Molecularly Imprinted Polymer (MIP) Based Electrochemical Sensor for Rapid Detection of PFAS On-Site

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MITRE

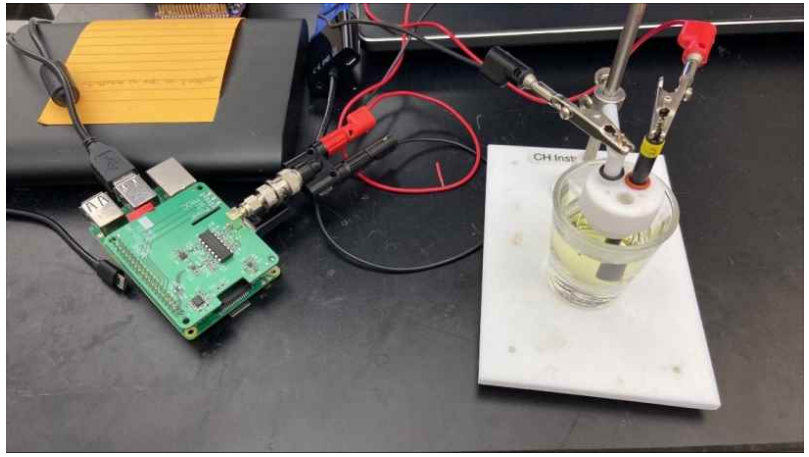
SOLVING PROBLEMS FOR A SAFER WORLD®

Rapid PFAS Screening

MITRE is working towards a sensor that can **screen for poly- and per-fluorinated alkyl substances (PFAS) in water or monitor destructive remediation technologies** for effectiveness.

Upon transmission of water quality data, a user can immediately explore the results in an interactive, web-based dashboard.

Current Technology Readiness Level (TRL) = 4



On-Site PFAS Testing

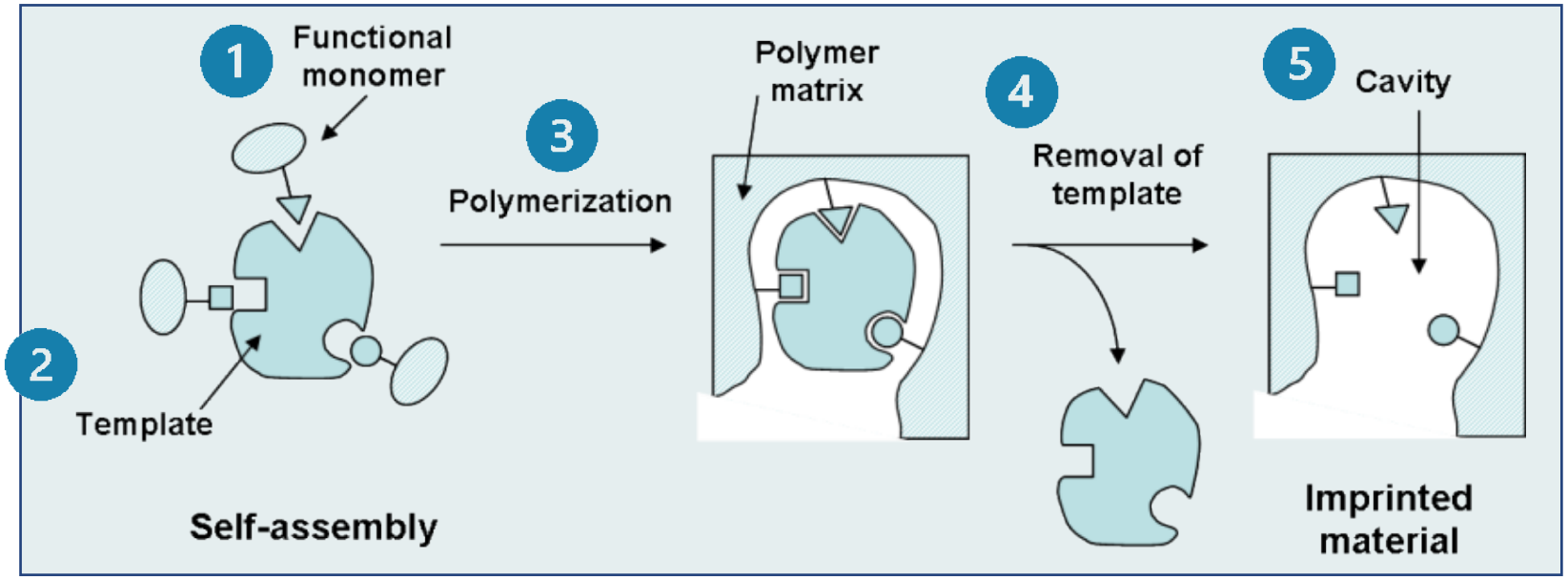
GAPS IN CURRENT CHALLENGES

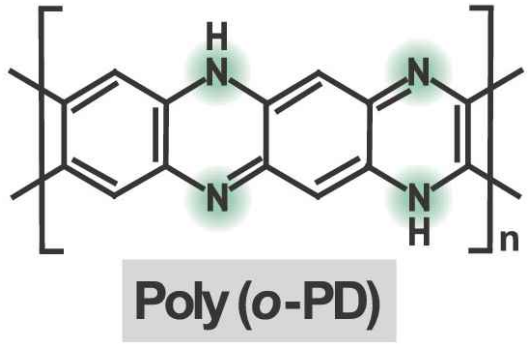
- Limited on-site decision support
- High cost for detecting PFAS
- Large number of samples collected
- Lag time in lab results
- No real-time analytics

