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NNSA Laboratory Directed Research & Development

Innovation Advancing Nuclear Security

# New Coatings for MEMS-Based Sensors for Enhanced Surveillance


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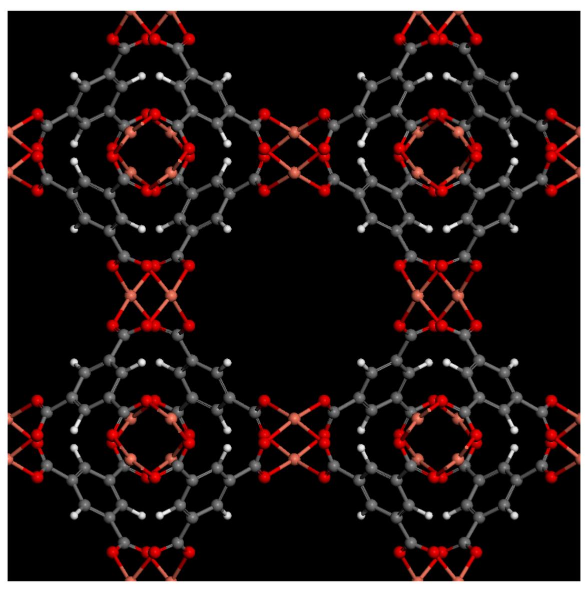
## What is the challenge?

- Age-related degradation (corrosion, oxidation, hydrolysis) of components in the enduring stockpile.
- The Integrated Stockpile Evaluation (ISE) program at Sandia has sought to provide advanced diagnostics to identify when and where aging occurs. Ultimately, this will ensure that aging does not adversely impact system performance.
- The challenge is to create in-situ sensors with the following properties:
  - extremely small size (distributed sensing near critical components)
  - very low power consumption (minimal energy for nuclear safety)
  - long-term stability
  - high selectivity
  - ability for self-calibration (an "Achilles heel" of many potential sensor systems)
- A fully instrumented weapon test platform could provide in-situ data to validate high-fidelity composition and transport models for gases within weapons.

## What is our innovation?

- We are developing microcantilevers (MCLs) as a platform for on-demand weapon atmosphere surveillance. These are extremely compact, high resonant-frequency, low-power devices in which the transduction mechanism is the stress at the cantilever surface induced by analyte adsorption.
- Sensors are coated with a new class of crystalline nanoporous materials known as metal-organic frameworks (MOFs) to provide both selectivity and high sensitivity. MOFs are flexible materials with ultrahigh surface areas (up to 6000 $m^2/g$), high radiation resistance, and synthetic tailorability for selective adsorption.
- We have demonstrated the use of MOF-coated MCL sensors for a variety of analytes: water vapor, alcohols, $CO_2$. Thus, practical MOF-based multigas sensors appear to be within reach.



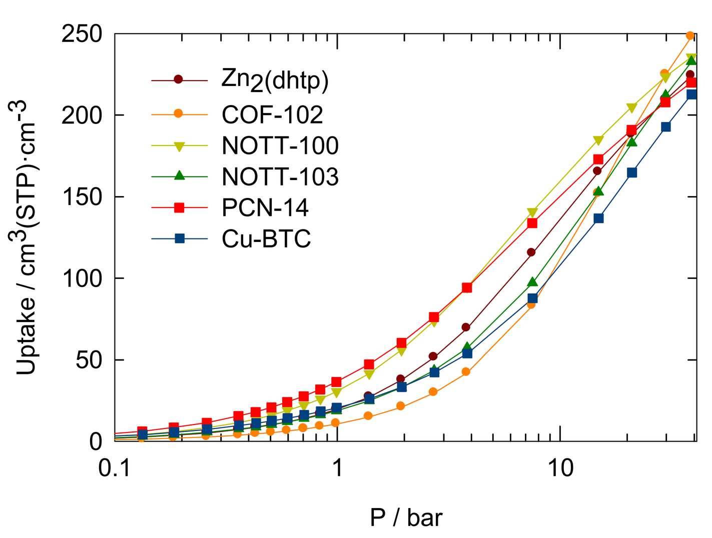
Structure of Cu-BTC, consisting of Cu(II) ions connected by benzene tricarboxylate (BTC) linkers. Unit cell shown is 2.6 nm x 2.6 nm.

