SAND2014-18524C

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Response Factor and Selectivity of Metal-Organic Framework Coatings on Surface Acoustic Wave Sensors

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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Abstract

Previous studies have been performed using Surface Acoustic Wave (SAW) sensors both with and without Metal Organic Framework (MOF) coatings. At Sandia, several studies have been done with SAWs at low temperatures with various coatings looking specifically at humidity sensitivity. Other studies have used polymer coatings; however, because of the polymer size and properties, the coatings often lack uniformity and ultimately affect sensitivity. For this experiment, we tested the response factor and selectivity of different MOF coating types with the introduction of three volatile species, n-hexane, dried acetone , heptane and water. MOFs are desirable for sensors in many ways, mainly in that they are customizable both for chemical sensitivity and selectivity and they are easy to make. They can also be customized to be selective for light gases, something that was unachievable with polymer-coated SAW devices in the past. SAWs are inexpensive, robust, sensitive and small, which is ideal for field applications. Example applications include portable sensors or weapons analysis and the detection of aging materials via decomposition products.

Introduction- Methods for Response Factors

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- Current methods use diffusion-equilibrium based methods that take minutes to hours to glean results.

- We proposed a dynamic method to reduce the time to determine the same results.

- Results of Interest:
  - Level of selectivity
  - Useful selectivity sensing based on size and functionality groups
  - Array sensing to increase confidence of measurements

Background - What is a SAW sensor?

- Surface Acoustic Wave sensors used to detect various chemicals
  - Dependent on gas sensitive coating
  - Increased mass from chemical absorption change the frequency response of the SAW.

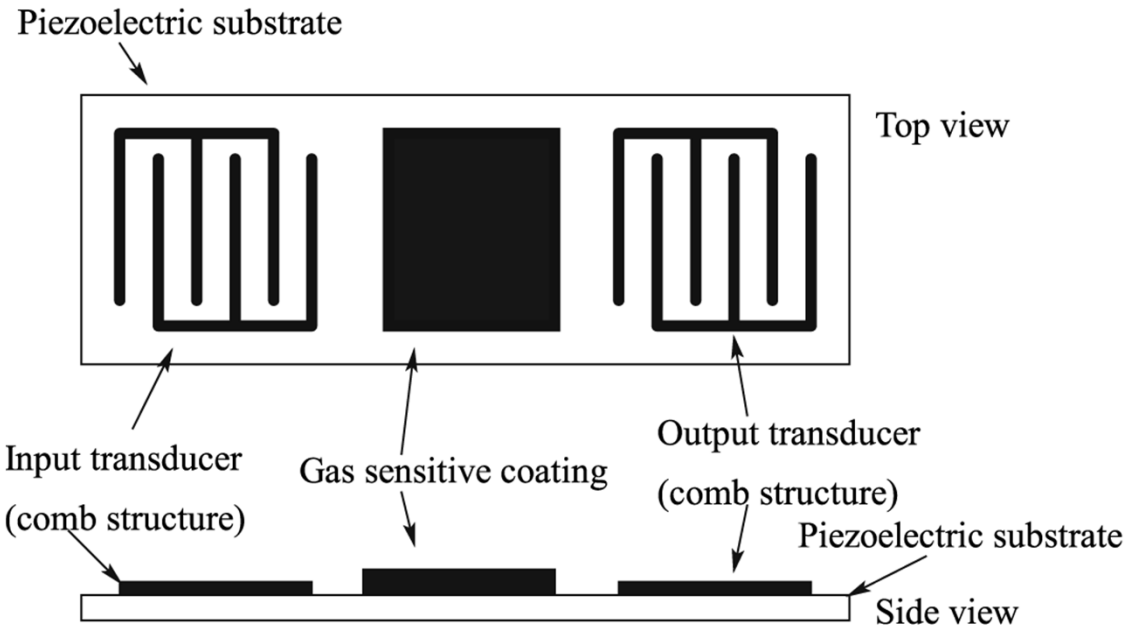

Image Credit: Arshak, K et al. A Review of Gas Sensors Employed in Electronic Nose Applications. Sensor Review. **24**, 2004, 181-198

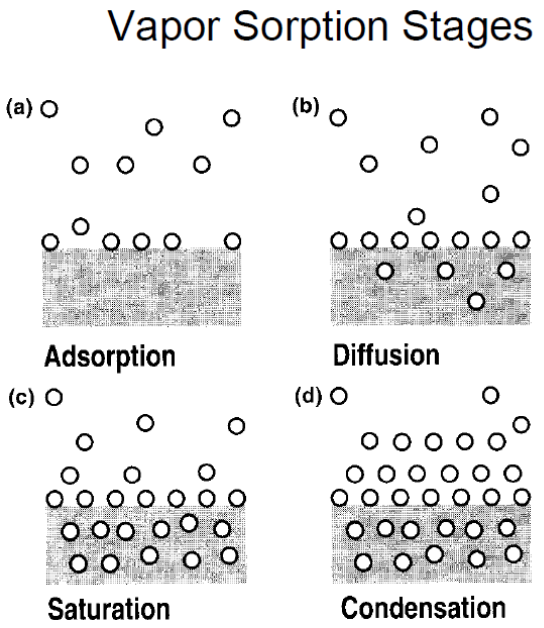

Image Credit: from Thompson, SLAWS 1997

Background - What is a Metal-Organic Framework?

