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Breathing City
Future Urban Ventilation Network

TAPAS
Tackling air pollution at school

Understanding indoor air quality for healthy buildings in a net zero world

ON-SITE CHARACTERIZATION METHOD FOR EMERGING SEMI-VOLATILE COMPOUNDS EMITTED BY MATERIALS - APPLICATION TO INDOOR AIR QUALITY IN SPORTS HALLS.

by Abigaël Souillier

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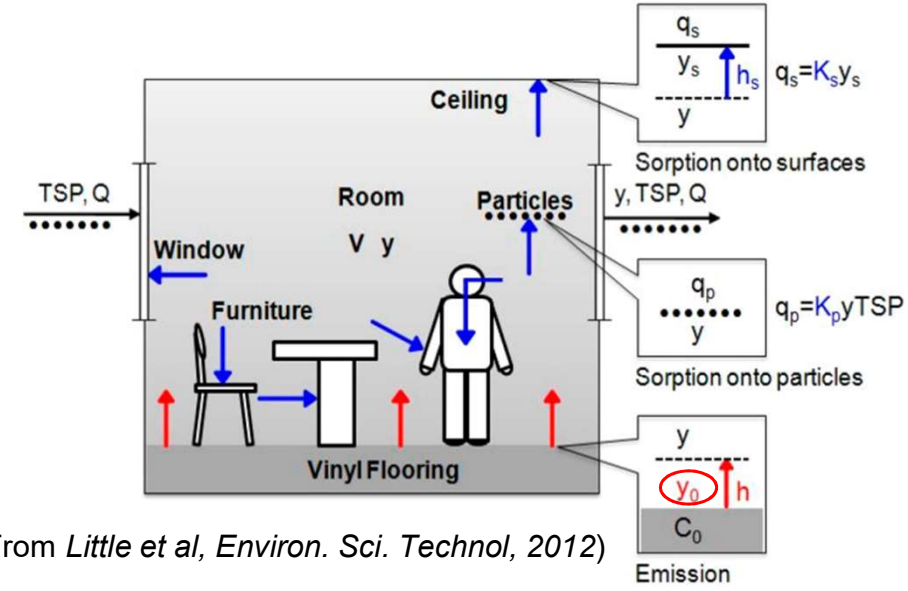
Context

- **SVOCs Definition :**
  - 10^{-5} à 10 Pa
  - 240 à 400°C
- **Compounds included in SVOCs :**
  - flame retardants
  - pesticides
  - phthalates
- **Adverse effects on health:**
  - ✓ endocrine disruption
  - ✓ reproductive disorder
  - ✓ cancer

- **In gaseous phase, major phthalates are DiBP, DEP and DBP (61-1300 ng/m^3)** *(Blanchard et al., Environ. Sci. Technol., 2014)*
- **In airborne and settled particles, major phthalate is DEHP (104-3214 µg/g)** *(Wang et al., Build. Environ., 2017)*

⇨ Multiple exposure pathways (inhalation, skin contact and ingestion)

⇨ Necessary to determine exposure level and sources



(From *Little et al, Environ. Sci. Technol, 2012*)

Gaseous concentration at the material surface (y_0) = key parameter

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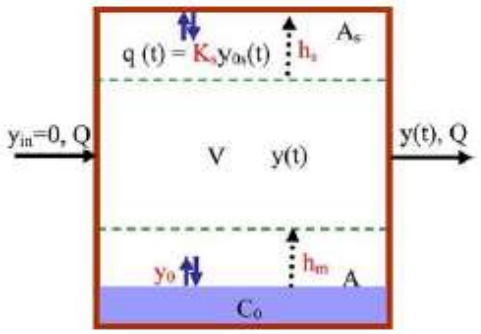
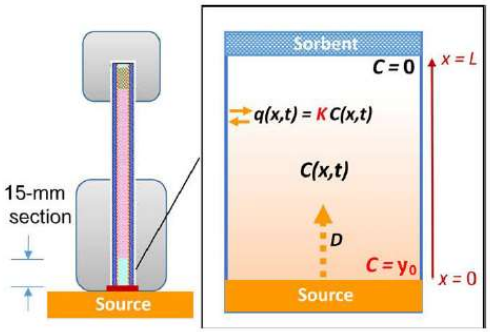
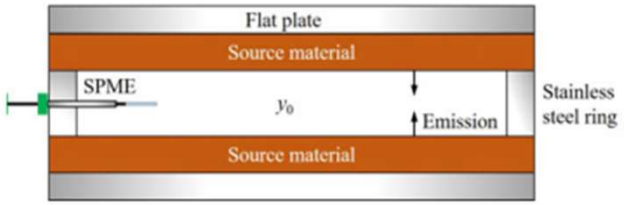
y_0 measurement methods for phthalates

Methods	Sampling type	Detected compounds	In situ ?	Experimentation time
Micro-chamber + GC **(ISO-16000-25, 2011)** *(Braish, 2019)*	Active	DnOP, DiNP	No	X
Passive Tenax sampling + GC *(Wu et al., Indoor Air, 2016)*	Passive	DiBP, DnBP, DEHP	Yes	> 200h
Sandwich-like chamber + GC *(Cao et al., Indoor Air, 2017)*	Passive	DEHP	No	24h