## What have we learned so far?

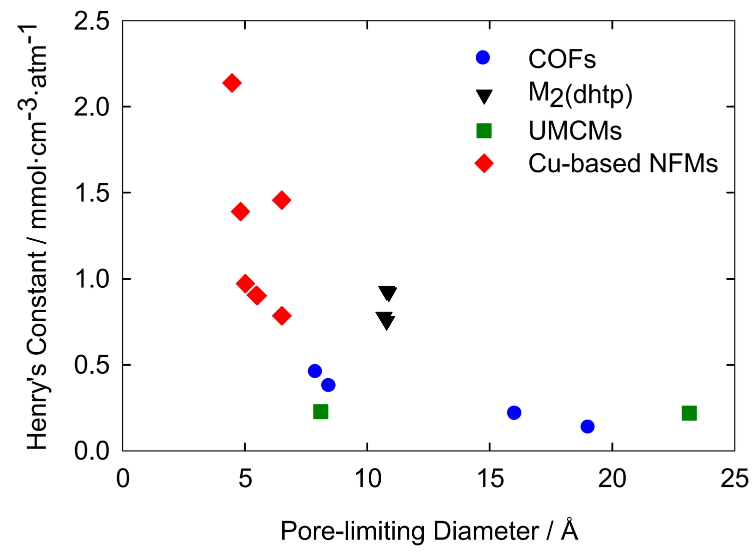
### Force field modeling to rapidly screen potential MOF coatings

- While MOFs are known for extraordinary gas storage and separation properties,[1] it has become apparent that low-level gas detection (< 5 mbar $P/P_o$) is also possible with these materials.[2]
- Computational modeling of adsorbate-MOF interactions allows for both efficient screening of existing structures and identifying desired molecular properties of potential new structures.
- Currently, we are using grand canonical Monte Carlo simulations of methane adsorption to screen candidate MOFs and related Covalent Organic Frameworks (COFs) for their low-level gas adsorption properties.