MITRE SENSOR GOALS

- Screens for a “Total PFAS” measurement
- Low-cost
- Minimal end user training requirements
- On-site decision support
  - Sample Screening
  - Remediation Tracking
  - Breakthrough Monitoring
- Real-time capable
- Store collected sensor data for geospatial analysis

Molecularly Imprinted Polymer (MIP) Technology





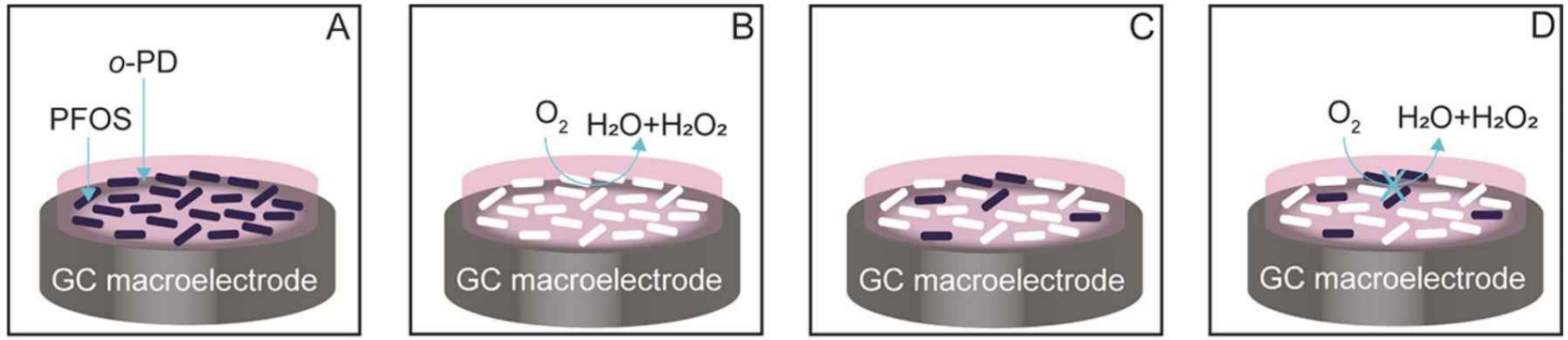
Polymeric *ortho*-phenylenediamine (*o*-PD) used in PFAS sensor
(M Glascott et al. Environ. Sci. Technol. Lett. (2020))

1. *Start with polymer molecule with affinity to template molecule*
2. *Template: analyte of interest*
3. *Polymerization creates attractive forces between template and polymer*
4. *Removal of template results in polymer substrate with imprinted cavities*
5. *Electrochemical signal is generated as new template molecule access the cavity*

Electrochemical MIP Sensor Technology

Features:

- Low-cost specialized equipment
- Simple data processing and interpretation
- Requires presence of electron mediator (e.g., oxygen, ferrocene derivative)
- ~ 10 ppt limit of detection for perfluorooctane sulfonic acid (PFOS)
- Electropolymerize the monomer in a controlled fashion directly on the electrode surface
- As pores of the MIP are filled, measured current will decrease
  - Concentration dependent relationship



Electrodeposition
Molecular imprinted polymer (MIP) is templated with PFOS and PFOS template is washed away

Oxygen Reduction
Pure MIP (white) shows high signal

Template Association
PFOS or other PFAS (black) bind to the MIPs

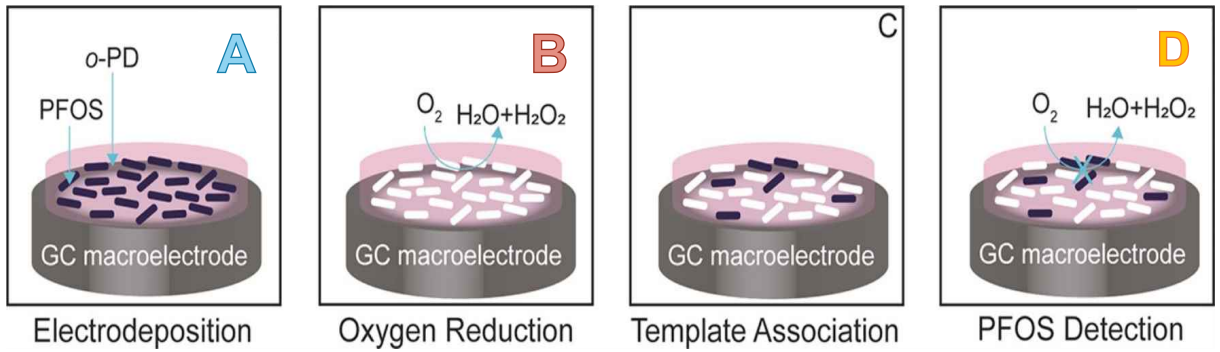
PFOS Detection
Bound PFOS block oxygen reduction and reduce electrical signal