- A gas sensitive coating that is crystalline and made of metal ions linked with organic ligands[2].
- Different MOF 'flavors' capture different chemical species based on geometry, polarity, and number of carbons in the chain[3] .

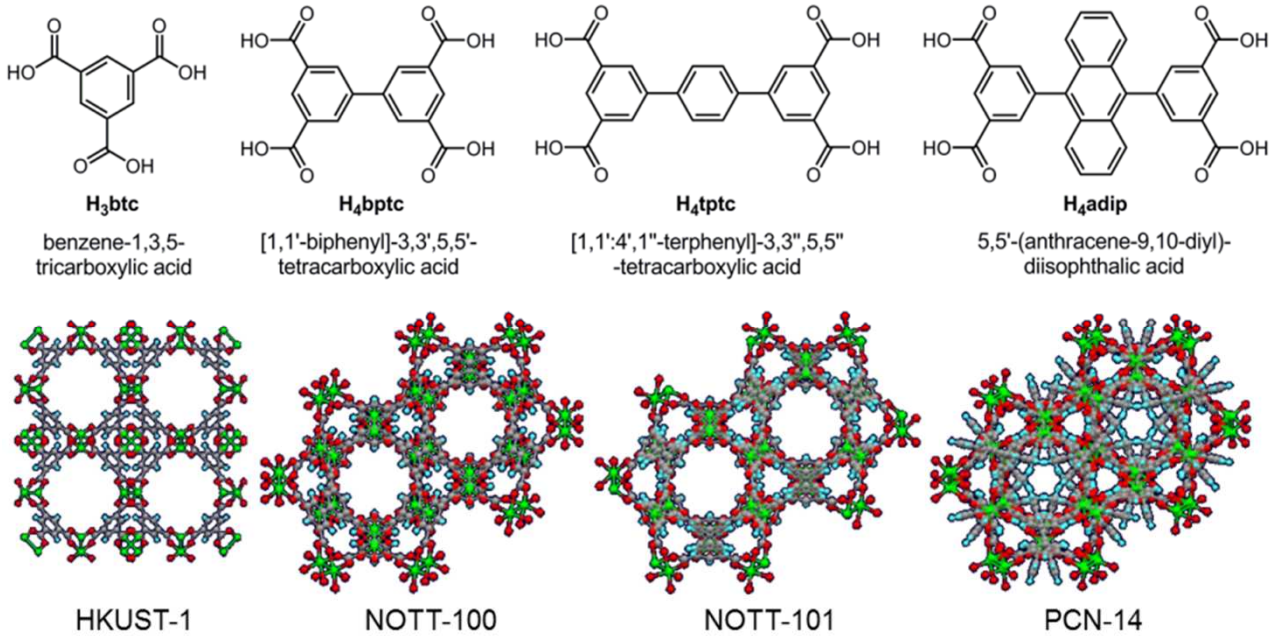

Image credit: Stavila, Vitalie et al. Tunable Suite of Copper (II) Paddlewheel MOF Thin Films of Small Molecule Chemical Detection

Why use MOF and SAWs Together?

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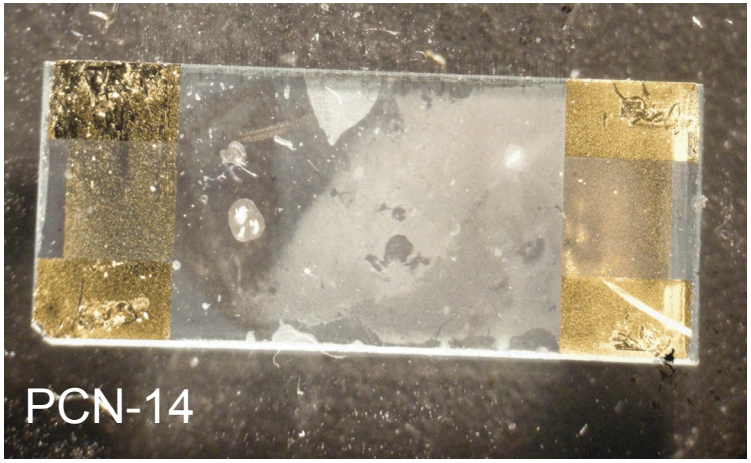
Sandia has performed many studies of SAWs with various coatings

Advantages

- Easy to challenge
  - Liquids and gases
- Measure interactions
- Response curve to change in concentration
- Evaluate MOF characteristics