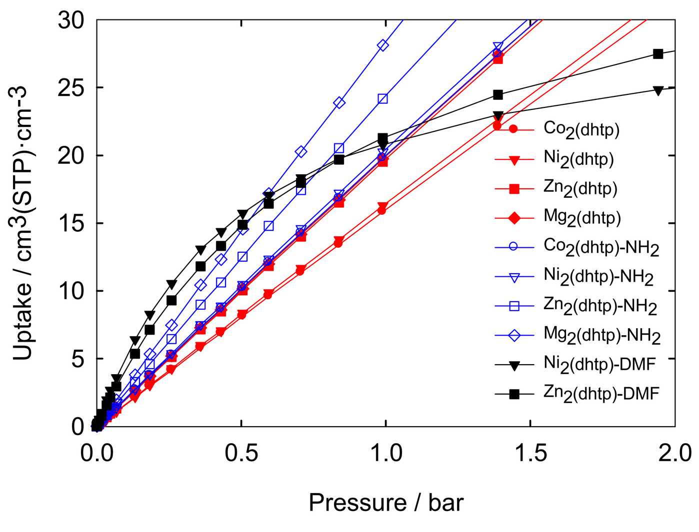
### Key results

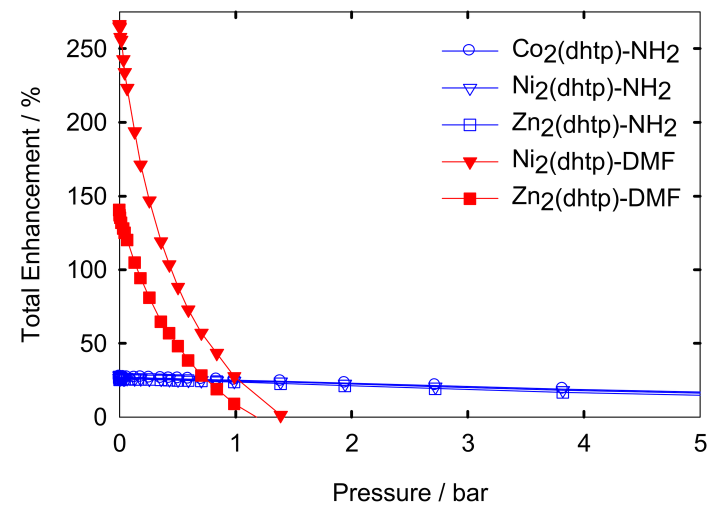



Methane adsorption isotherms for selected MOFs. The relative performance of a group of MOFs with respect to uptake is pressure dependent.

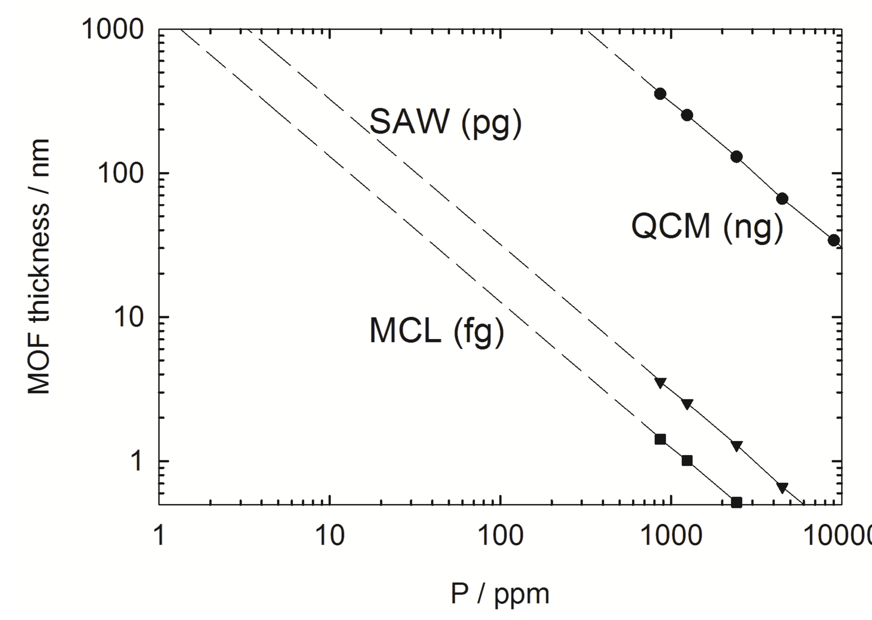



Henry's constant for methane uptake versus pore-limiting diameter for selected materials. MOFs with smaller pore diameters have a greater ability to adsorb methane at low pressures. In particular, the Cu-based MOFs studied here show significant methane uptake at low pressure.




Above left: Methane adsorption isotherms at 298 K for the $M_2$(dhtp) series with coordinating solvent. Above right: amine ($NH_2$) functionalization enhances uptake by 20-25% below 1 bar. Dimethylformamide (DMF) functionalization significantly enhances methane uptake.