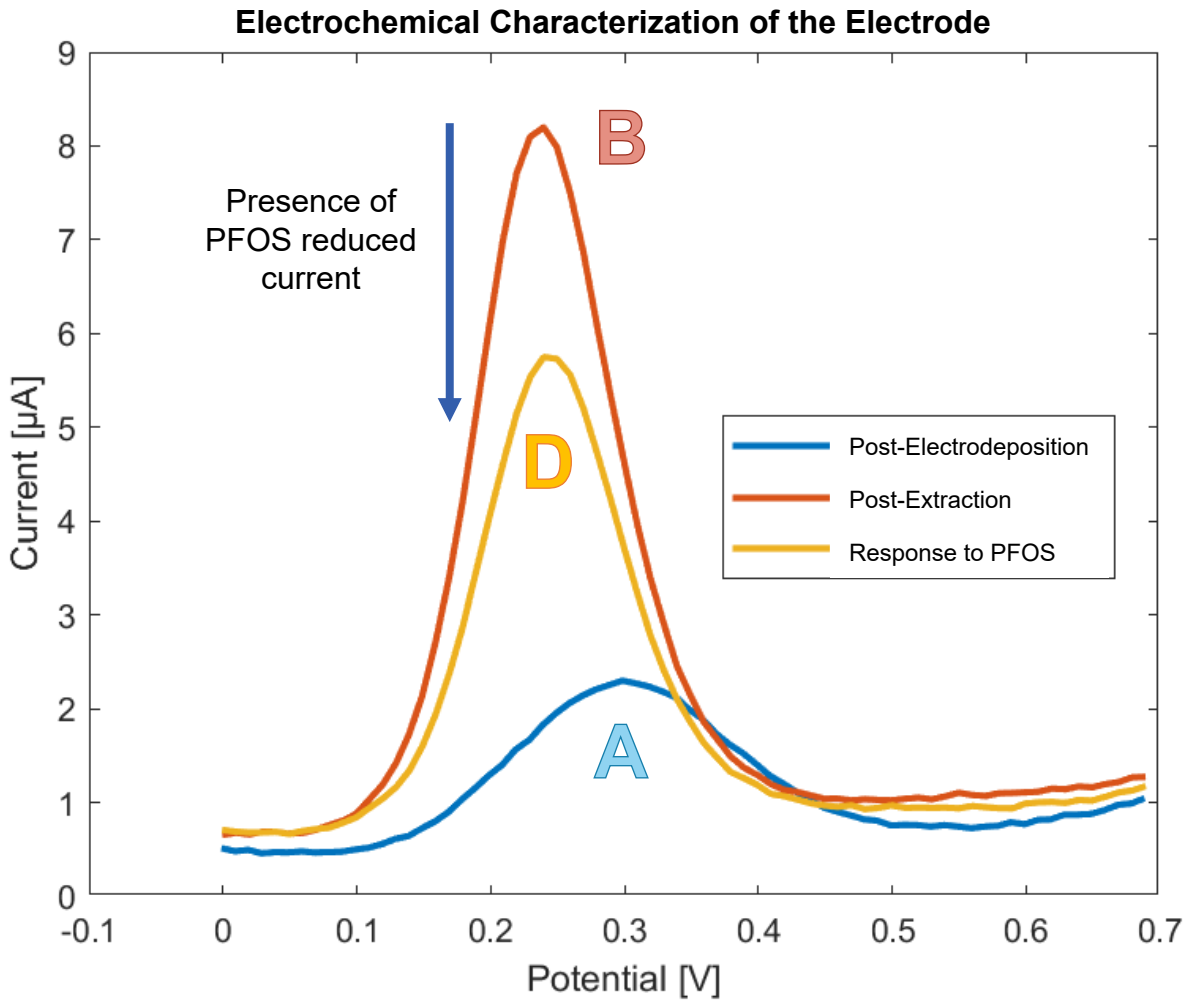
Image: R. Clark & J. Dick, ACS Sensors (2020)

Electrochemical Response of MIPs

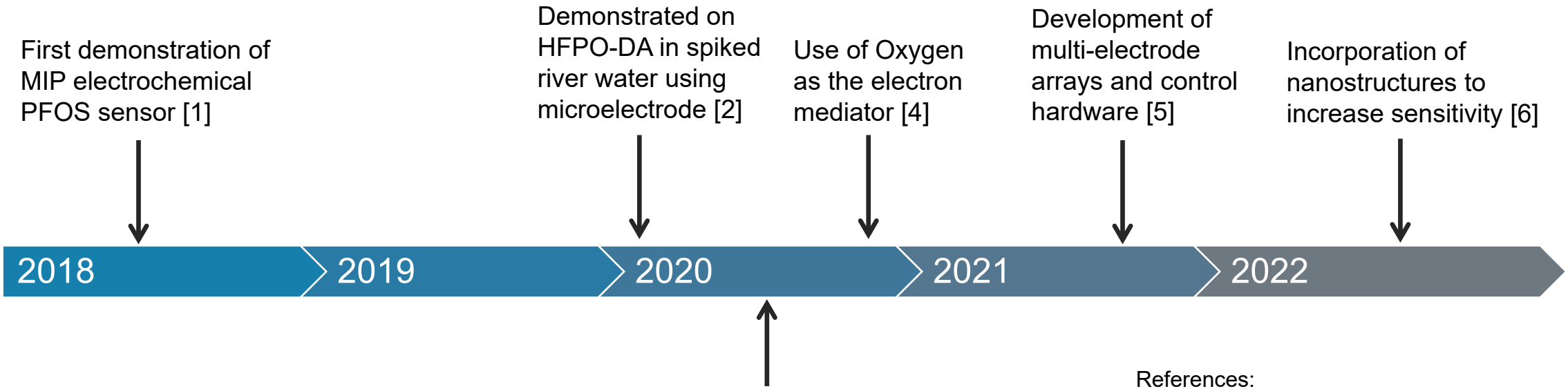
- The electrodeposited MIP impedes access to the electrode
  - Current is reduced
- Extraction removes the template, opening pores to allow access the electrode again
  - Current grows to the “maximum” current for the sensor
- Exposure to the analyte refills the pores, blocking electrode access
  - Current reduces as a function of concentration

Image: R. Clark & J. Dick, ACS Sensors (2020)





