> JOURNÉE ANNUELLE DES DOCTORANTS - CSTB

Innovative materials for the detection of VOCs in the field of cultural heritage: α-pinene sensing by Metal-Organic Frameworks

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CONTEXT

Volatile Organic Compounds (VOCs) emitted by building materials, furnishings and cultural heritage are major contaminants of indoor air, impacting people's health, as well as altering the cultural assets of patrimonial institutions (museums, bookstores, and others).

Cultural heritage objects.

Within VOCs, terpenes are found from different sources and are known to accelerate the degradation processes of cultural artefacts. To better control and avoid this phenomenon, the on-line detection of terpenes is thus required, even if it remains challenging since they are present at trace level (from ppb to a few dozen of ppm).

GOAL

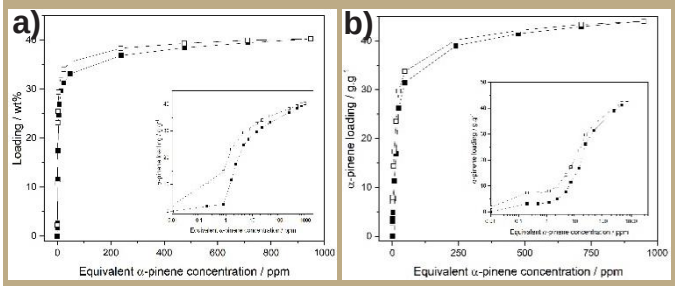
We aim at designing a terpene sensor, via the incorporation of a sorbent into a transducer. This sorbent belongs to the Metal-Organic Frameworks (MOFs) family, a recent class of porous hybrid materials attractive for the selective sorption of a wide range of indoor and outdoor contaminants, including VOCs,[1] while their ability to adsorb terpenes was rarely explored.[2,3] α-pinene is considered as a representative terpene molecule, since it is the most abundant of this family of pollutants.

Based on a preliminary study, two candidates (DUT-4(Al) and MIL-100(Fe)) were identified as promising for α-pinene detection. The quality of the MOFs films, deposited by drop-casting onto Quartz Crystal Microbalance (QCM), was evaluated by SEM. The sensor response was recorded for traces concentrations of α-pinene to reflect the real conditions.

[1] Li X. et al, Separation and Purification Technology, 235, 2020, 116213
[2] Gu Z. et al, Chem. Commun., 51, 2015, 8998-9001
[3] Hou, X et al, ACS Appl. Mater. Interfaces, 9, 2017, 32264−32269

MAIN RESULTS

Gravimetric sorption isotherms of α-pinene by DUT-4(Al) and MIL-100(Fe) (T = 303 K)



*α-pinene gravimetric sorption isotherm by **a)** DUT-4(Al) and **b)** MIL-100(Fe). Closed symbols mean adsorption branch and open symbols mean desorption branch.*

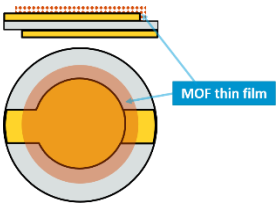
DUT-4(Al) and MIL-100(Fe) show high uptake at low concentrations and negligible hysteresis.

→ ideal behavior as sensing materials toward α-pinene detection at trace levels.

ON-GOING WORK

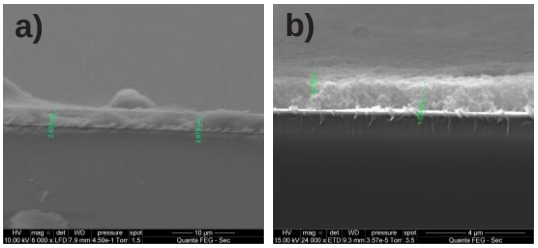
Development of the sensor platforms

DUT-4(Al) and MIL-100(Fe) were deposited as a thin film on a QCM transducer by drop-casting.



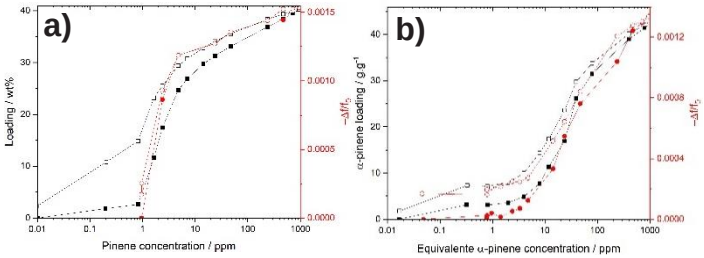
Sauerbrey equation

$$\Delta F = -\frac{2F_0^{\,2}}{\sqrt{\rho_Q \mu_Q}} \frac{\Delta m}{A}$$



*Scanning Electron Microscope (SEM) for **a)** DUT-4(Al) and **b)** MIL-100(Fe).*

The films are dense and homogeneous, with 2.835 µm and 1.229 µm thickness for DUT-4(Al) and MIL-100(Fe), respectively.



*Sensor response (red circles) compared to the gravimetric sorption isotherm (black squares) for **a)** DUT-4(Al) and **b)** MIL-100(Fe). Closed symbols mean adsorption branch and open symbols mean desorption branch.*

The sensor response is reversible and suitable for the detection of α-pinene traces.

CONCLUSION AND PERSPECTIVES

1. Proof-of-concept: MOFs are suitable for α-pinene sensing at traces level
2. On-going work:
   - Investigation of additional sensor metrics in terms of repeatability, response/recovery time, long-term stability and selectivity.

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