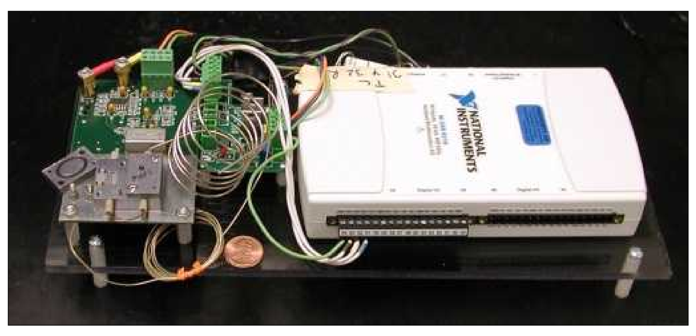

Minimum film thickness for a MOF (PCN-14) required to achieve detectable levels of methane in three typical sensing devices: MCL, surface acoustic wave (SAW), and quartz crystal microbalance (QCM). Dashed lines indicate values extrapolated based on the Henry's constant for methane adsorption by PCN-14. Approximate detection limits are given in parentheses.

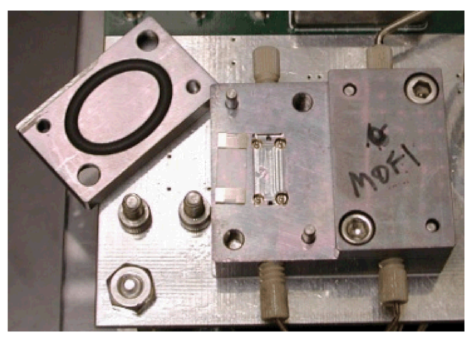
### Trace gas detection using MOF-coated MEMS sensors

- The unique adsorptive properties of MOFs (high intrinsic surface areas, guest-induced expansion/contraction) suggest several routes to chemical sensing using micro-electro-mechanical systems (MEMS).
- Potential transduction mechanisms:
  - stress induced at the MOF-MCL interface, detected with a built-in piezoresistive stress sensor
  - change in the resonant frequency of an oscillating MCL sensor induced by mass adsorption
  - change in the resonant frequency of a SAW sensor through changes in mass loading and film moduli
- We have demonstrated humidity sensing by SAWs coated with a MOF (Cu-BTC) over a very broad concentration range, as well as detection of alcohols and $CO_2$. MOF-coated SAWS for methane detection are currently undergoing testing.

