Alternative method for the measurement of formaldehyde and carbonyl compounds in indoor environments

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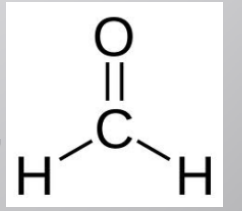
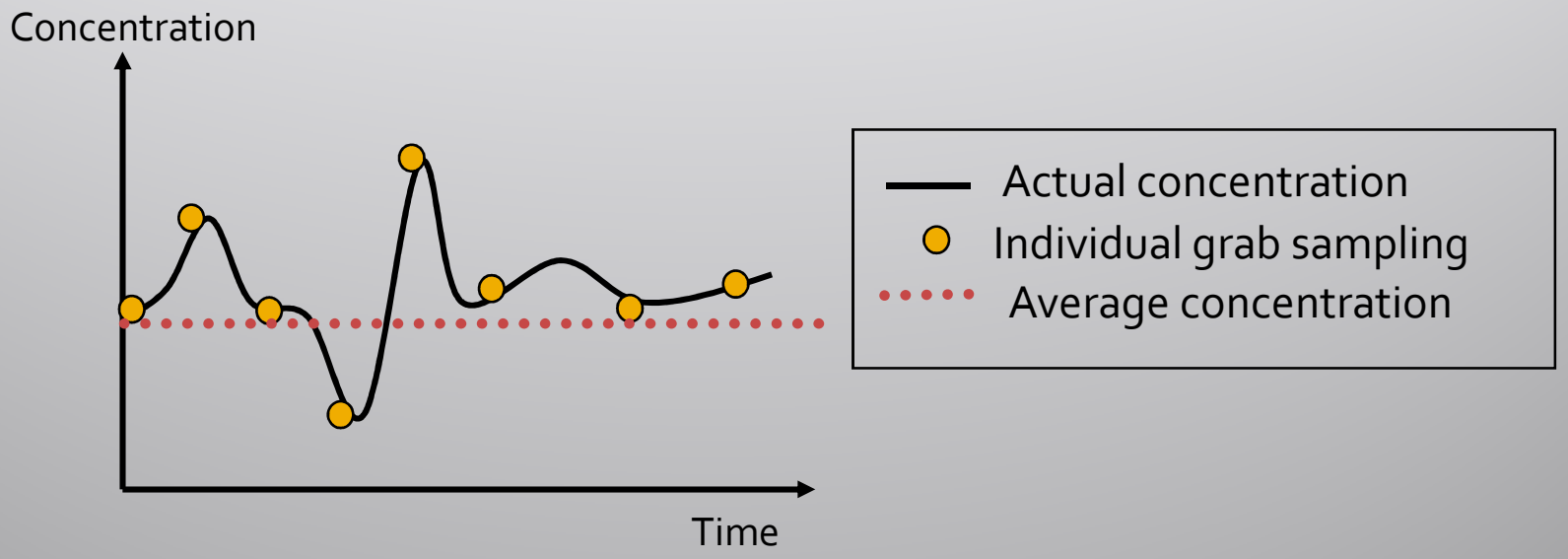
Formaldehyde and carbonyls compounds



- **Formaldehyde:**
  - Frequently found in indoor environments (building materials, combustion, chemical reactions…)
  - « ***Carcinogenic to humans*** » (class 1, IARC), priority substance (OQAI)
  - French Guide Value for Indoor Air: **10 µg.m^{-3} (**long term exposure)
- **Acetaldehyde**:
  - Main sources: plywood products, chemical reactions,…
  - « May be carcinogenic to humans » (class 2B, IARC), priority substance (OQAI)
- **Hexanal:**
  - Plywood panels, wood treatment products, solvent based paints, …
  - Relatively high concentrations:1 – 106 µg.m^{-3} *(dwelling campaign, OQAI, 2001)*
- …

Two sampling strategies



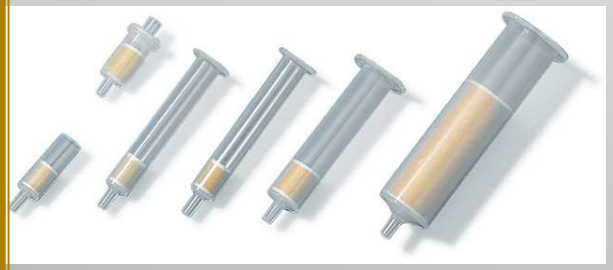
➡ **GRAB SAMPLING**

Which gives information about the evolution of pollutant concentration.

➡ **TWA SAMPLING**

Which allows the determination of average concentration for the evaluation of long term exposure.