MIP-Based PFAS Sensors in the Literature



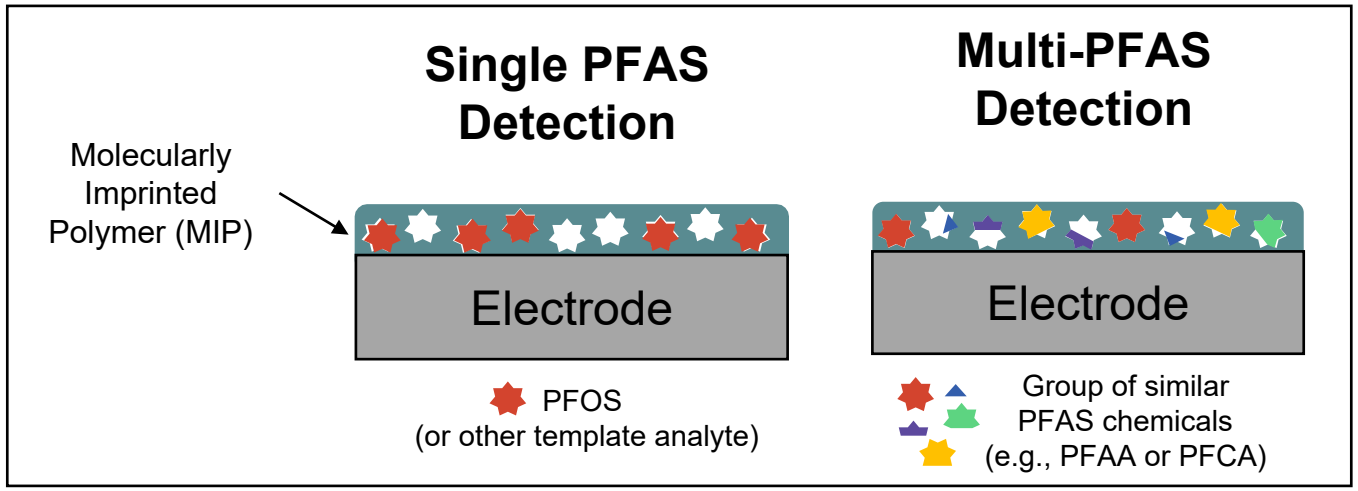
References:

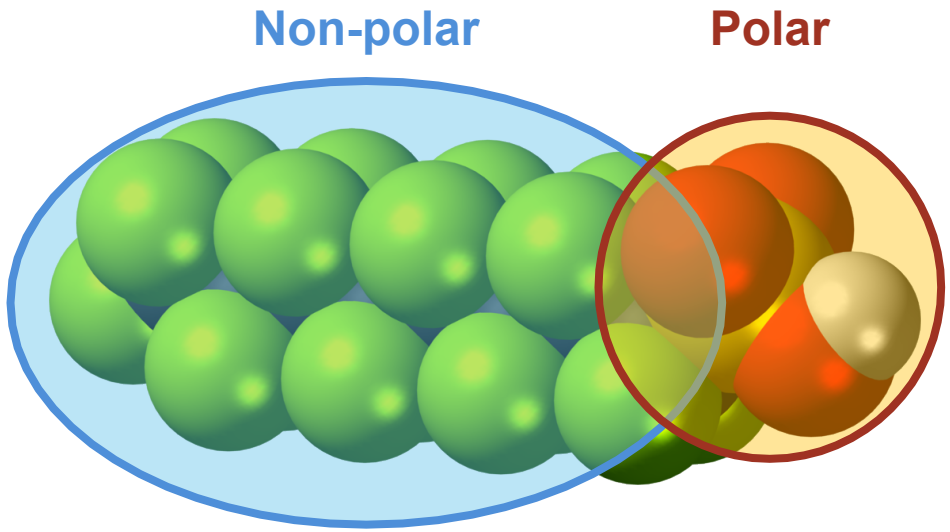
1. *N Karimian et al., ACS Sensors (2018).*
2. *MW Glasscott et al., Environ. Sci. Technol. Lett. (2020).*
3. *R Kazemi et al., Anal. Chem. (2020).*
4. *RB Clark & JE Dick, ACS Sensors (2020).*
5. *RB Clark & JE Dick, RCS ChemComm (2021).*
6. *D Lu et al., Sensors & Actuators B: Chem.(2022).*

Academic research is active in proof-of-concept electrochemical MIP sensors for PFAS.
MITRE aims to advance the TRL of these rapid PFAS sensors from academic demo to commercializeable prototype.

Total PFAS Screening

- Previous work has shown that a PFOS templated MIP **also responds to perfluorooctanic acid (PFOA)**
- MIP interactions are based on attractive forces. If molecules share similar structures, they should all be capable of interacting with the template
  The main components of per- and polyfluoronated alkyl acids (PFAAs) are:
  - A polar acidic group
  - A nonpolor chain of C-F bonds
- A “total” PFAS sensor (targeted primarily at PFAA) should work based on a single template