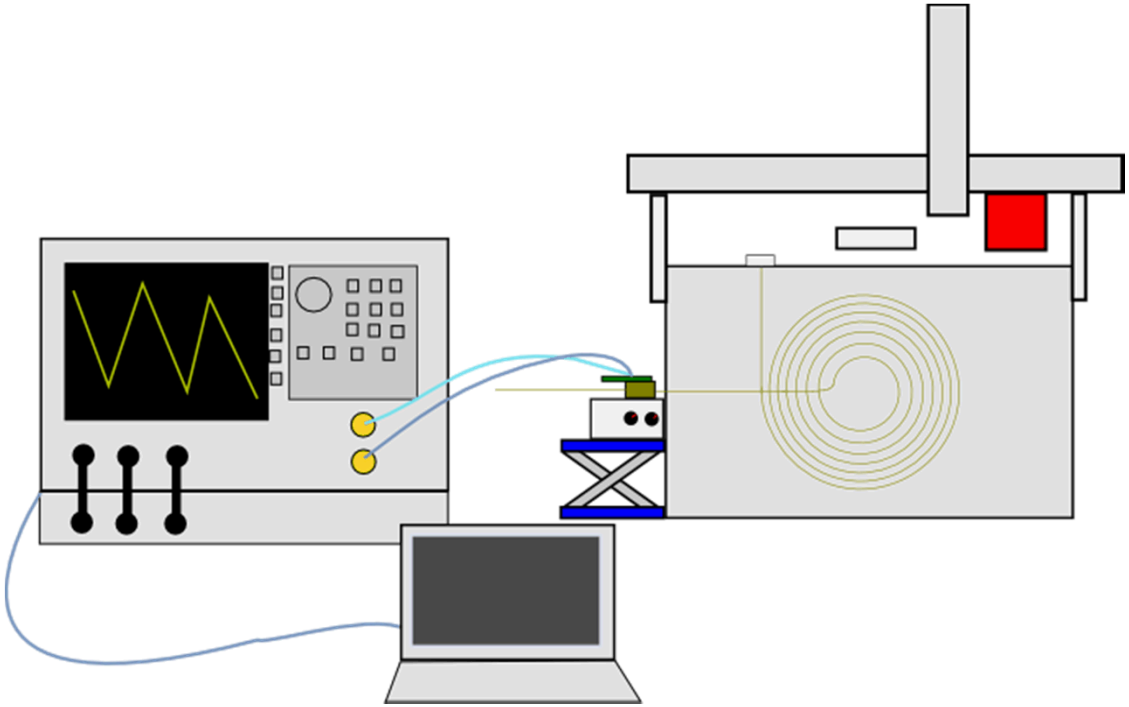
Disadvantages

- Mixed tests
- No cross sensitivity
- Dynamic challenge



Methods and Materials

It is hypothesized that using a GC in series with a MOF coated SAW sensor will more quickly determine the associated chemical response factors than diffusion-equilibrium methods.



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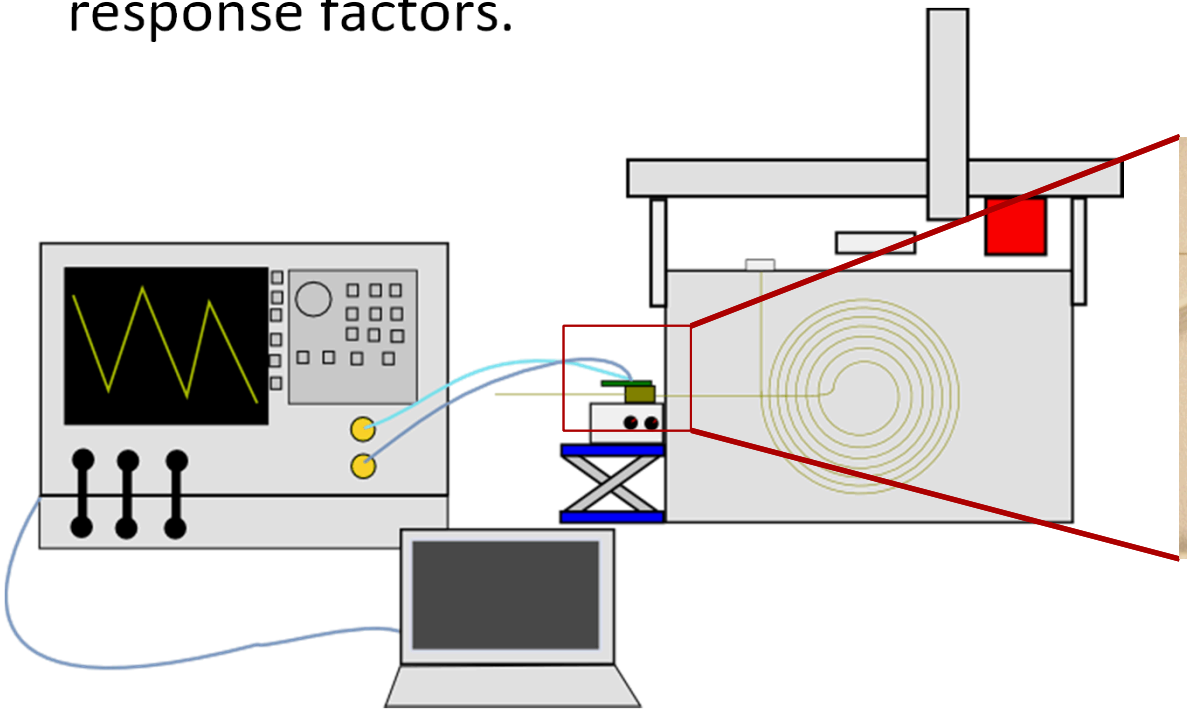