Grab sampling: active method
(NF ISO 16000-3, 2002)



On-site sampling with DNPH cartridges

Desorption in Acetonitrile

HPLC Analysis
UV Detection

☹

✓ Long sampling time (up to 24 hours [1] for $[HCHO]_{air} \approx 5\ \mu g.m^{-3}$)

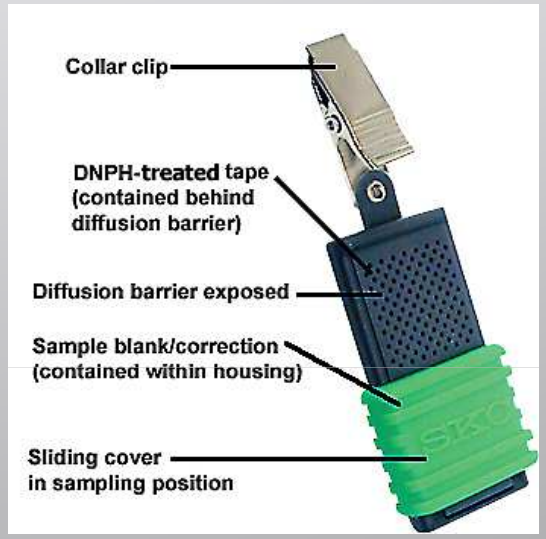
✓ Implementation: needs pump, flow-meter, tubing…

✓Solvent desorption

[1] *Mesure des aldéhydes dans l'air ambiant à Paris*, Véronique Eudes et al., Laboratoire Central de la Préfecture de Police de Paris

TWA sampling: passive method
(NF ISO 16000-4, 2006)

