Sandia National Laboratories

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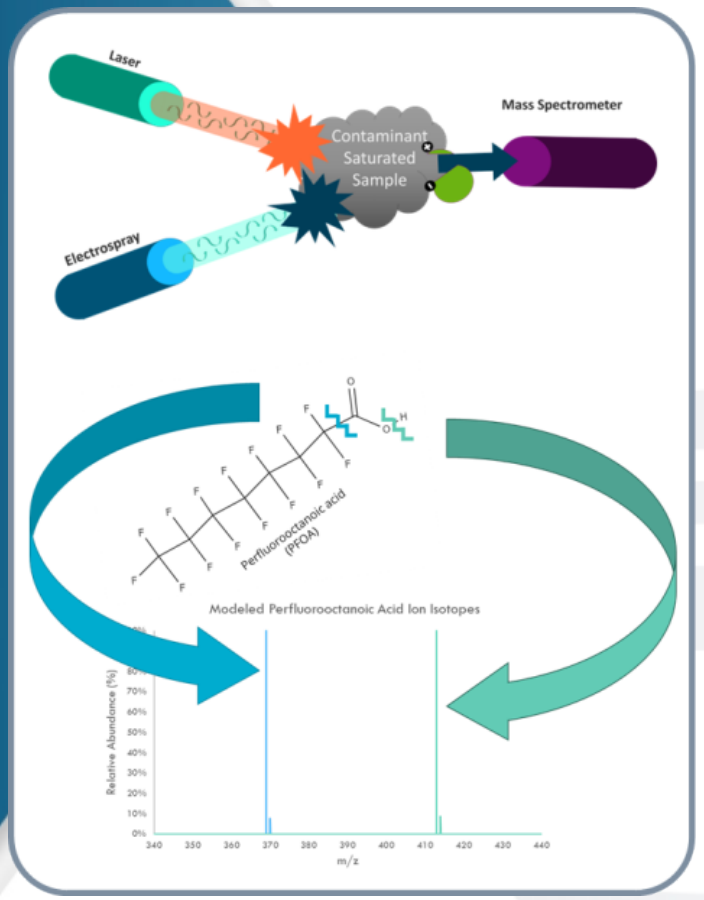
NOVEL METHODS FOR DIRECT ANALYSIS OF PFAS ON ADSORBENTS

Investigating rapid methods for Pollutant Detection



Presented by Nathan R. Bays

Work by Nathan R. Bays, Samantha Kruse, Mohammad Shohel, Jessica A. Lafond, David Schafer, Andre Benally, Jessica Kustas, Andrew W. Knight, Ryan D. Davis

For ACS FALL 2024 session on ‘Analytical Advancements for Emerging Contaminants’

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PFAS ARE INCREASINGLY COMMON AND DANGERO

- Perfluoro-alkyl substances (PFAS) have found wide use in society
  - Grease, water, and stain resistant coatings
  - Also firefighting and other uses

U.S. Fire Administration

- PFAS are highly stable due to strong C-F bonds
  - Poor environmental degradation
- Per U.S. EPA's 'Health Effects Support Documents for PFOA'…
  - Easily distributed throughout the body with long half life (>2 years)
  - Associated with high cholesterol, increased liver enzymes, decreased vaccination response, thyroid disorders, evidence of carcinogenic potential

