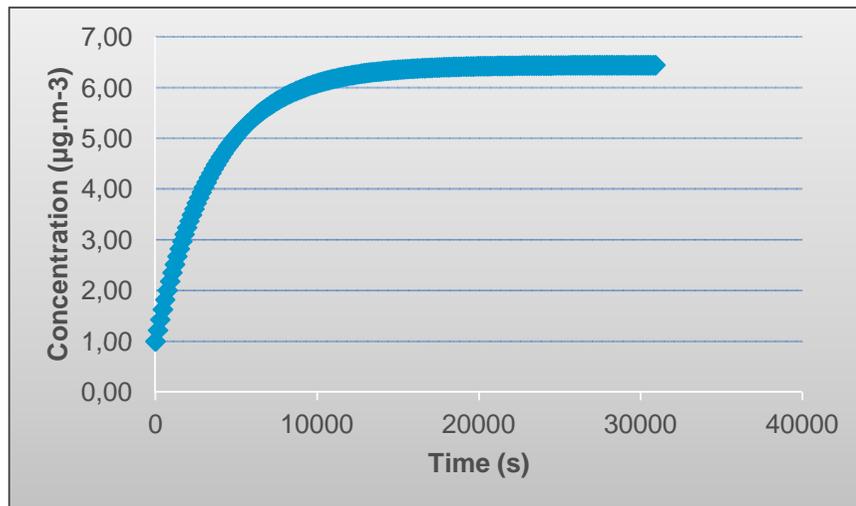
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# Indoor air modeling: application to formaldehyde

$$U_{\text{dep}} = 0 \text{ m.s}^{-1}$$
$$C_{\text{ext}} = 1 \text{ }\mu\text{g.m}^{-3}$$
$$\lambda_{\text{air}} = 0.98 \text{ vol/h}$$

Calculated formaldehyde concentration:  $6.4 \text{ }\mu\text{g.m}^{-3}$

Measured formaldehyde concentration:  $7.0 \pm 1.0 \text{ }\mu\text{g.m}^{-3}$



=> In accordance with the future French regulation ( $10 \text{ }\mu\text{g.m}^{-3}$ )



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- Emission rate calculated from the air/material interface concentration
- Modeling considering the air exchange rate and the “real” material contribution
- Possibility to try different scenarii in order to evaluate the impact of various parameters of building management: ventilation, materials....

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# Conclusion

- ✓ Fast, sensitive, easy to implement analytical method for the evaluation of **both VOCs and formaldehyde** was developed. Further comparisons with the standard methods will now be done.
- ✓ On-site determination of material emissions
- ✓ Modeling of indoor air quality:
  - First experiment in a new building very encouraging
    - The box model will be adjusted with a 6 month study in a newly built high school
      - Predictive tool of indoor air quality



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Thank you for your attention

Questions?



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