Radiello® tubes



UME^{x} Sampler

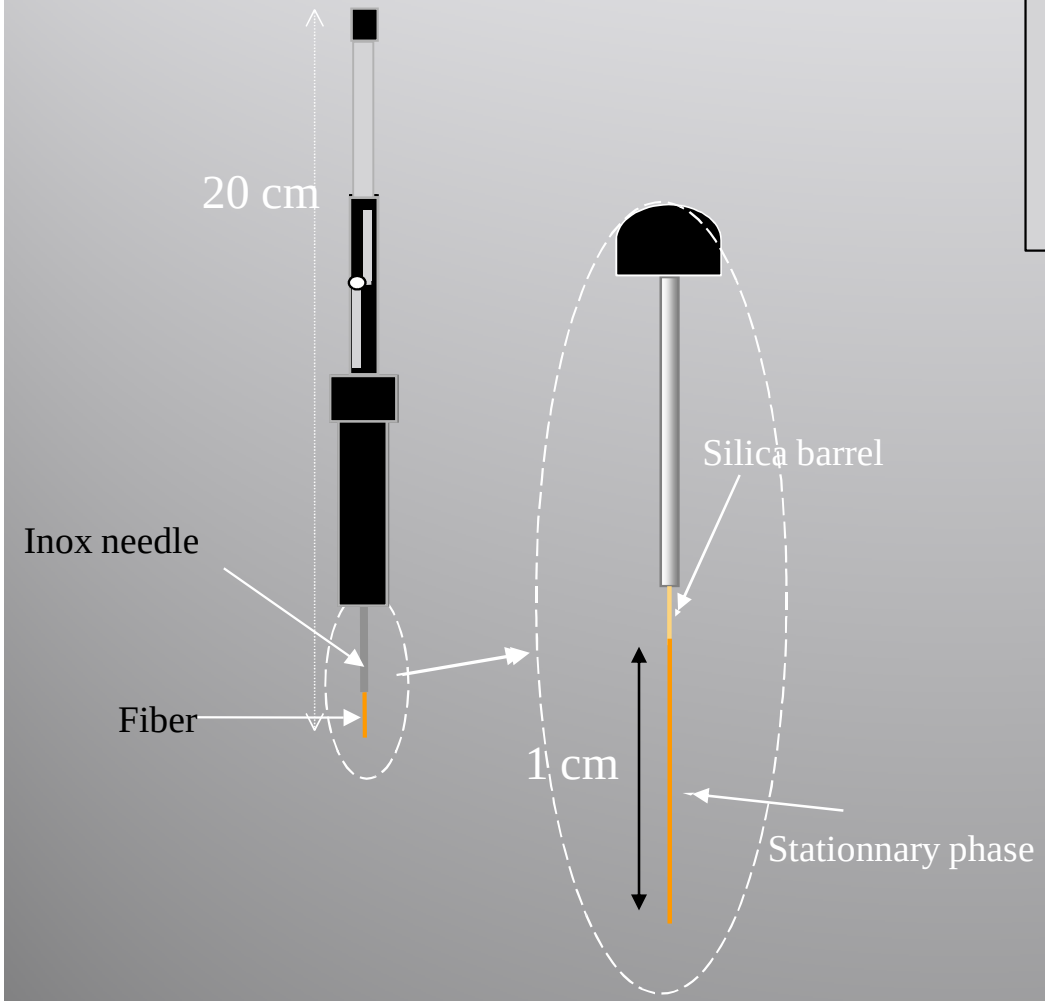
☺

- ✓ No pump
- ✓ Easy to use
- ✓ Time weighted average

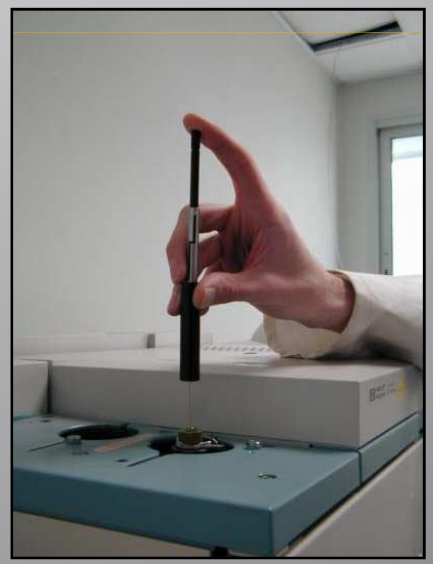
☹

- ✓ Solvent desorption

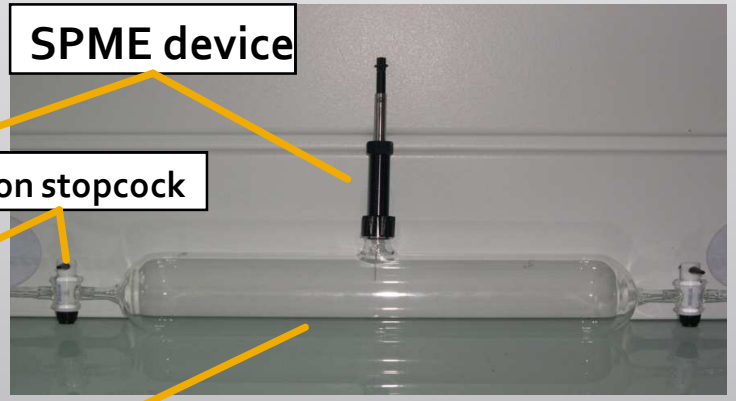
Solid Phase Micro-Extraction (SPME): An Alternative Passive Technique

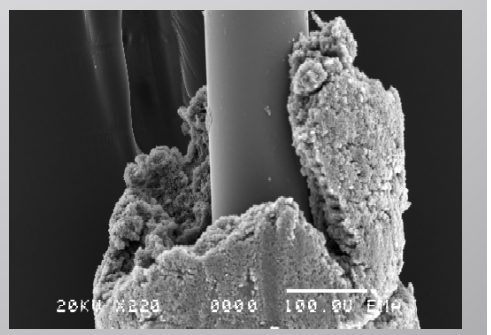


- Easy to use (passive sampling)
- One step thermal desorption in a classic GC injection port
- Solvent-free technique



First application: Grab sampling of VOCs[2]





PDMS/Carboxen fiber

- Air sample is enclosed in a glass bulb
- A SPME fiber is exposed to the air: PDMS/Carboxen fiber chosen
- GC Analysis with FID or MS detection

Equilibrium:
3 hour extraction in 250 mL
⇒ Mean LOD: 0.2 µg.m^{-3}

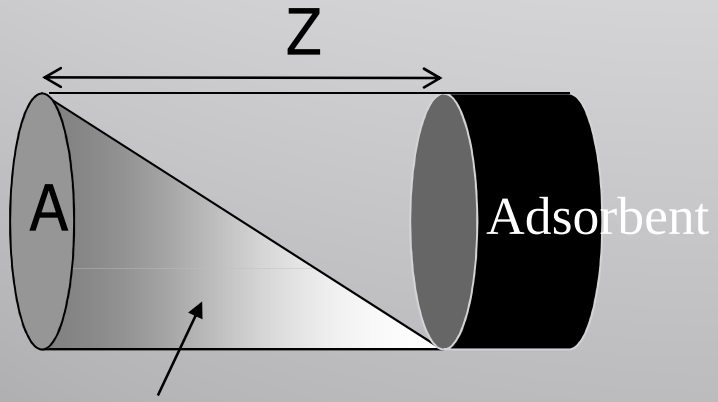
Non-equilibrium

First Fick's Law

[2] Larroque V, Desauziers V, Mocho P, *J. Environ. Monit.*, 2006, **8**, 106-111