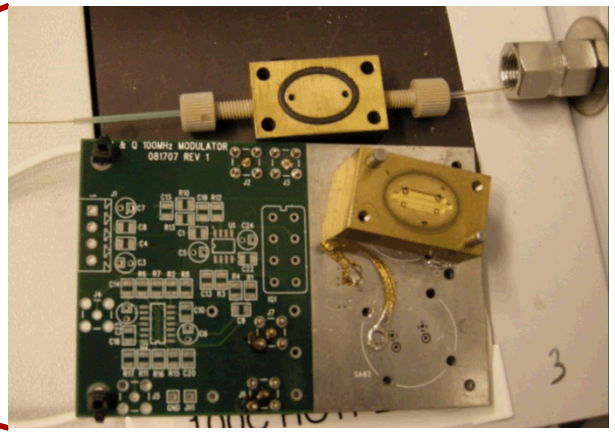

Methods and Materials

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Instruments

- Agilent 6890N GC
- MPS2 Twister Gerstel Autosampler
- HP 8751A Network Analyzer
- Dell Latitude E6500 Laptop with LabView 2013 installed

GC Setup

- Oven: 40^{o}C isothermal
- Pressure: 21 psi, 50:1 split
- Column: DB5
  30m x 0.32mm x 0.25µm
- Mobile phase: He gas
- Analyte: 0.2 uL liquid
- Run time: 2-5 minutes