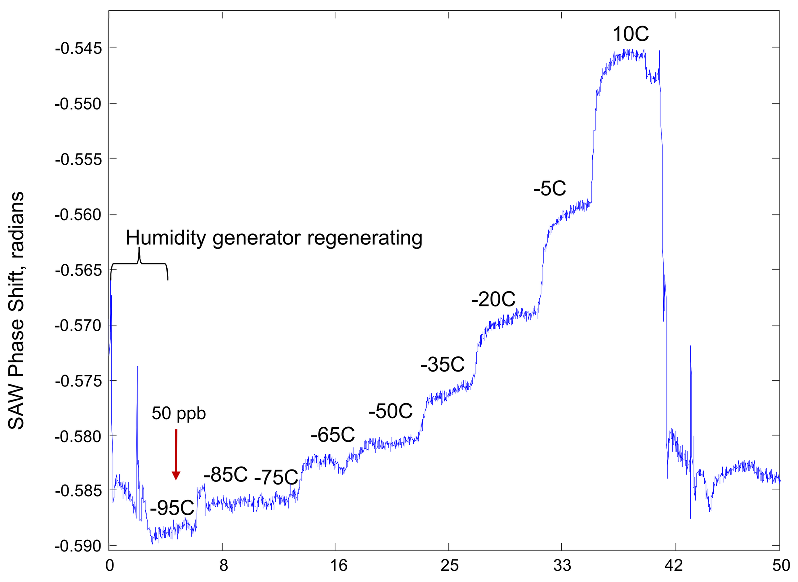
### Key results

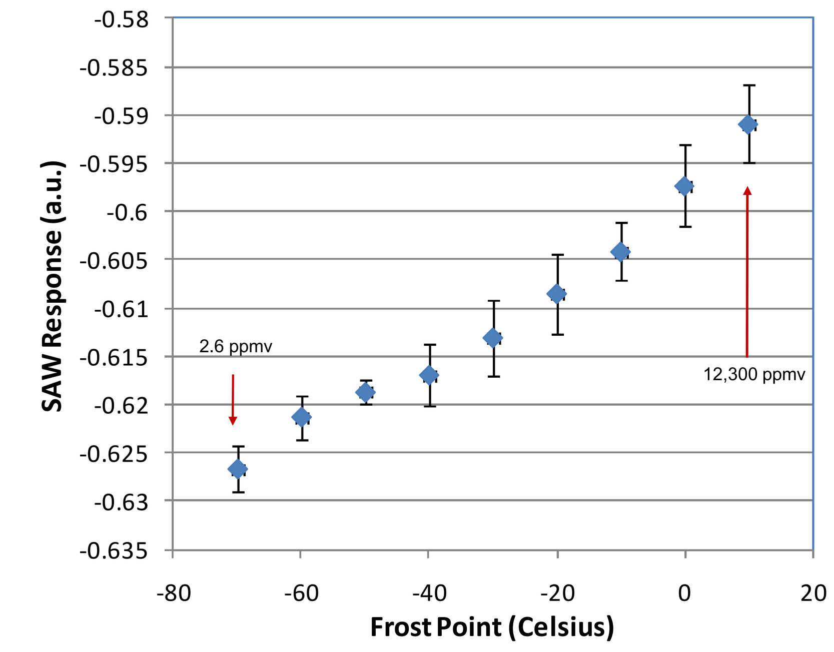
**Setup for gas detection using MOF-coated SAWS**



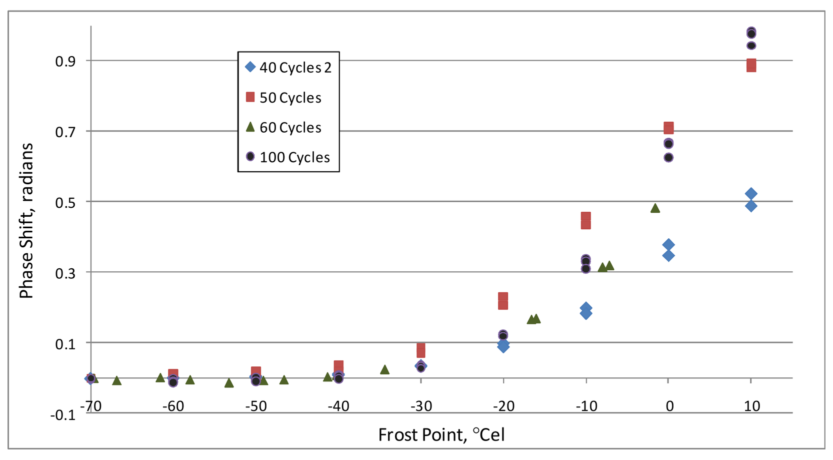


SAW sensor fixture and data acquisition hardware. At right, a close-up of a SAW on the opened fixture.




Detection of water vapor by a MOF-coated SAW at various frost points (–95 °C frost point corresponds to 50 ppb water at 1 atm). An approximately linear response covering 4 orders of magnitude in water vapor concentration is observed.




We are optimizing device response by tuning the thickness of the MOF coating. This graphs shows the response of CuBTC-coated SAWs with different number of coating cycles to various humidity steps. 100 cycles corresponds to a coating thickness of ~350 nm.

## Why is this important for our nation?

- A state-of-health predictive capability is a critical aspect of the Integrated Stockpile Evaluation (ISE) embedded-evaluation contribution to Common-Adaptable-System-Architecture (CASA) stockpile transformation objectives.
- A second key application is deployment in the emerging ISE component surveillance program (CSP). DoD has analogous needs: a prognostic health monitoring system is required in all new major systems.
- DHS-related real-time chemical detection schemes could also benefit from this technology.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