First Fick's law of diffusion

➡ Used for passive samplers



Concentration gradient when $C_{sorb}=0$

$$n_f = D * \frac{A}{Z} \int (C_a - C_{sorb}) dt$$

n_f : Extracted amount on the adsorbent (µg)
D : Diffusion coefficient ($cm^2.min^{-1}$)
A : adsorbent section (cm^2)
Z : Diffusion length (cm)
Ca : concentration in air ($\mu g.cm^{-3}$)
C_{sorb} : Surface concentration ($\mu g.cm^{-3}$)
t : Extraction time (min)

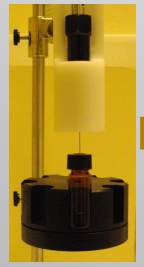
➡ At the beginning of sampling, C_{sorb} can be neglected:

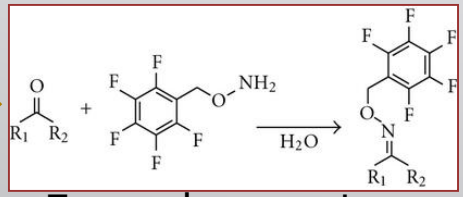
$$n_f = \underbrace{D * \frac{A}{Z}}_{\text{Uptake rate (U)}} * C_a * t \quad \Rightarrow \quad \boxed{n_f = U.(C_a * t)}$$

Performances for VOCs analysis (GC/MS)

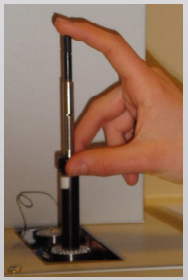
Compound	Ions for quantification (m/z)	Limits of detection in µg.m^{-3} (1L – 4 min)	Limits of quantification in µg.m^{-3} (1L - 4 min)	Reproducibility (n=5) (% RSD)
Acetone	43+58	1.4	4.5	5
Benzene	78	2.2	7.4	4
Cyclohexane	84+56	0.7	2.2	20
Trichloroethylene	95+130	0.8	2.5	9
Toluene	91	2.9	9.5	6
Butyl acetate	56+43	2.7	9.2	19
p-xylene	91+106	0.5	1.8	10
α-Pinene	93	0.4	1.3	7
n- decane	57+43	5.3	17.5	12
		Mean = 1.9	Mean: 6.2	Mean = 10.2

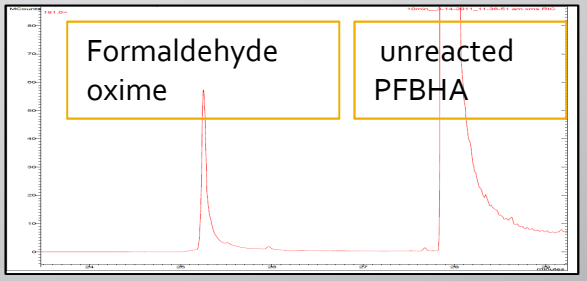
Formaldehyde SPME sampling





Example: reaction with PFBHA





GC/MS analysis (PDMS-DVB fiber)

- Loading of the derivatization reagent on the fiber
- On-fiber derivatization during the exposure to gaseous formaldehyde [3]
- Thermal desorption into a GC injector
- GC analysis (FID or MS detection)

[3] Jacek A. Joziel, Japeth Noah and Janusz Pawliszyn, *Environ. Sci. Technol*. 2001. **35,** 1481-1846

Development of the analytical method for formaldehyde SPME sampling

Three different coatings:

- PDMS/Carboxen
- PDMS/ DVB*
- PDMS/DVB*/Carboxen

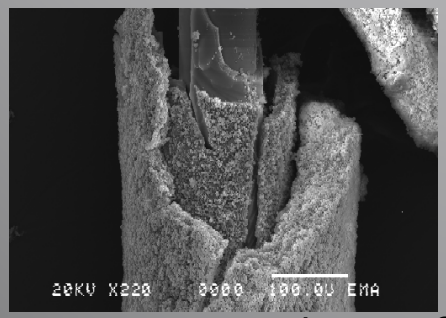
* DiVinylBenzene

Stationary Phase	BET** Surface ($m^2.g^{-1}$)	Porous volume ($mL.g^{-1}$)		
		Micro	Meso	Macro
DVB	720	0.29	0.26	0.23
Carboxen	750	0.11	0.85	0.58

** BET: Brunauer, Emmet, Teller

Two derivatization reagents:

- Pentafluorophenylhydrazine (PFPH)
- (o-2,3,4,5,6-pentafluorobenzyl)hydroxylamin (PFBHA)