- Not suitable for on-site measurement
- No direct determination of y_0



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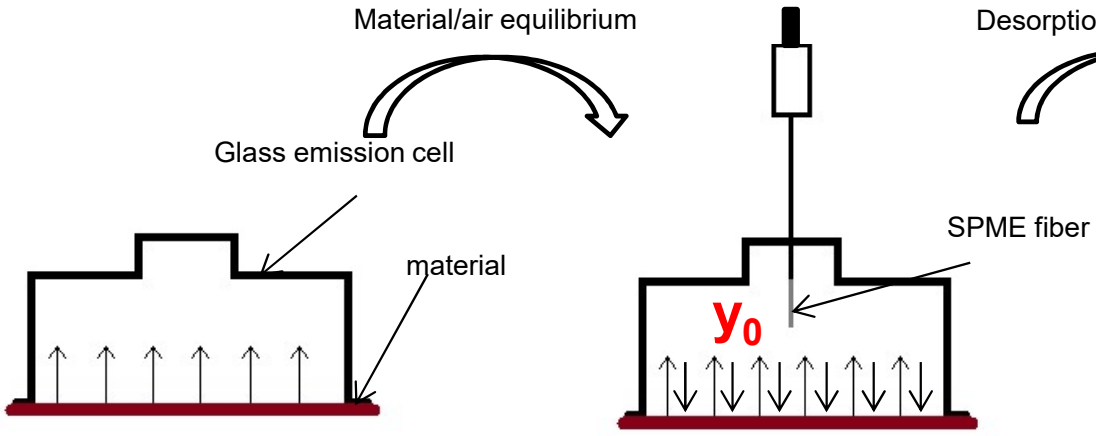
SPME-MOSEC based method

(Ghislain et al., Anal Bioanal Chem, 2017; Plaisance et al., Anal. Chim. Acta, 2021)

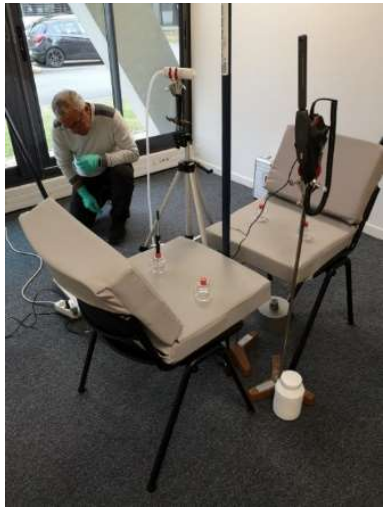
MOSEC = Midget On-Site Emission Cell



1- Material emission

2- SVOC sampling
Solid-Phase Microextraction (SPME)

3- SPME fiber thermal desorption and analysis by GC-MS-FID



Easy to perform at laboratory and on site, but:

Quantification is challenging : well controlled calibration atmosphere needed

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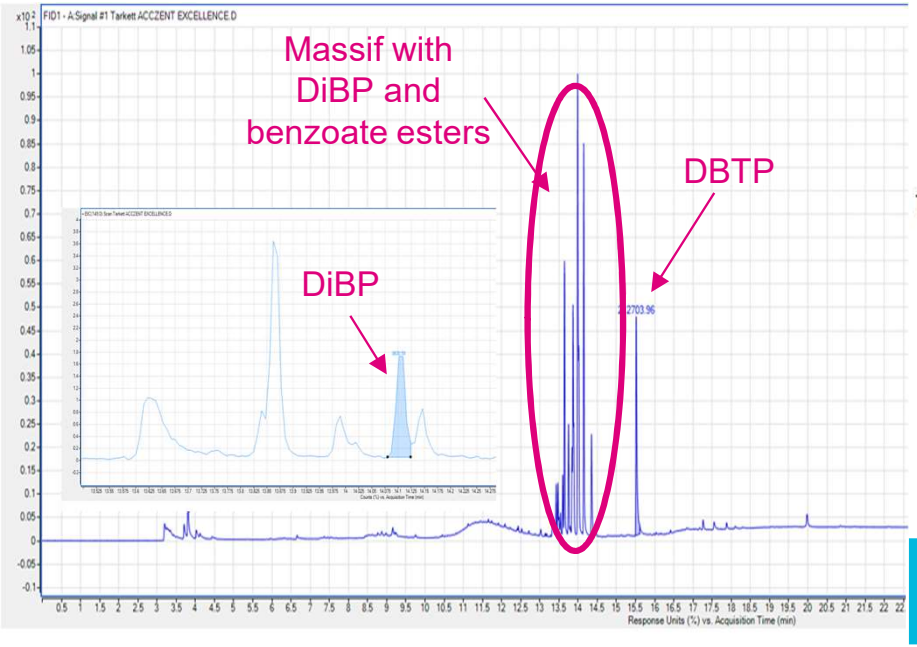
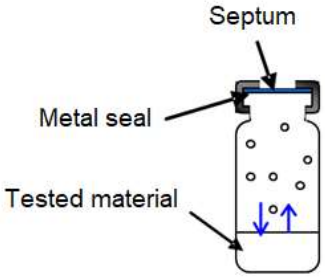
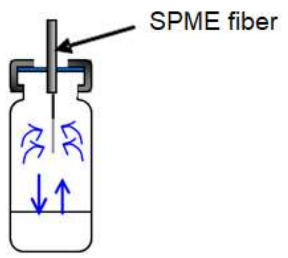
PVC floorings and compounds studied