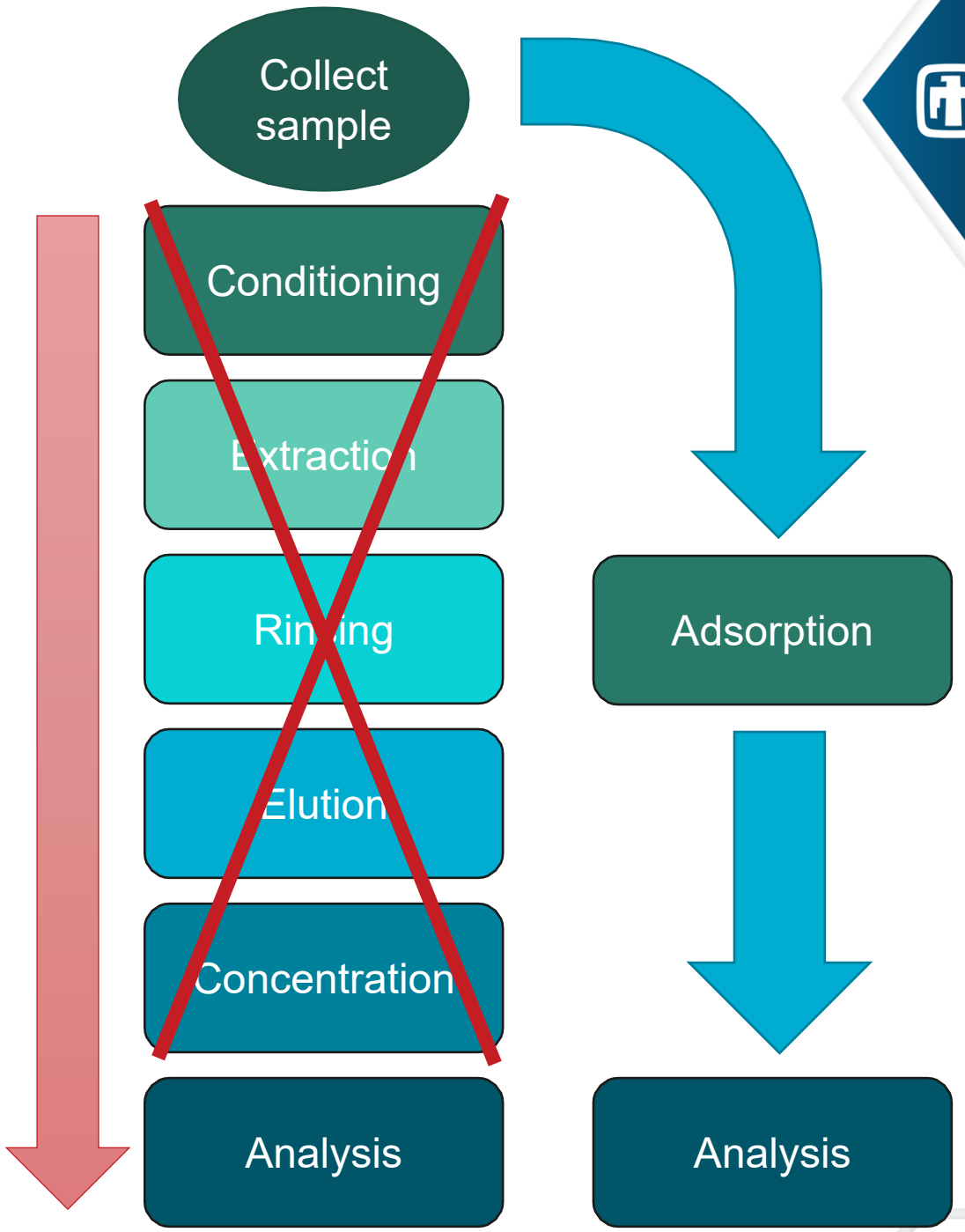
U.S. Environmental Protection Agency (EPA). (2016). Health Effects Support Document for Perfluorooctanoic Acid (PFOA). EPA 822-R-16-003

OBJECTIVE – RAPID THROUGHPUT

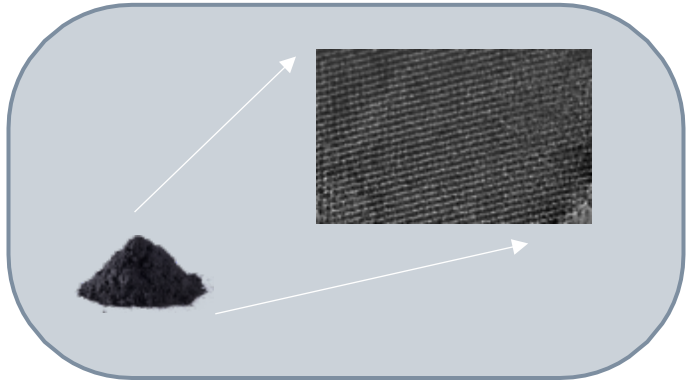
- Frequent complaint – PFAS analysis too slow