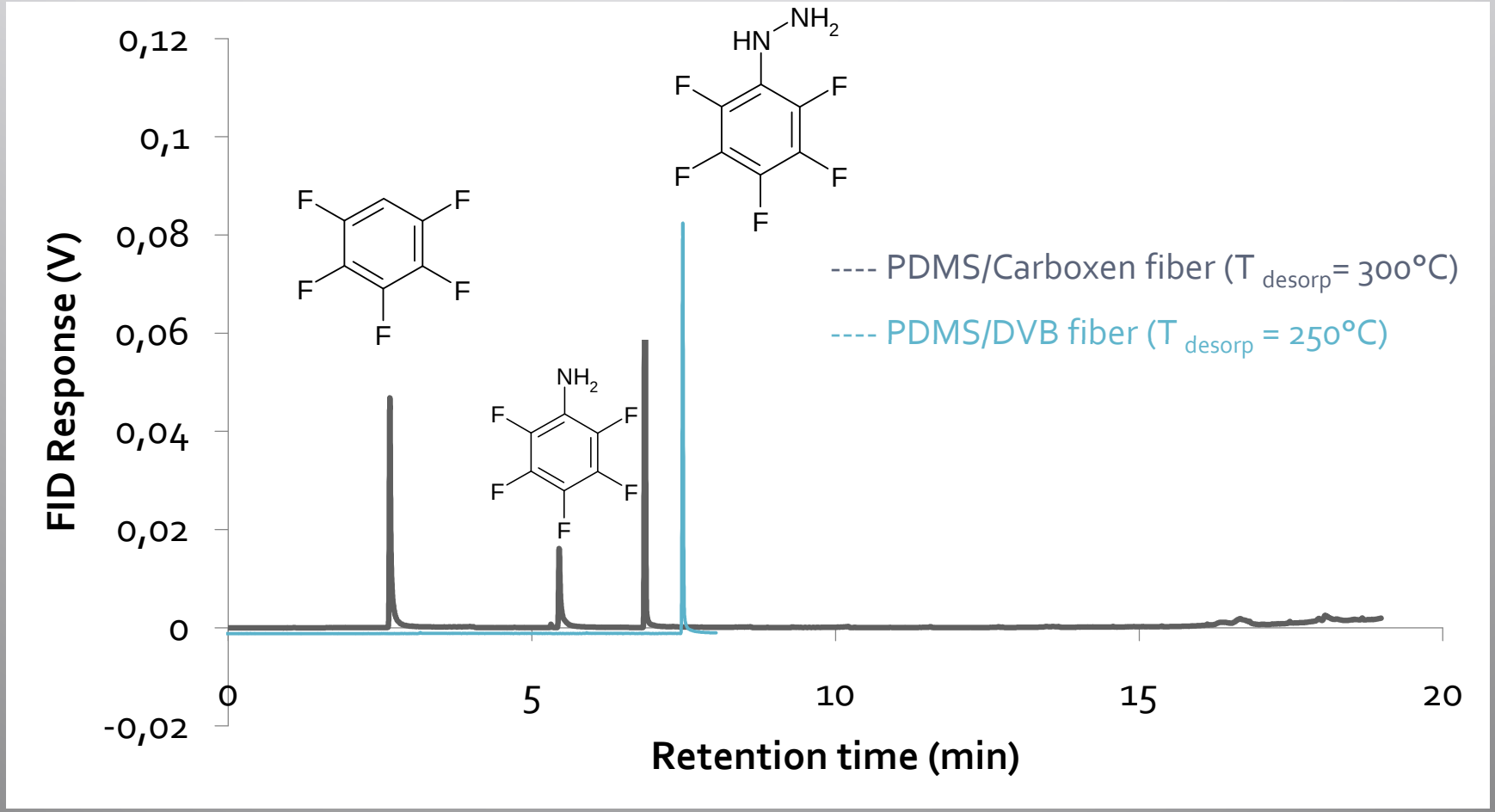


PDMS/DVB/Carboxen fiber

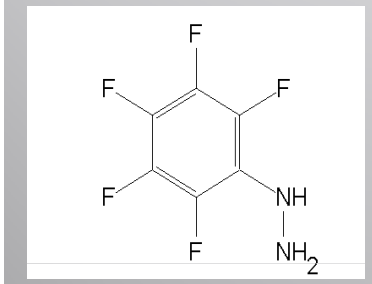
Loading processes:

- Pure product heated
- From an aqueous solution

Choice of the fiber coating

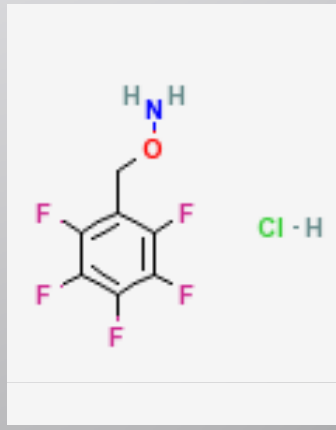


Choice of the derivatization reagent



PFPH

- PDMS/DVB Fiber loaded with the derivatization reagent
- Fiber exposed to standard atmospheres of formaldehyde (permeation device)
- Analysis by GC/MS of the derivatives formed on the fiber