Step 1 : heating (60°C) and equilibration (4h)



Step 2 : SPME sampling (PDMS 100 µm fiber, 10 min)

Step 3 : GC-MS/FID analysis

DiBP, DBTP and benzoate esters detected in PVC 1-4

DBTP and benzoate esters reported as phthalate alternatives

(Stimpson et al., 2012; Bonhert et al., 2014)

	DiBP	DEHP	DBTP	Octyl benzoate	Heptyl benzoate
Boiling point (°C)	278	385	278	234	220
Molecular formula	$C_{16}H_{22}O_4$	$C_{24}H_{38}O_4$	$C_{16}H_{22}O_4$	$C_{15}H_{22}O_2$	$C_{14}H_{20}O_2$
Pv (Pa at 25°C)	$6.34x10^{-3}$	$1.30x10^{-3}$	N.D.	N.D.	N.D.
CAS n°	84–69–5	117-81-7	1962–75–0	94-50-8	7155-12-6

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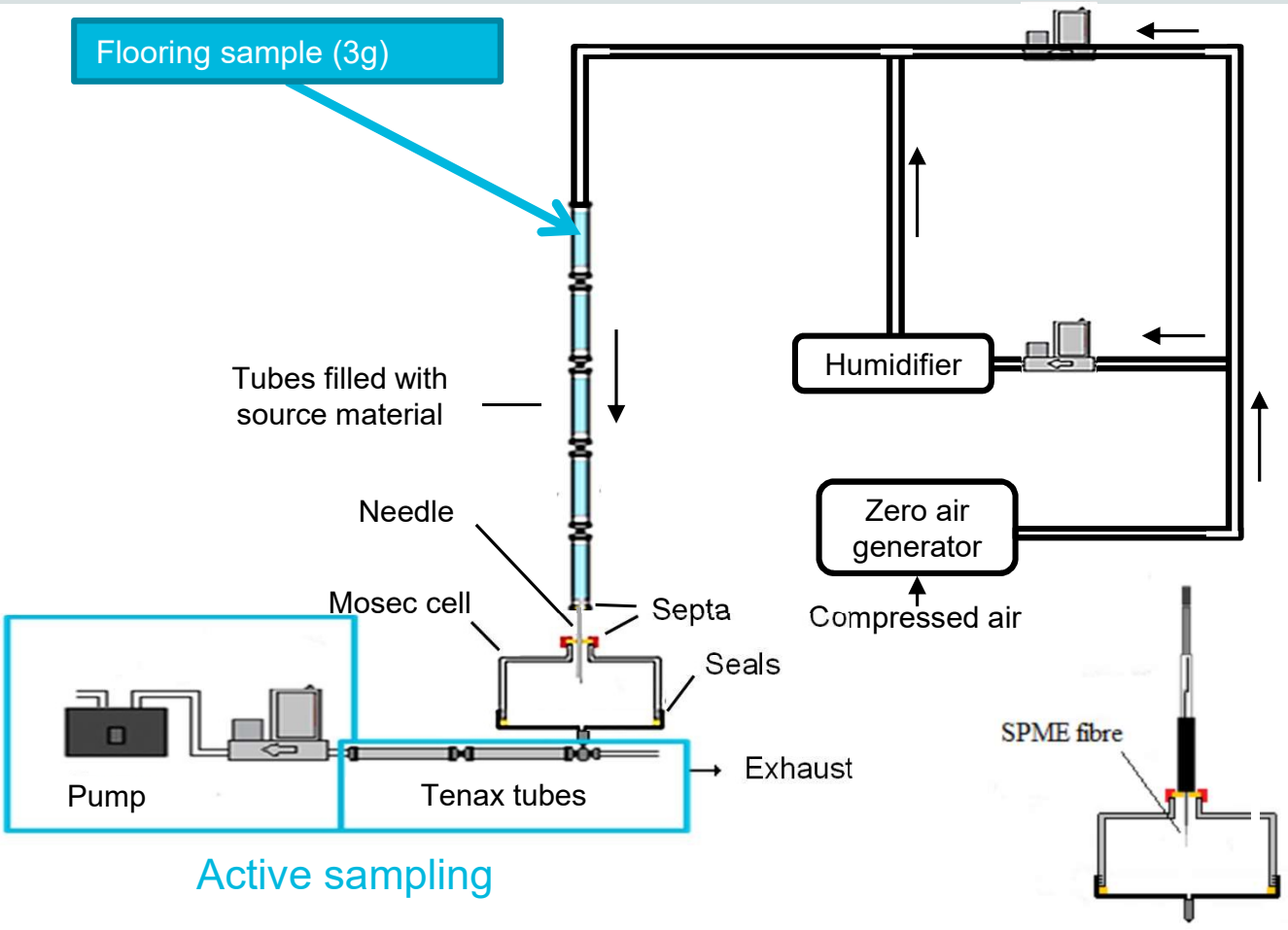
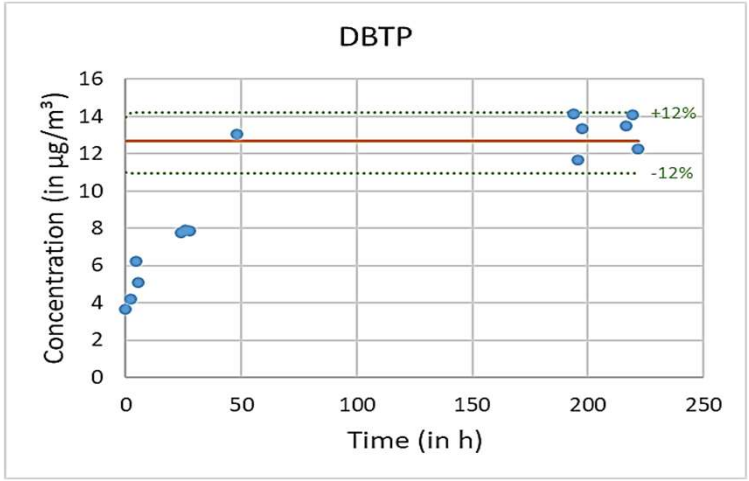
Calibration gas generation using emissive material