- Often a **multi-step** process
  - Solid-phase extraction (SPE): hours
  - LC-MS Analysis: 10-30 min *per sample*

- Direct analysis of adsorbent
  - **One-step** separation and concentration
  - As low as 5 minutes total per sample

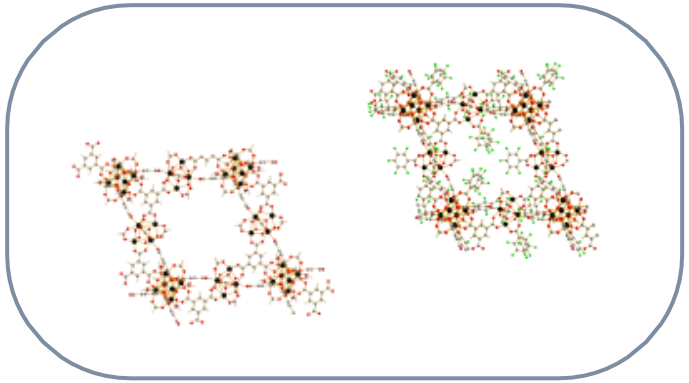


ADSORBENTS USED IN THIS STUDY



- *Novel* and *commercial* adsorbent testing

- **Mesoporous carbons**
  - *CMK-3*, Disordered Carbon (DC), customized materials
- **Metal organic frameworks (MOFs)**
  - *MOF-808*, MOF-808F, NU1000
- **Other commercial adsorbents**
  - Molecular sieves, *activated alumina*



- <u>See Mohammed Shohel's talk here at ACS for more details</u>
  - Wednesday (21st), 3:50-4:05

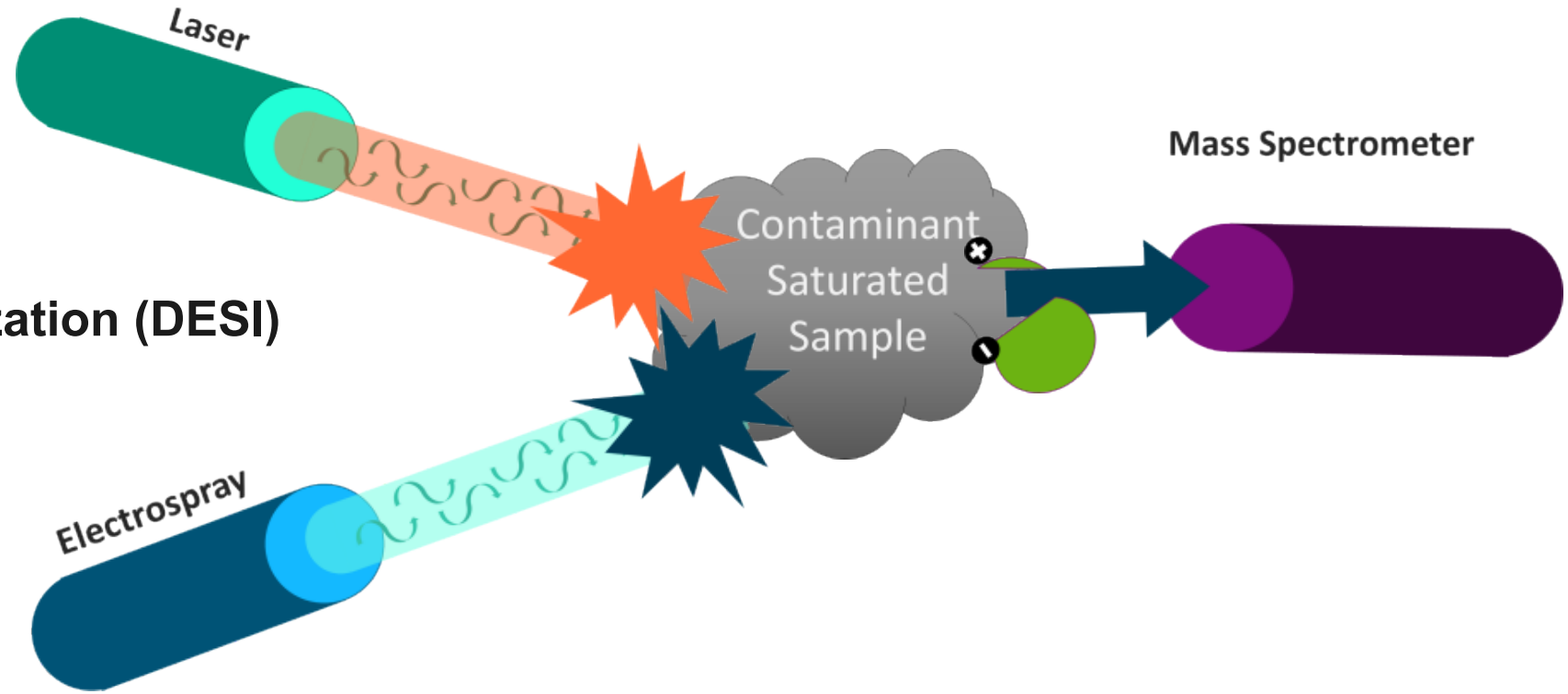
TECHNIQUES FOR DIRECT MS ANALYSIS OF SOLIDS