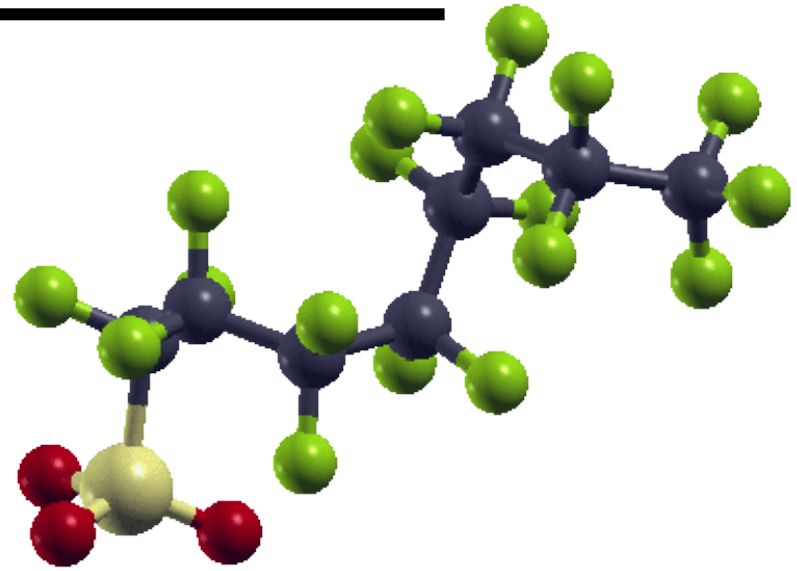


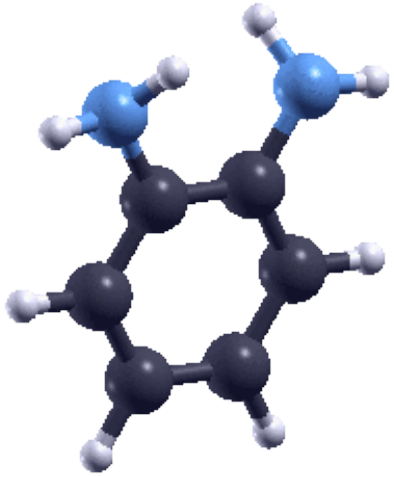


Using Molecularly Modeling to Optimize and Understand Sensor Performance

- Optimizing MIP fabrication conditions
  - Extraction solvent
  - Polymer : PFAS ratios
  - Polymer chemistry

- Understand and characterize:
  - Factors that control binding affinity to wide array of PFAS and common co-contaminants
  - Kinetics of species diffusion through the MIP
  - PFAS self-assembly effects on fabrication and measurements
  - Polymer dynamics and aging during storage and use conditions





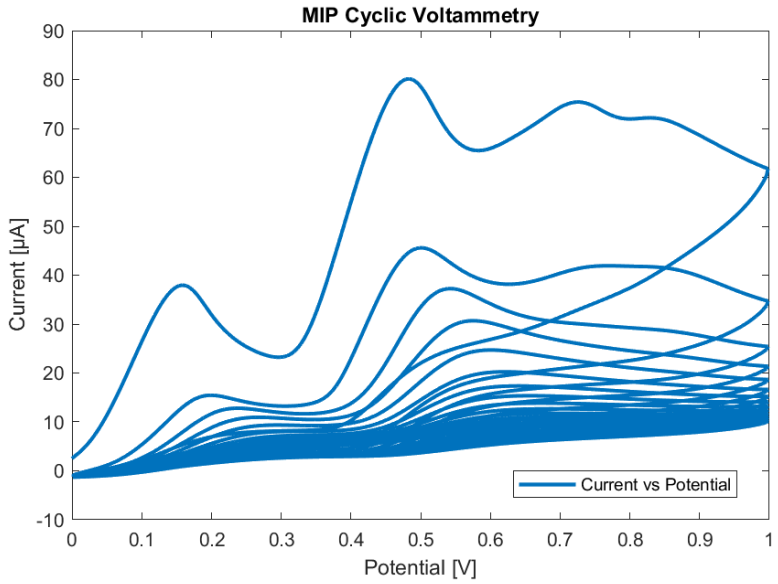
Making a MIP Sensor

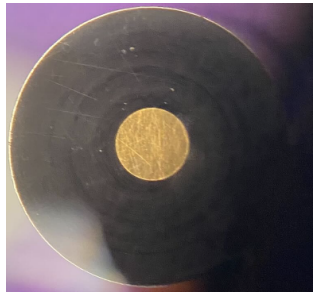
1. Prepare your electrode surface

2. Combine *o*-PD and PFOS in solvent and buffer

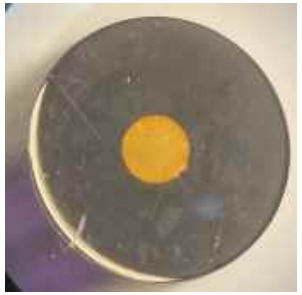
3. Electropolymerize the *o*-PD onto the electrode surface by performing cyclic voltammetry (CV)
   - CV applies a sweeping voltage for a set number of cycles