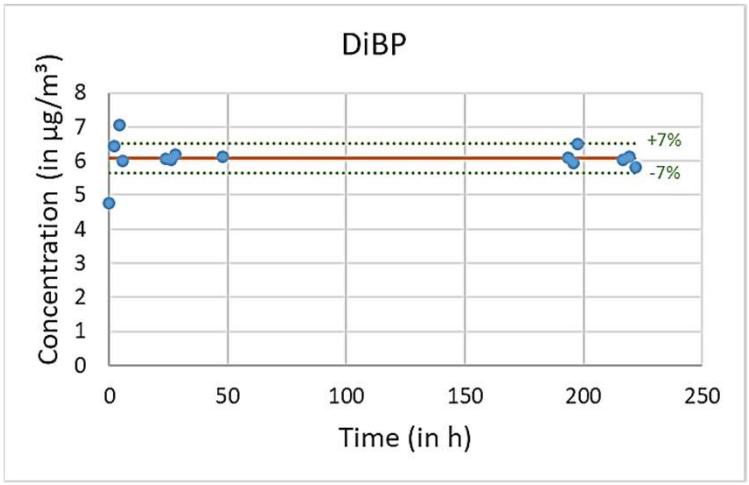
(Plaisance et al., Analytica Chimica Acta, 2021)



Active sampling

Calibration gas stabilization





Stabilization time : 50 h

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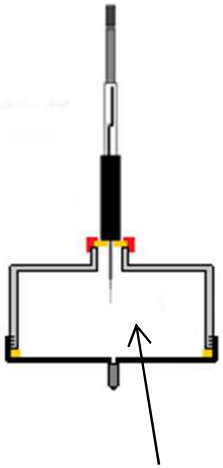
Calibration gas generation using emissive material

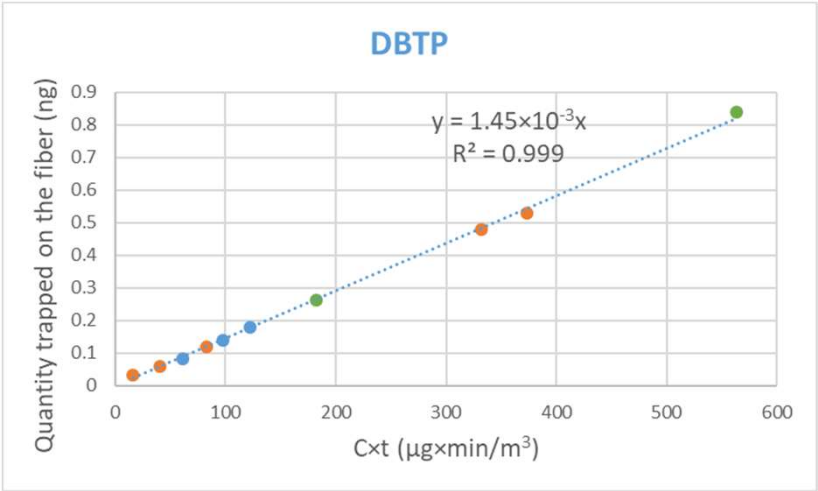


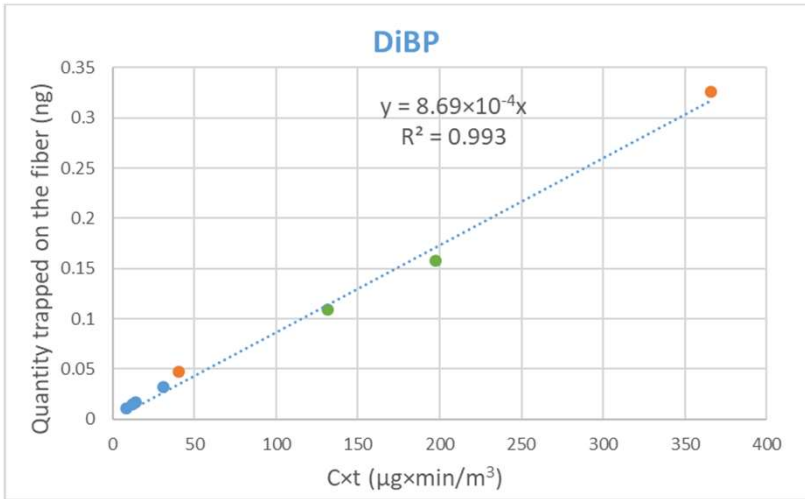
Concentration C :
- C(DiBP) = 6.1 µg/m³
- C(DBTP) = 13.2 µg/m³