Results

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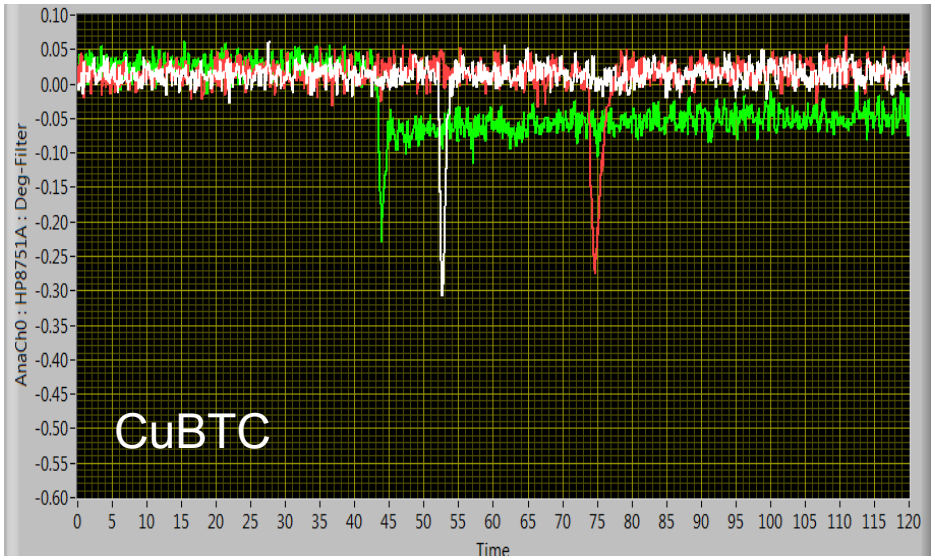
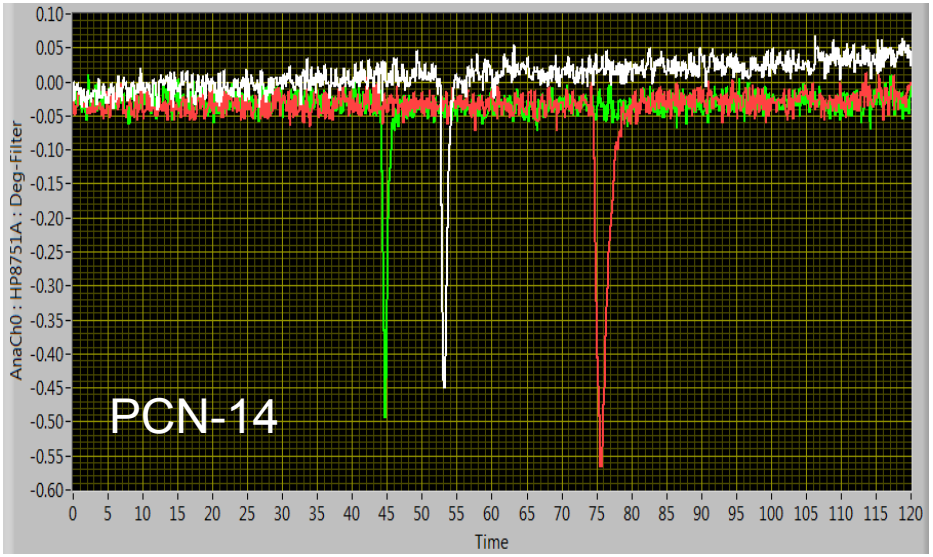