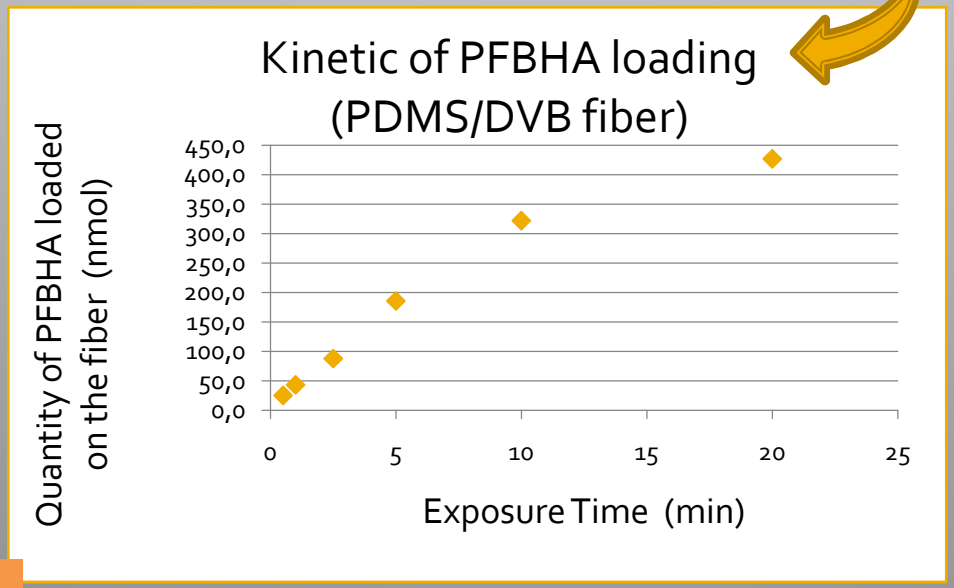
PFBHA

Derivatization not easy to implement

On-fiber derivatization easily performed at room temperature

Development of the loading process

	Pure product 50 c	Aqueous solution 23 C
Equilibrium time	10 min (?)	20 min
Quantity of PFBHA loaded on the fiber (nmol)	80	420
Reproducibility (% RSD)	32	5



Loading applied:

30 s

25 nmol PFBHA

0.75 µg HCHO…

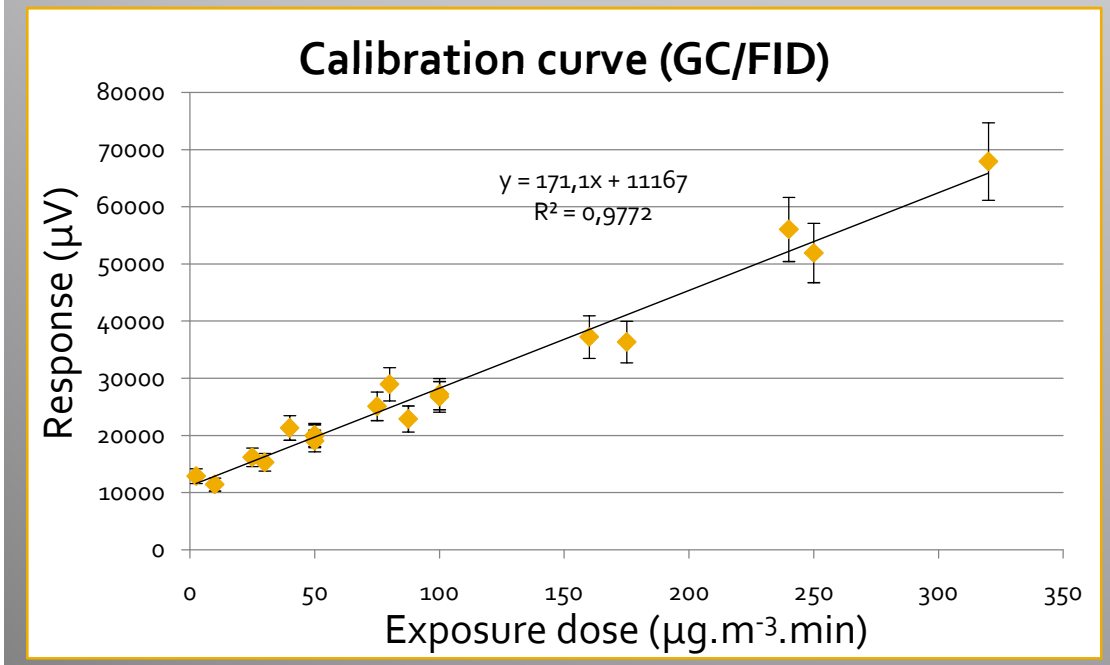
…in 250 mL: 3 $mg.m^{-3}$

Analytical Performances

- Fiber exposed to standard atmospheres
- SPME extraction in static mode into a 330 mL glass bulb