- ❑ SPME fiber: PDMS 100 µm
- ❑ Different exposure times in the cell (2 to 90 min)

SPME = passive sampler → n = f(C xt)

SPME Tenax





Obtained by combining three series of measurements (renewed material in stainless tubes)

$R^2 > 0.99$

- ➢ No significant deviation between the three series
- ➢ Linear range extended up to :
  24 µg/m³ for DiBP and 38 µg/m³ for DBTP (15 min SPME extraction time)

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Method performance

DiBP	FID	TIC (MS)	EIC 149 (MS)
LOD (µg/m³)	0.5	1.0	1.0
LOQ (µg/m³)	2.0	4.0	4.0
RSD (n=6)	28%	8.8%	10.7%

DBTP	FID	TIC (MS)	EIC 205 (MS)
LOD (µg/m³)	2.0	0.4	0.4
LOQ (µg/m³)	5.0	2.0	1.0
RSD (n=6)	19.1%	3.7%	3.2%

- LOD : 0.4 – 4.0 µg/m³
- LOQ : 1.0 – 5.0 µg/m³
- RSD : 3.2 – 28%

Conditions:

- **SPME sampling time : 15 min**
- **RSD :**
  - DiBP concentration level : 0.8 ± 0.2 µg/m³
  - DBTP concentration level : 3.0 ± 0.5 µg/m³

	SPME sampling time	
	20 min	40 min
DiBP:		
LOD (µg/m³)	0.2	0.1
LOQ (µg/m³)	0.8	0.4
DBTP:		
LOD (µg/m³)	0.6	0.3
LOQ (µg/m³)	2.1	1.0

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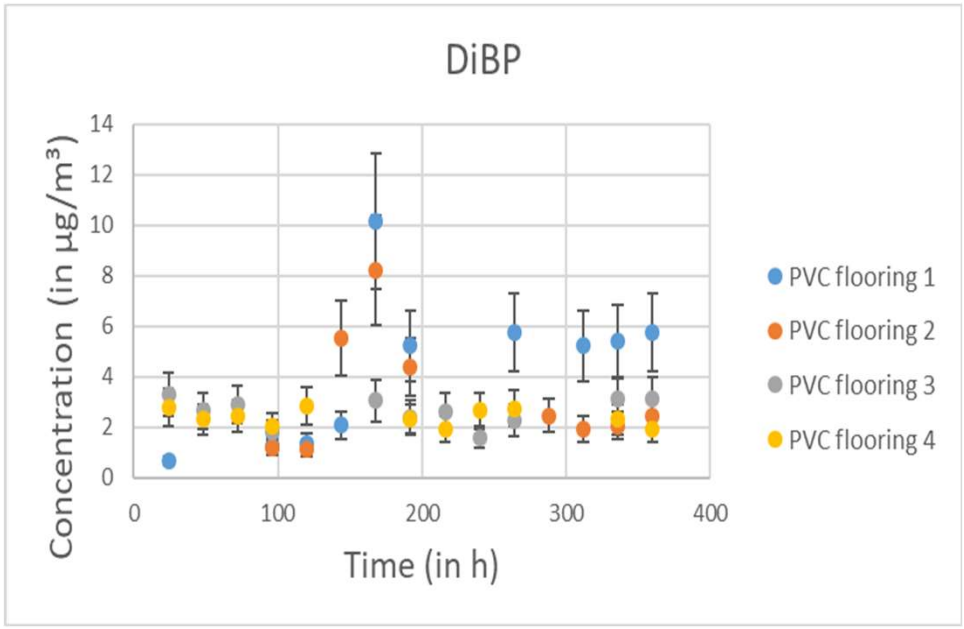
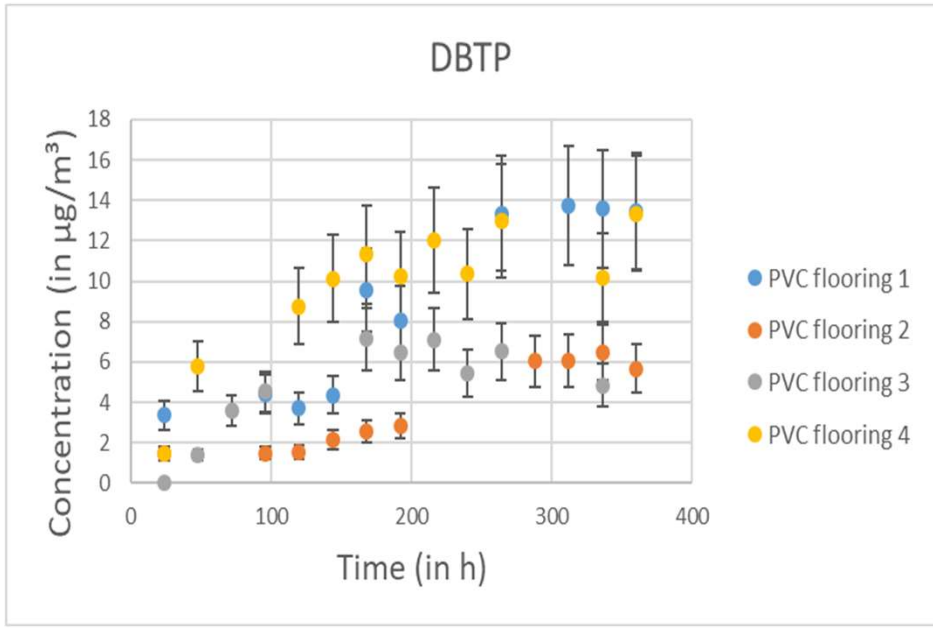
y_0 for studied floorings: determination of equilibrium time