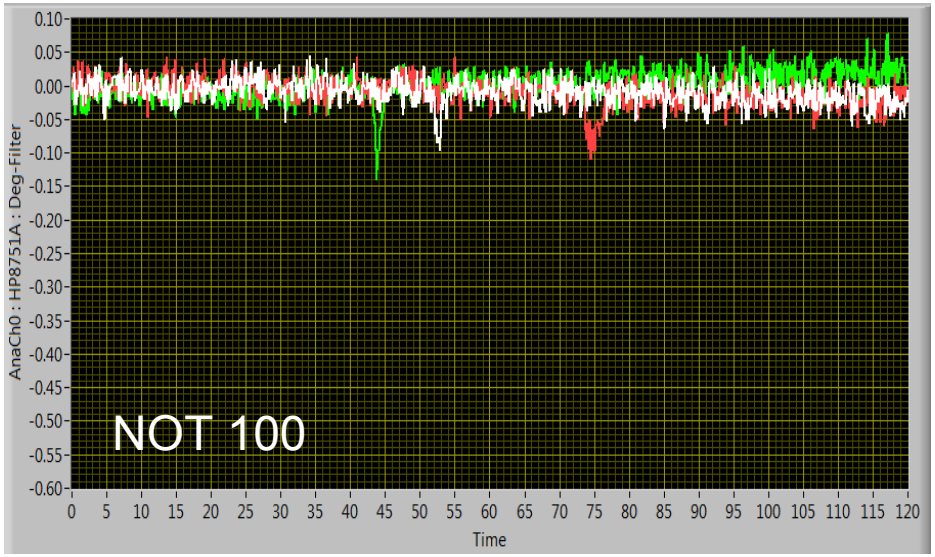
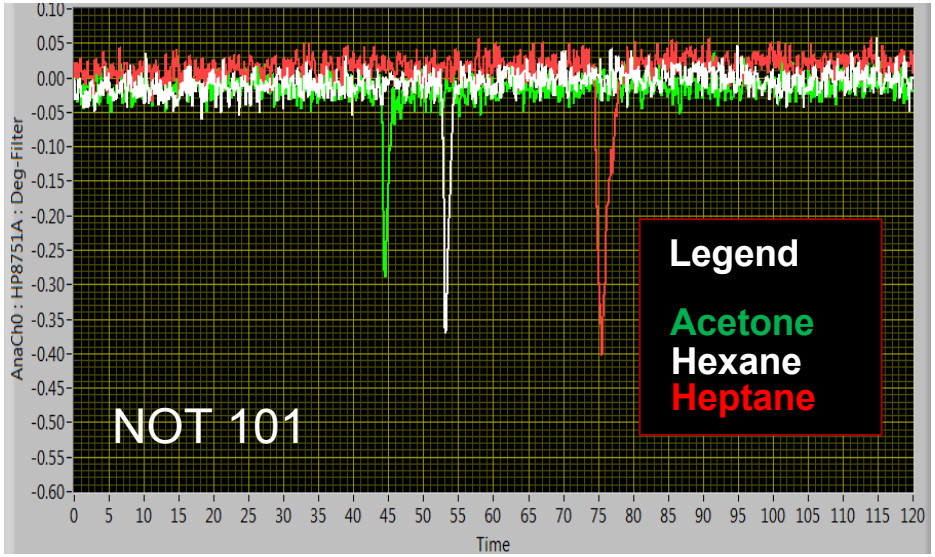
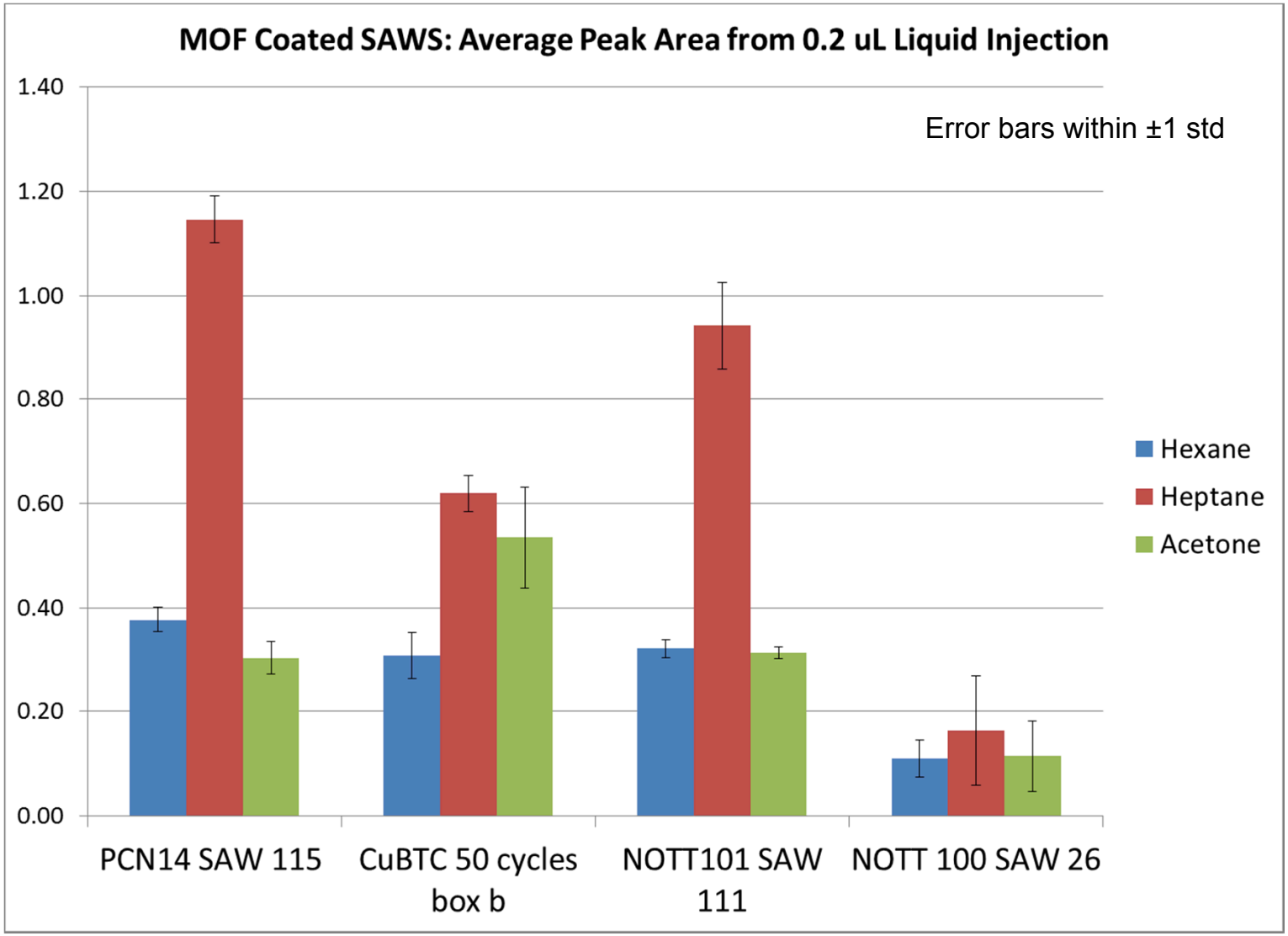