Matrix-Assisted Laser Desorption Ionization (MALDI)

Typically performed with a matrix co-crystal

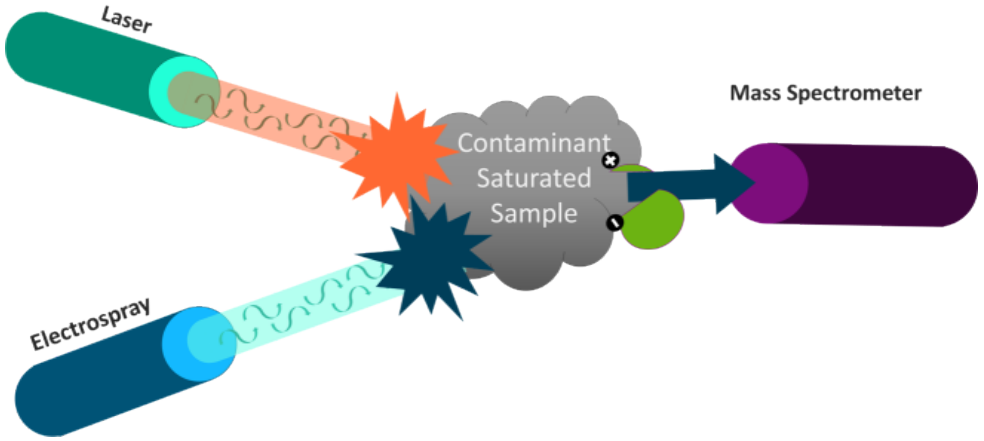
Desorption Electrospray Ionization (DESI)