SPME sampling time : 15 min





DiBP concentration stabilization time : 24h

DBTP concentration stabilization time : 300h

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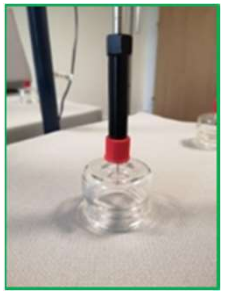
y_0 for studied floorings : results



Equilibration time : 360h
SPME sampling time : 15 min

⇩

- y_0 for DBTP between 2.0 and 6.0 µg/m^3
- y_0 for DiBP between 6.0 and 14.0 µg/m^3

Flooring n°	y_0 for DiBP (µg/m^3)	y_0 for DBTP (µg/m^3)
1	6.0 ± 0.3	14.0 ± 0.1
2	2.0 ± 0.3	6.1 ± 0.3
3	3.0 ± 0.6	6.0 ± 1.0
4	2.0 ± 0.4	12.0 ± 2.0

To compare, y_0 measured for DiBP in litterature is :

- 68 µg/m^3 *(Cao et al., Environ. Sci. Technol., 2016)*
- 49.8 µg/m^3 *(Liang et Xu, Environ. Sci. Technol., 2014)*

More recently :

- 13.5 µg/m^3 *(Yang et al., J. Hazard. Mater., 2020)*

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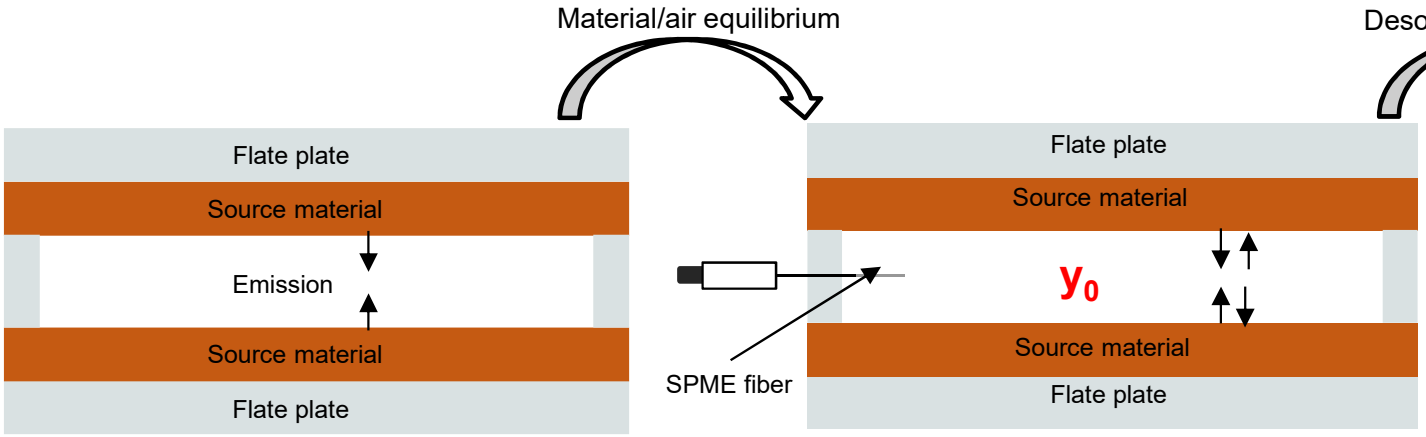
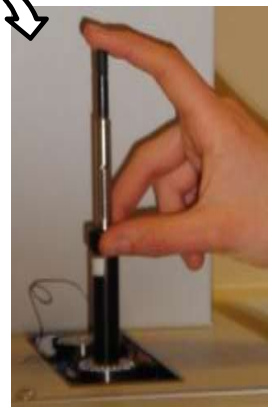
SPME-sandwich cell method