Formaldehyde concentration (C): 2.5 – 80 µg.m^{-3}
Exposure time (t): 0.5 – 60 min

Exposure dose C*t (µg.m^{-3}.min)

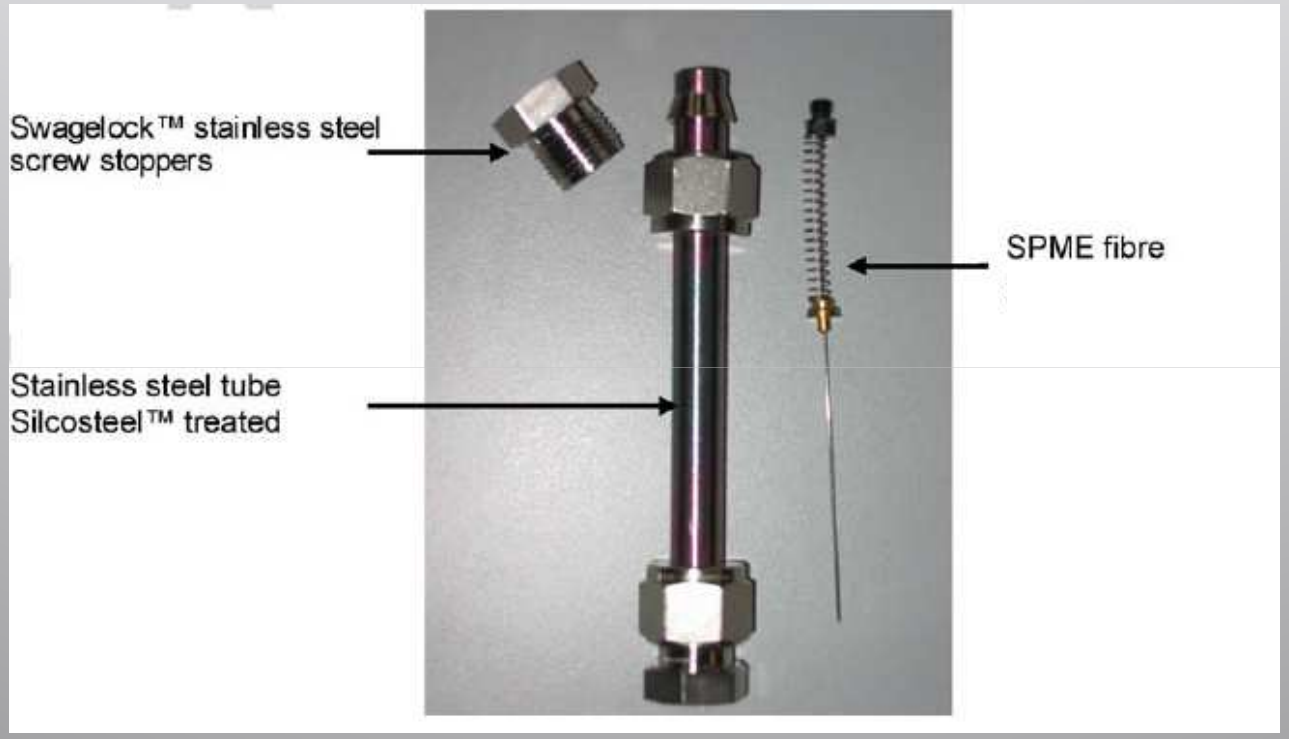


	GC/FID	GC/MS SIM Mode (m/z 181)
LOD	0.9 µg.m^{-3}	1.2 µg.m^{-3}
LOQ	2.7 µg.m^{-3}	3.7 µg.m^{-3}

20 min exposure

Repeatability: 14% RSD (n=6)

Sample storage[4]