Charged solvent sprays surface

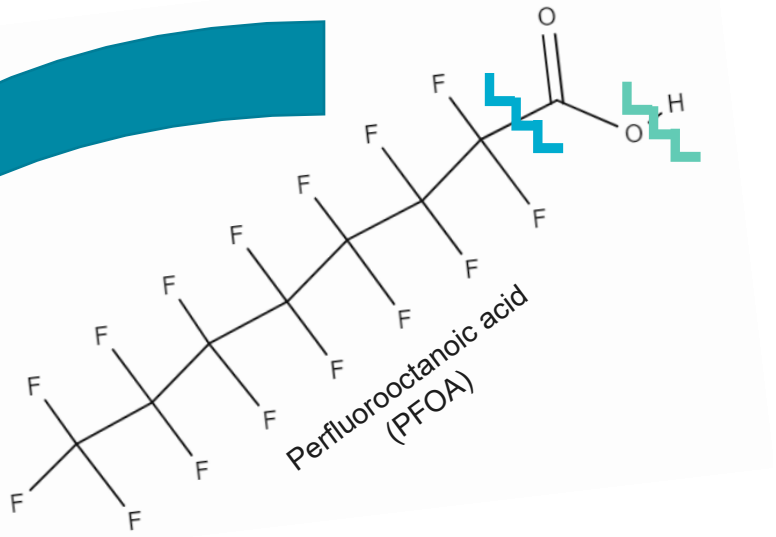


IONIZATION OF PFOA

- m/z = 412.97
- m/z = 368.98
  - Freq. used for quantification
- **Both can be present**