Used for intercomparison with MOSEC-SPME based method

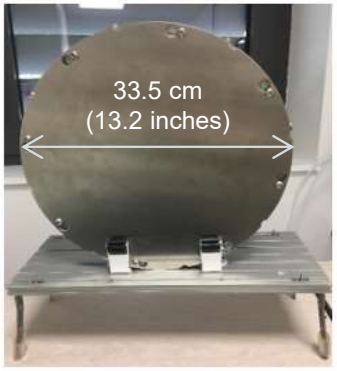


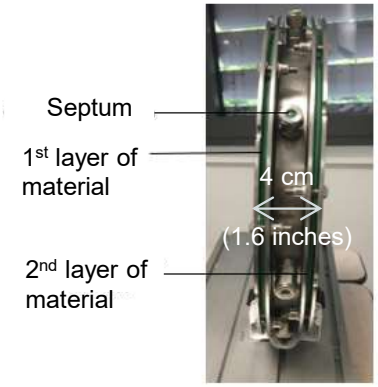
Step 1 : equilibration phase

Step 2 : SPME sampling



Step 3 : SPME fiber thermal desorption and analysis by GC-MS-FID





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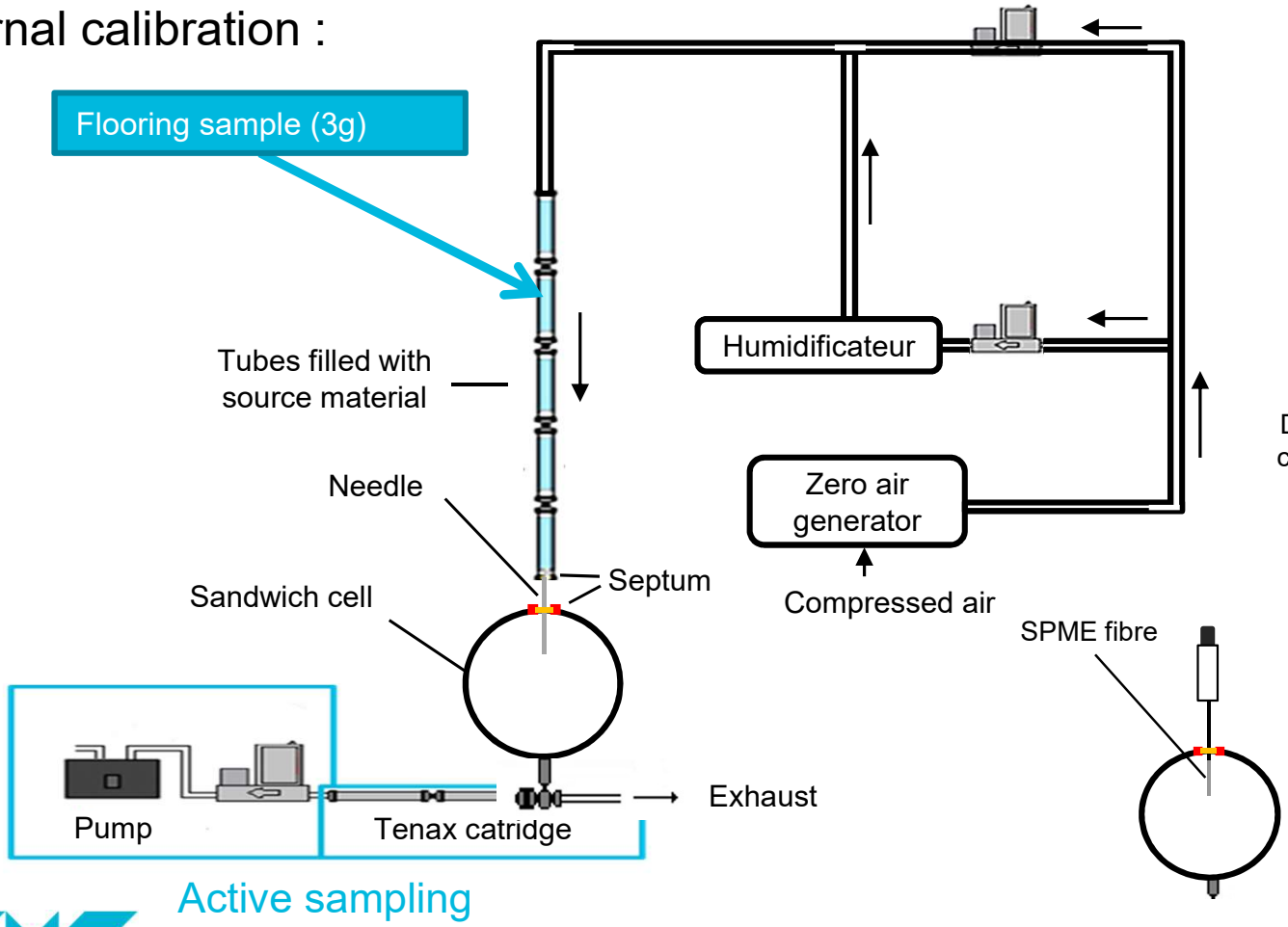
Calibration of the SPME-sandwich cell method

External calibration :



Active sampling

Modelisation :