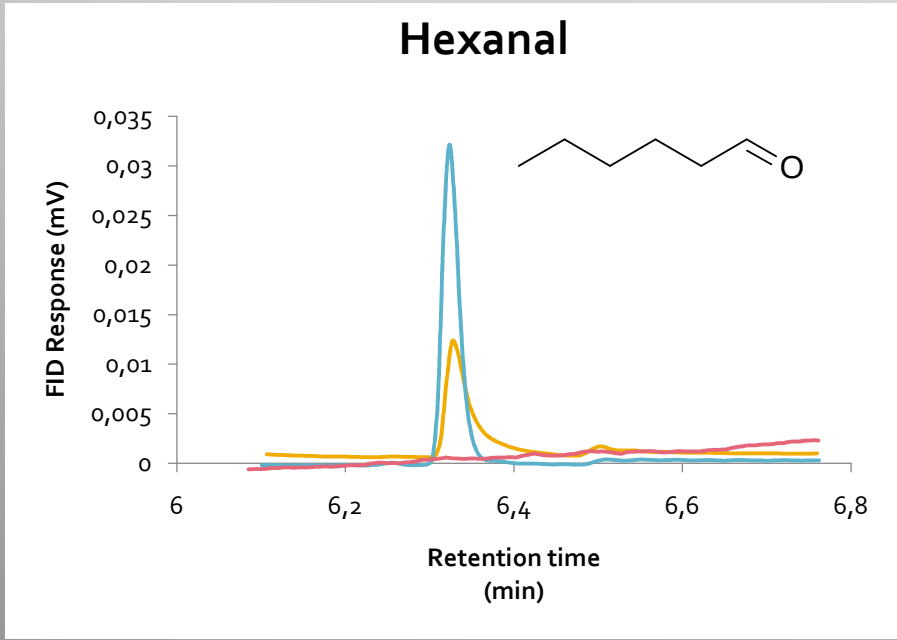


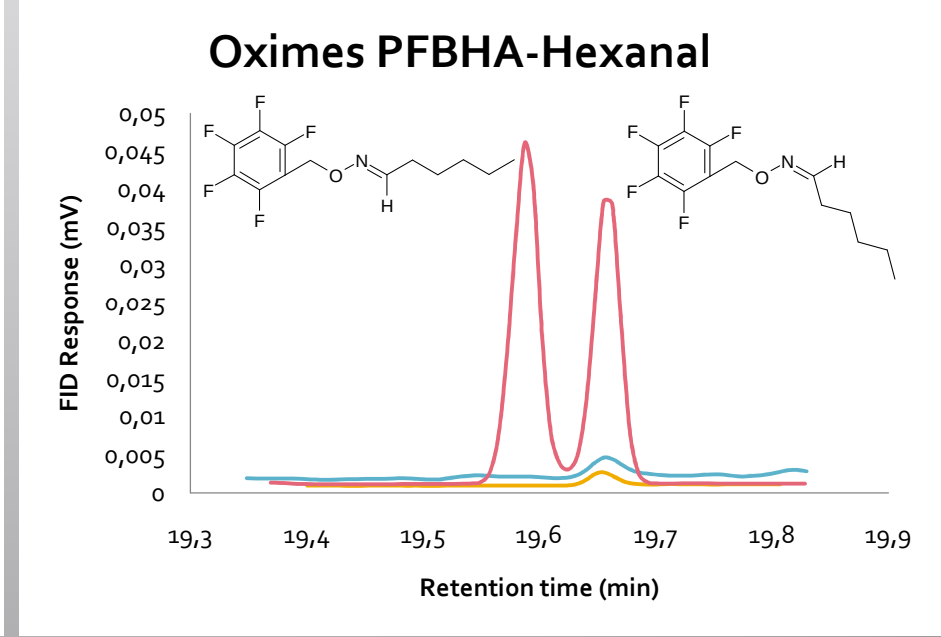
- 3 days before sampling: 77% (n=6)
- 3 days after sampling: 100 % (n=6)

[4] Virginie Larroque, Valérie Desauziers et Pierre Mocho, *J. Chromatogr. A*, **1124** (2006) 106-111

Other carbonyl compounds: hexanal

[Hexanal] $_{air}$ = 510 µg.m^{-3} GC/FID Exposure time: 15 min





----- PDMS/CAR (T_{desorp} = 300°C) ----- PDMS/DVB (T_{desorp} = 250°C) ----- PDMS/DVB + PFBHA (T_{desorp} = 250°C)

- ✓ Quantitative reaction
- ✓ Higher sensitivity
- ✓ Apparition of two peaks instead of one => carbonyl compound

Conclusion
Analytical Development

We have…

✓ Sensitive, fast and easy-to-use analytical method for carbonyl compounds

⇒ LOD < 1µg.m^{-3} with a 20 min sampling (formaldehyde)

Next step….

✓ Validation: comparison with the standard method (NF ISO 16000-3)

✓ Combined sampling of VOCs and carbonyl compounds (2 fibers in one bulb)

✓ Passive sampler for on-site measurement of material emissions in buildings

Future Prospects

Application of these methods in new buildings

- Kinetic study of building material emissions

Development of a prediction model for indoor air quality

Health recommendations for the delivery of new or renovated buildings

Help for the new french regulation

Thank you for your attention.

Questions?