4. Extract the PFOS template by allowing the electrode to sit in a mixture of 1:1 acetone:water





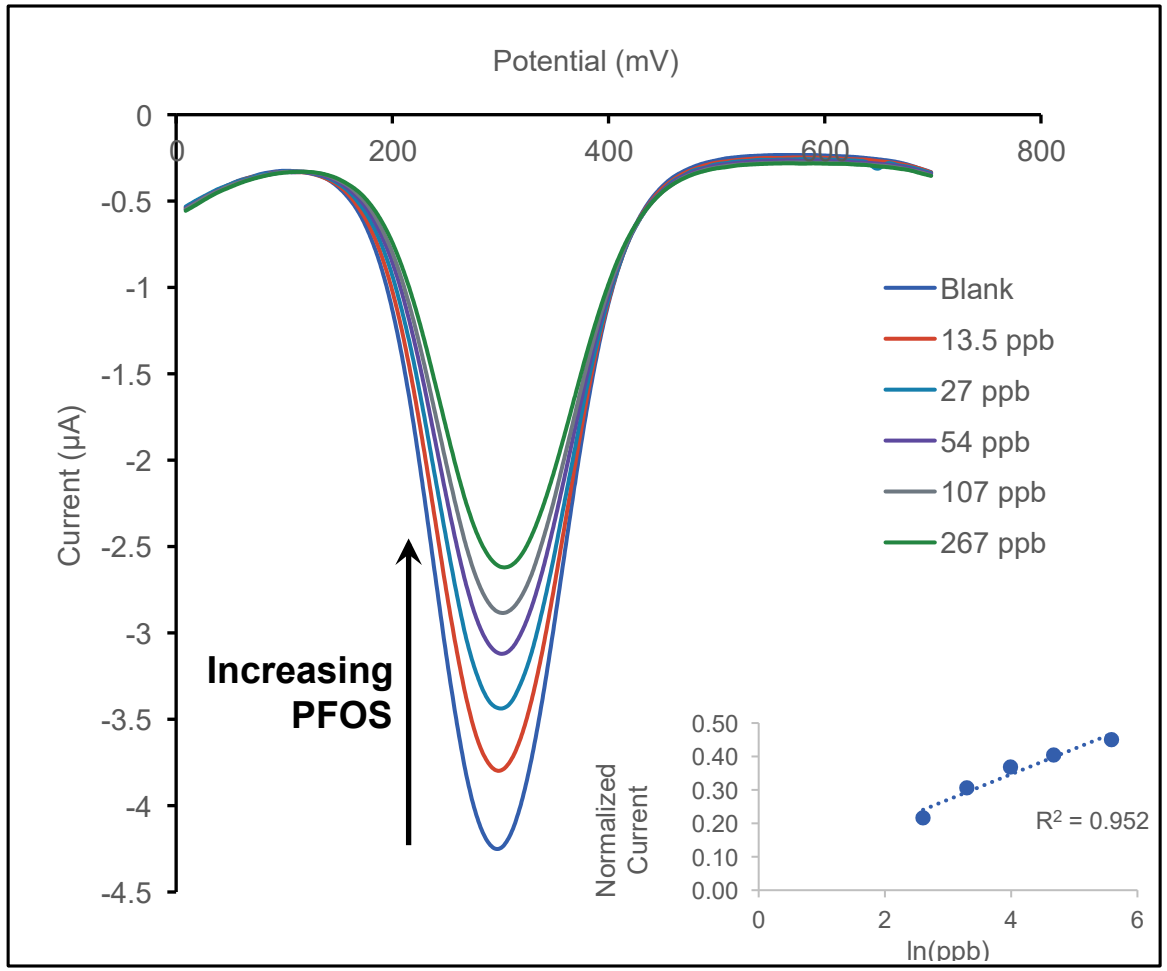
Bare Electrode



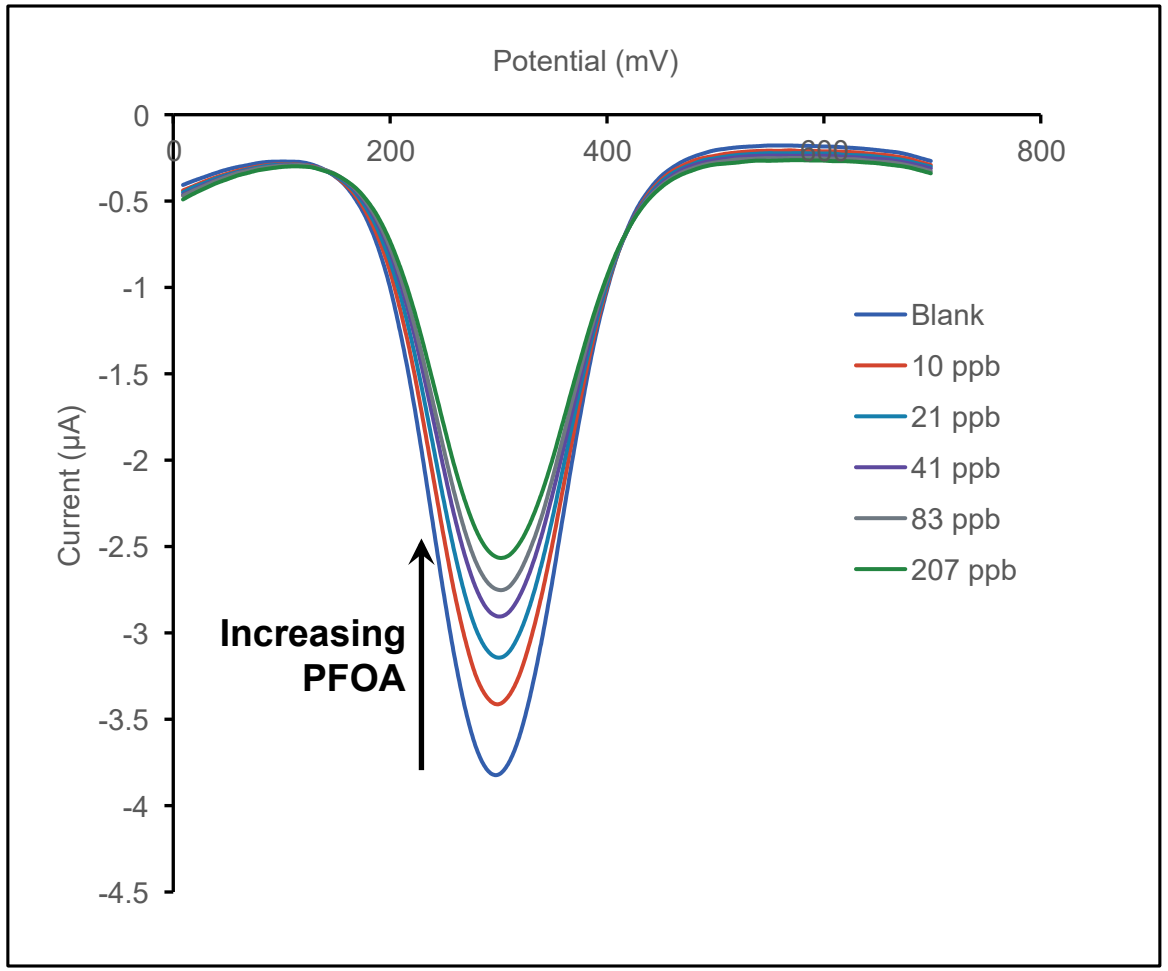
MIP Coated Electrode

Screen-printed Gold Electrode (Pine Instruments)

Measuring PFOS & PFOA



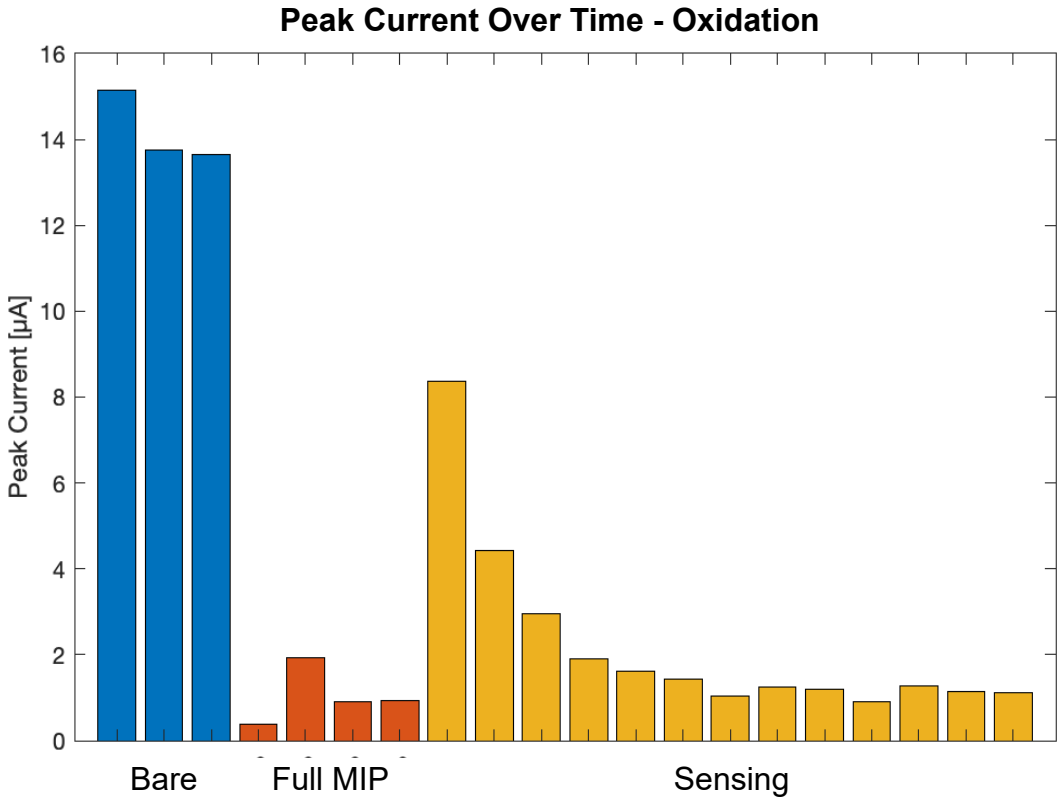
Initial Response to PFOS



Re-extracted Response to PFOA

Time Dependent MIP Behavior

- The response of the MIP in solution is time dependent
- The decay shown on the right has **NO PFAS**
  - Blue represents the bare electrode
  - Red represents the prepared MIP
  - Yellow represents the sensing of an extracted MIP to an electron mediator
- MIP appears to be responding to the blank
  - **WHY?**