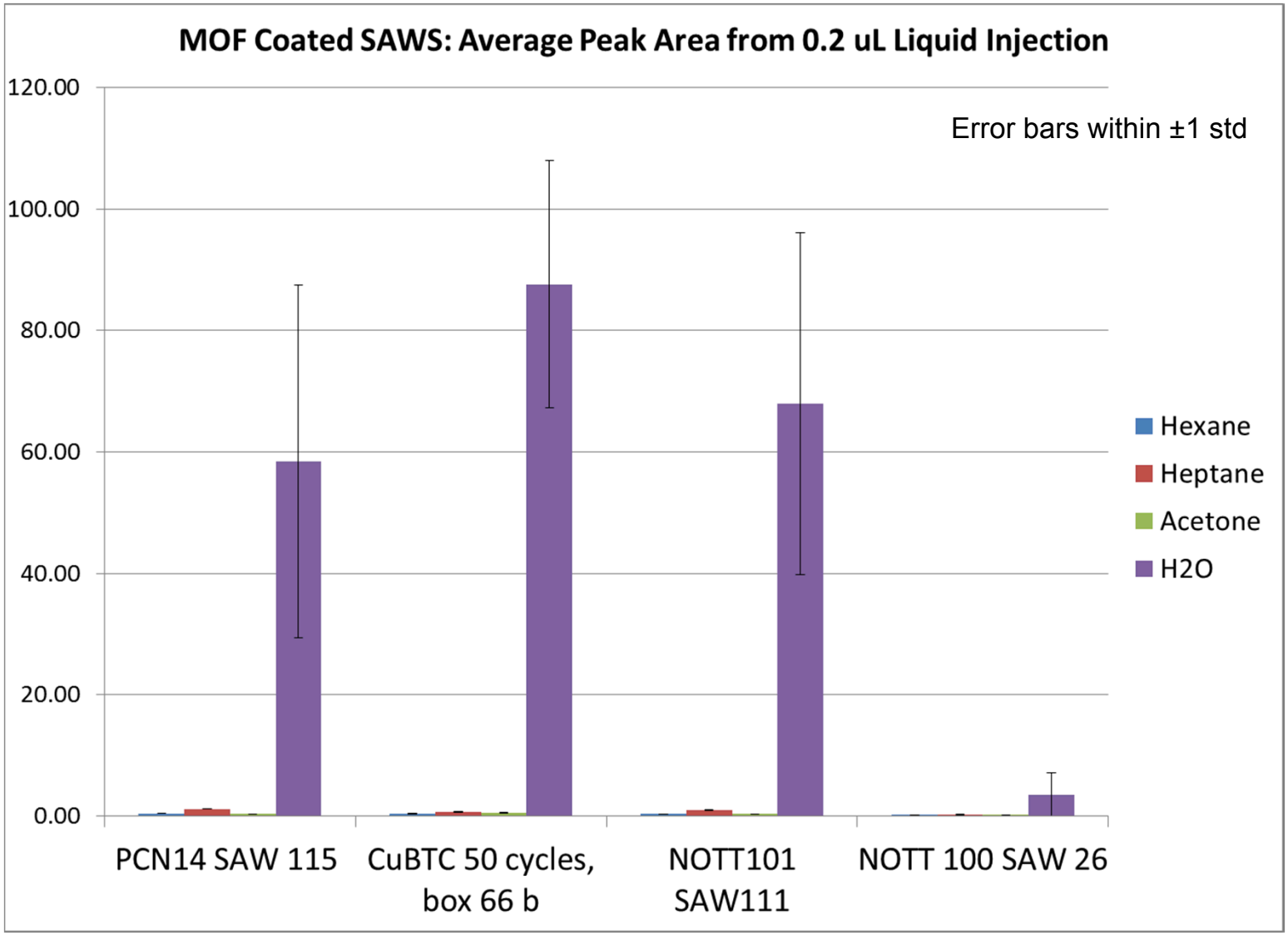


Results – Organics



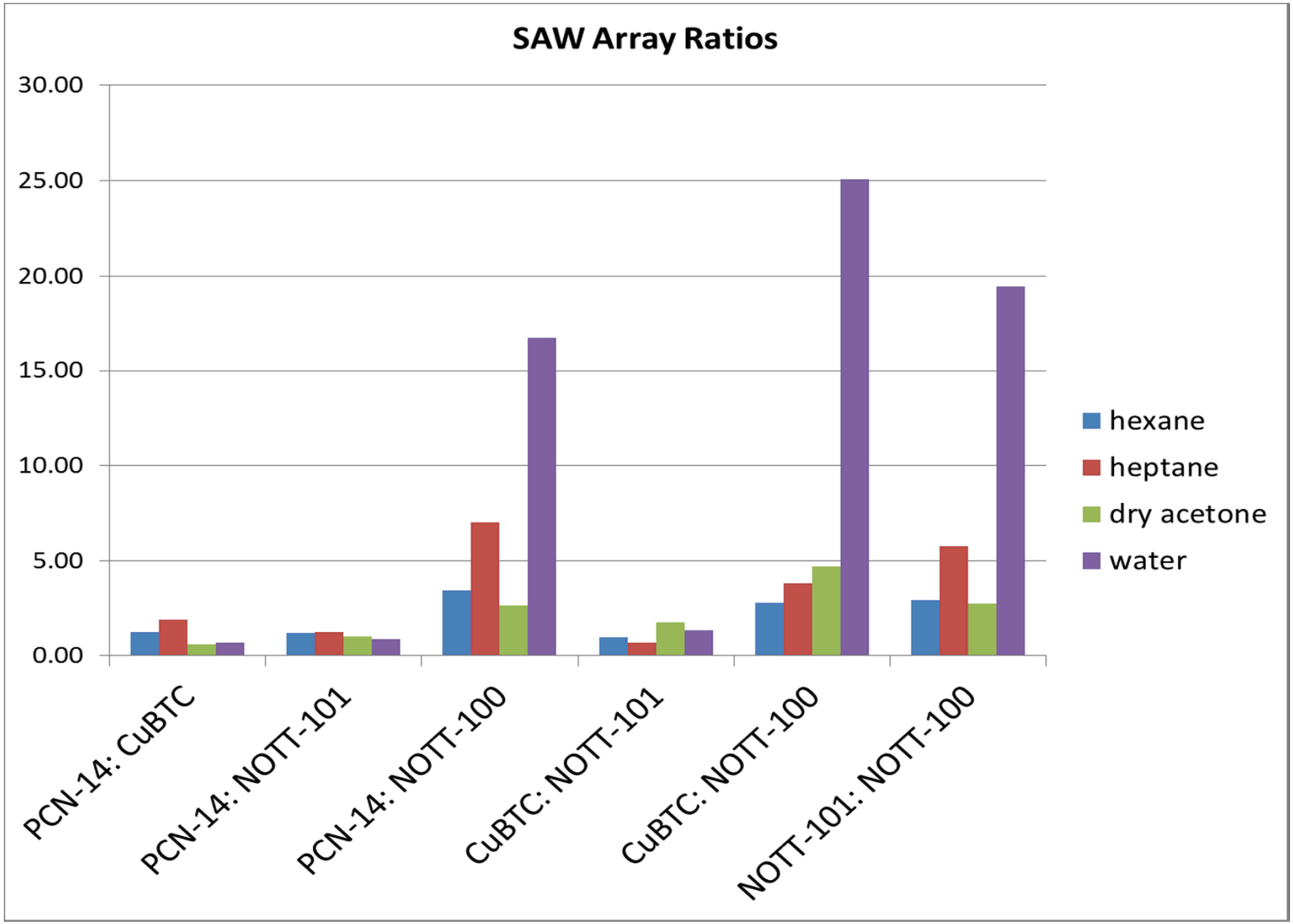
Insertion Loss: -14.8 dB -14.8 dB -15.6 dB -14.2 dB

Results – Organics & Water



Insertion Loss: -14.8 dB -14.8 dB -15.6 dB -14.2 dB

Results –SAW Array Ratios



Outcome of Results

- Response factors
  - Ratio of water to organics peak area is large, as seen in previous studies[2].
  - Signal of each chemical species varied for the different flavors of MOF, as expected.
  - Peak Areas between polar and non-polar species (acetone and hexane) not as different as expected.
  - Results differed from diffusion-equilibrium methods
- Selectivity
  - Response seen for all chemical species for all MOFs tested