Slope of the equation n = f(t)

$$y_0 = \frac{a}{D_a \times S}$$

Diffusion coefficient of the compound in the air (m²/s)

$$S = 4\pi L\sqrt{1-\gamma^2}/\ln\left(\frac{1+\sqrt{1-\gamma^2}}{1-\sqrt{1-\gamma^2}}\right)$$

$$\gamma = D/L$$

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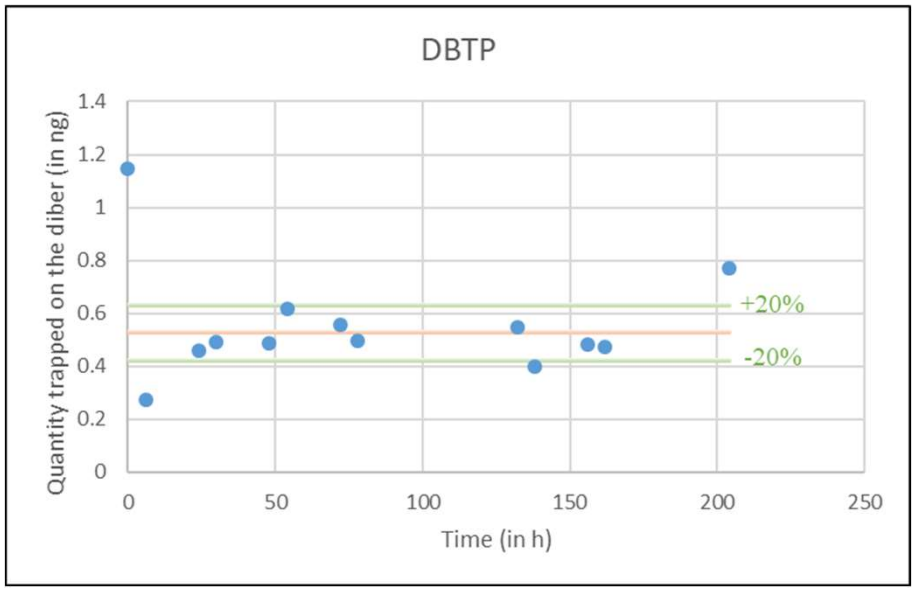
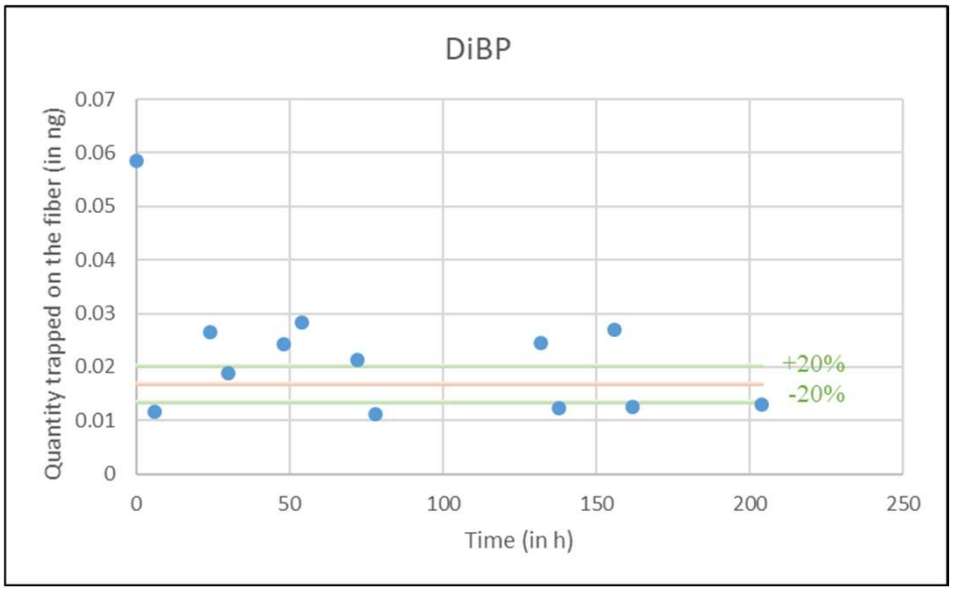
(Plaisance et al., Analytica Chimica Acta, 2021)

y_0 for studied floorings: determination of equilibrium time

SPME sampling time : 15 min





Stabilization time for DBTP : 24h

Stabilization time for DiBP : 6h

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Conclusion

SPME-MOSEC method :

- The MOSEC-SPME based method is suitable to characterize phthalates and their alternatives (terephthalate + benzoate esters) emitted by PVC floorings.
- Calibration has been successfully realized for DiBP and DBTP and calibration curves show a satisfying linearity ($R^2 > 0.99$), Calibration for DEHP is in progress,
- LOD and LOQ below µg/m^3 reached for 20-40 min SPME extraction times

SPME-sandwich cell method used to compare y0 results:

- Stabilization time of 6h for DiBP and 24h for DBTP

Upcoming :

- SPME-sandwich cell method calibration (DBTP, DiBP and DEHP)
- Dynamic sandwich cell method
- In-situ measurements in sports halls (QAI-Sport project, suported by ADEME)

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THANK YOU FOR YOUR ATTENTION