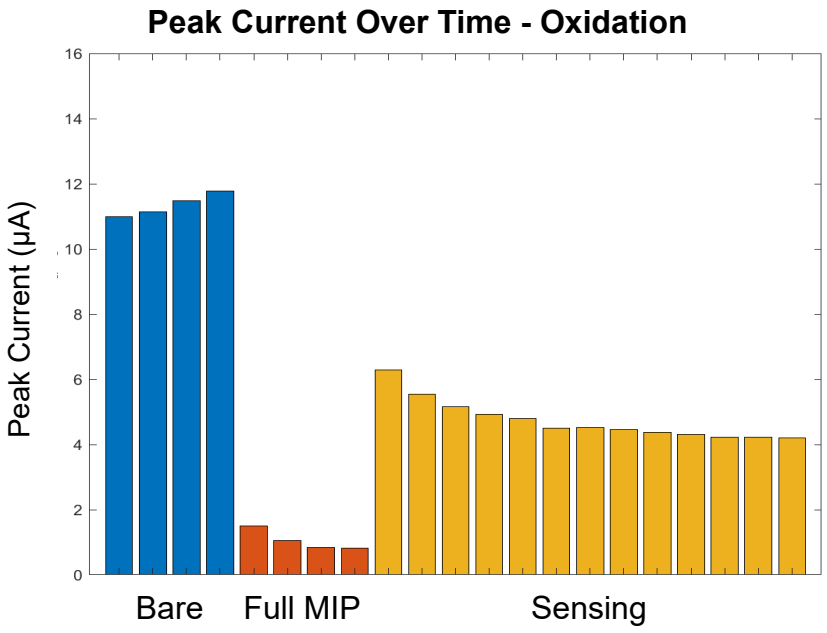


Each bar represents a 10-minute time point

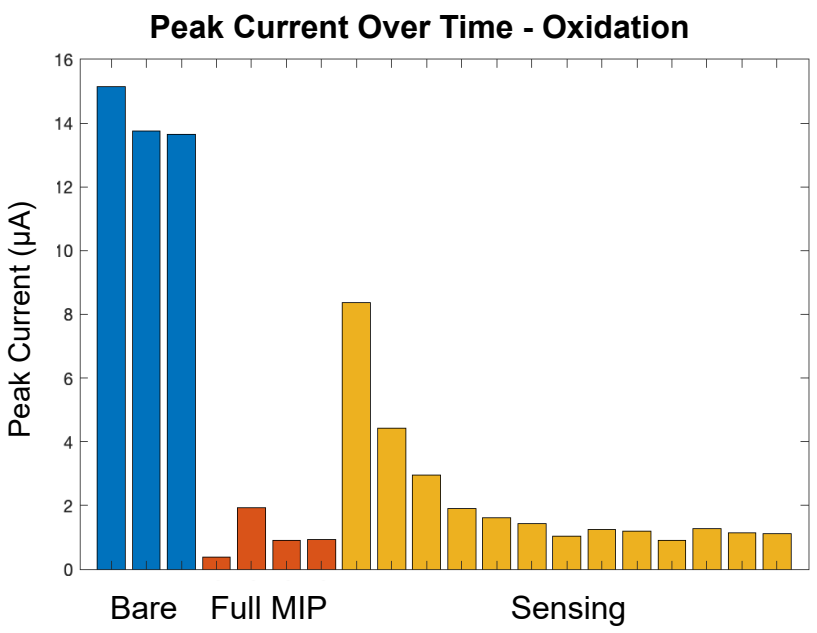
Kinetic Evaluation of Time Dependence

- Three situations with very different reproducible results
- The difference in rate of decay indicates a kinetic effect that needs to be evaluated further to determine what data it can provide

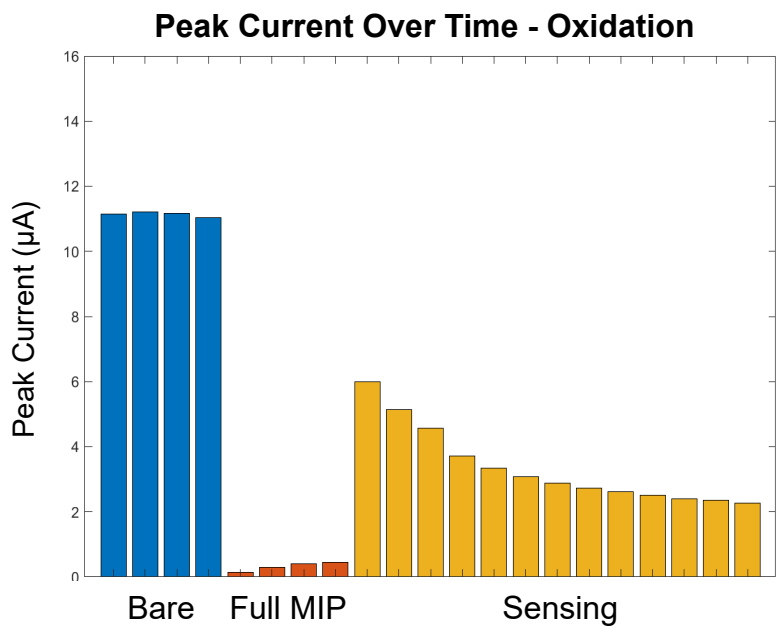
Non-Imprinted Polymer (NIP)



MIP with only Electron Mediator



MIP with 500 ppt PFOS and Electron Mediator



Each bar represents a 10-minute time point

Conclusions

- **The commercialization of a MIP PFAS sensor is still early in development**
- **Current sensor iteration has reproducible responses to PFOS and PFOA**
  - Plans to test other PFAA
- **Need to clearly understand the time dependence and kinetic behavior**
  - Magnitude and time-dependence are needed to fully characterize a sample
- **Sensors are robust and durable**
- **Initial field test has been performed**
  - More are planned for 2023

Future Directions

Limits of Detection (LOD)

- Determine baseline for sensor sensitivity
- Develop a ROC curve

Storage Conditions

- Determine effect on LOD on time from fabrication of sensor to use

Sampling Time

- Length of time sensor can be immersed in water; subsequent effect on LOD
- Variables: length of time immersed, PFAS concentration in solution

Reversibility

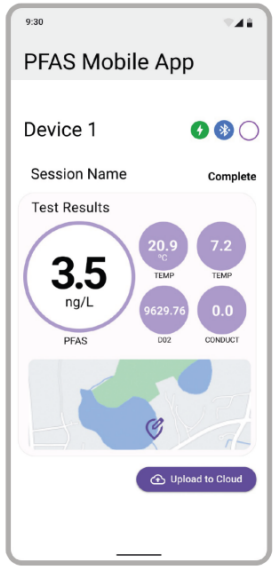
- Investigate mechanisms for reverting sensitivity back to baseline, to include time and materials required

Operating Temperature

- Effect of LOD after temperature cycling
- Determine expected temperature range and number of cycles

Interferents

- Determine effect on LOD from common or predicted interferents



Prototypes for a field sensor suite

Acknowledgements

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