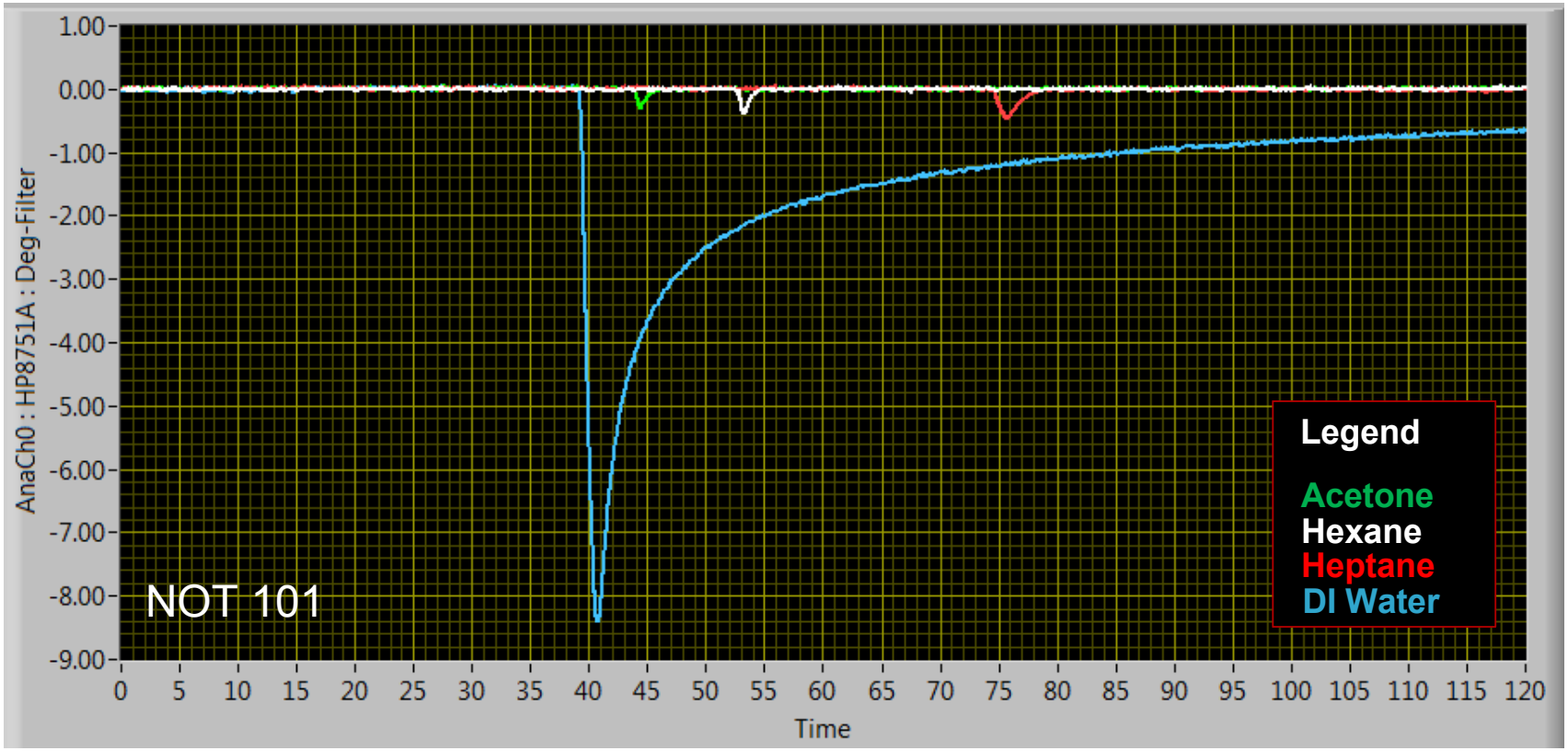
Conclusions and Future work

- Retention times from the GC method and resultant peak areas can be used to determine reference signals and selectivity of MOF coated SAWs.
- Results seen in 2-5 minutes dependent on desired analyte.
- Results from dynamic method not directly comparable to diffusion-equilibrium methods.
- Selected MOFs not as selective as anticipated. Determine other species to test for greater selectivity.

References

1) Robinson, Alex et. Al. Ultrasensative Humidity Detection Using Metal-Organic Framework-Coated Microsensors. *Anal. Chem.* **2012,** 84, 7043-7051.
2) Stavila, Vitalie et. Al. Tunable Suite of Copper(II) Paddlewheel MOF Thin Films for Small-Molecule Chemical Detection. *Advanced Functional Materials.* **2013**.
3) Davydovskaya, P., Ranft, A., Lotsch, B.V., Pohle, R. Analyte Detection with Cu-BTC Metal Prganic Framework Thin Films of Mass-Sensitive and Work-Function-Based Readout. *Anal.Chem.* **2014**, 86, 6948-6958.

Water Peak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-2.00
-3.00
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-6.00
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-8.00
-9.00
AnaCh0 : HP8751A : Deg-Filter
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120
Time
NOT 101
Legend
Acetone
Hexane
Heptane
DI Water