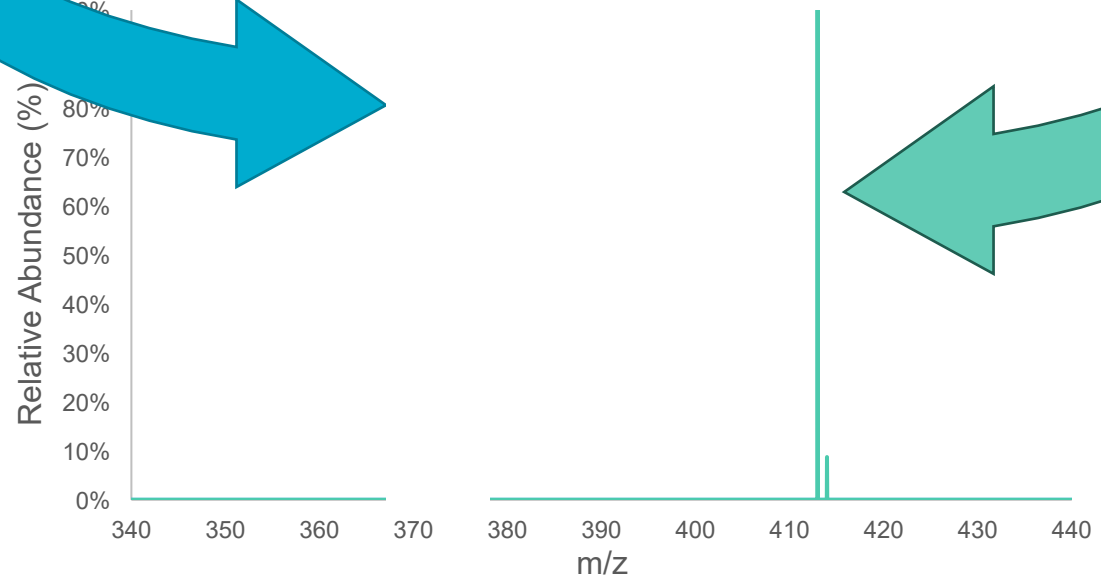


Higher energy



"Gentle" ionization

Modeled Perfluorooctanoic Acid Ion Isotopes



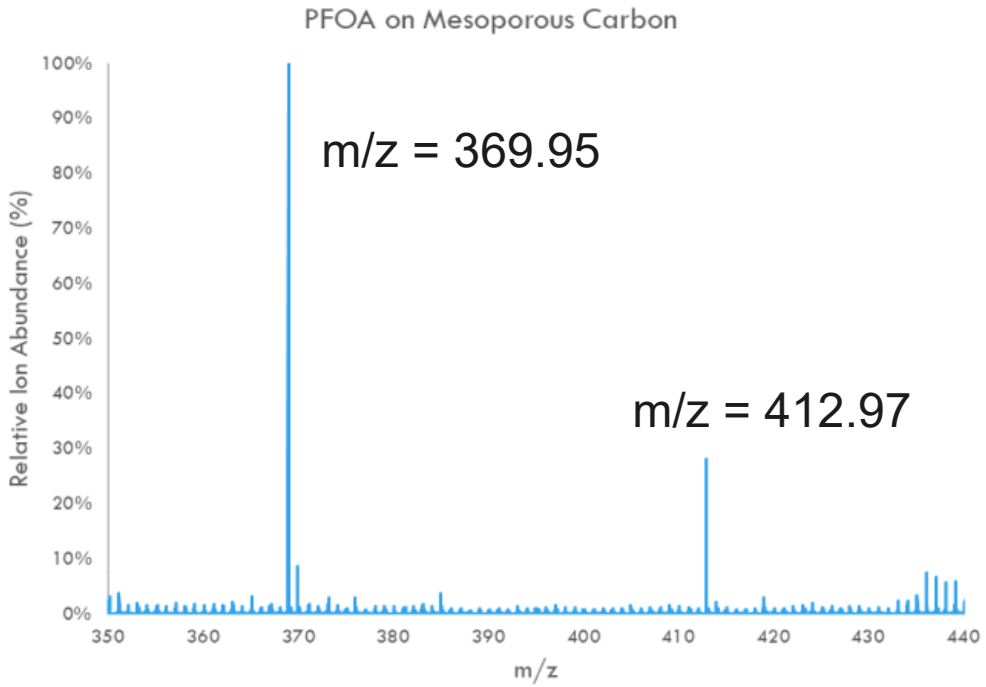
INITIAL RESULTS - SMELDI

200 PPM initial concentration

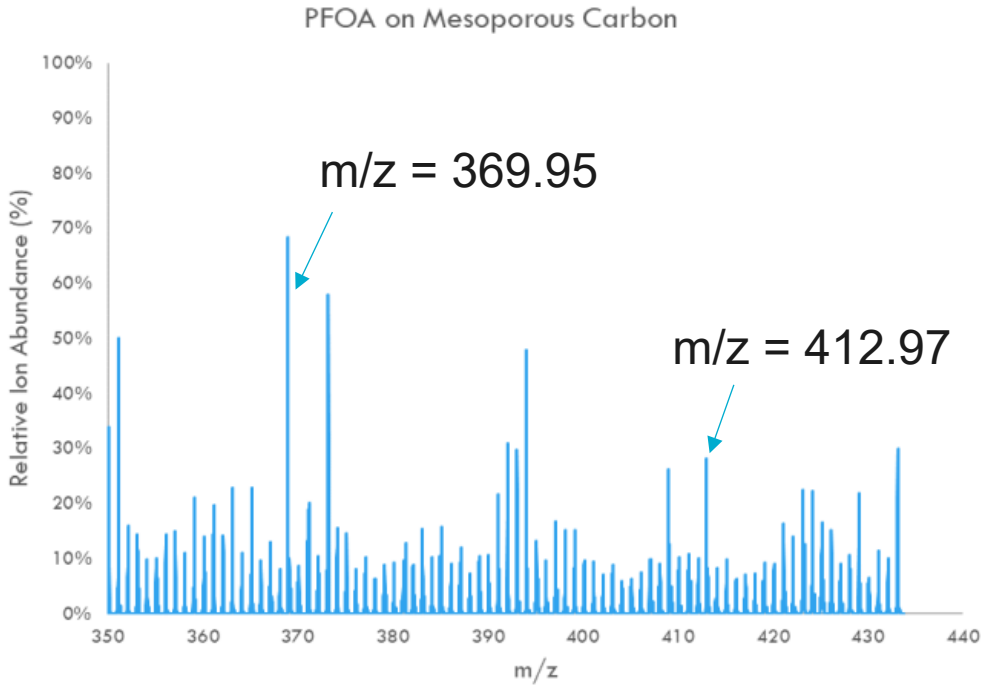
Very High

Areas to improve:

- Consistency
- Lower concentration
- Improve sample prep



Very inconsistent…



The other ~99% looks like this

SMELDI – ALTERNATE ADSORBENTS

- Is this technique specific to carbon?
- No! ☺

Still requires high concentrations

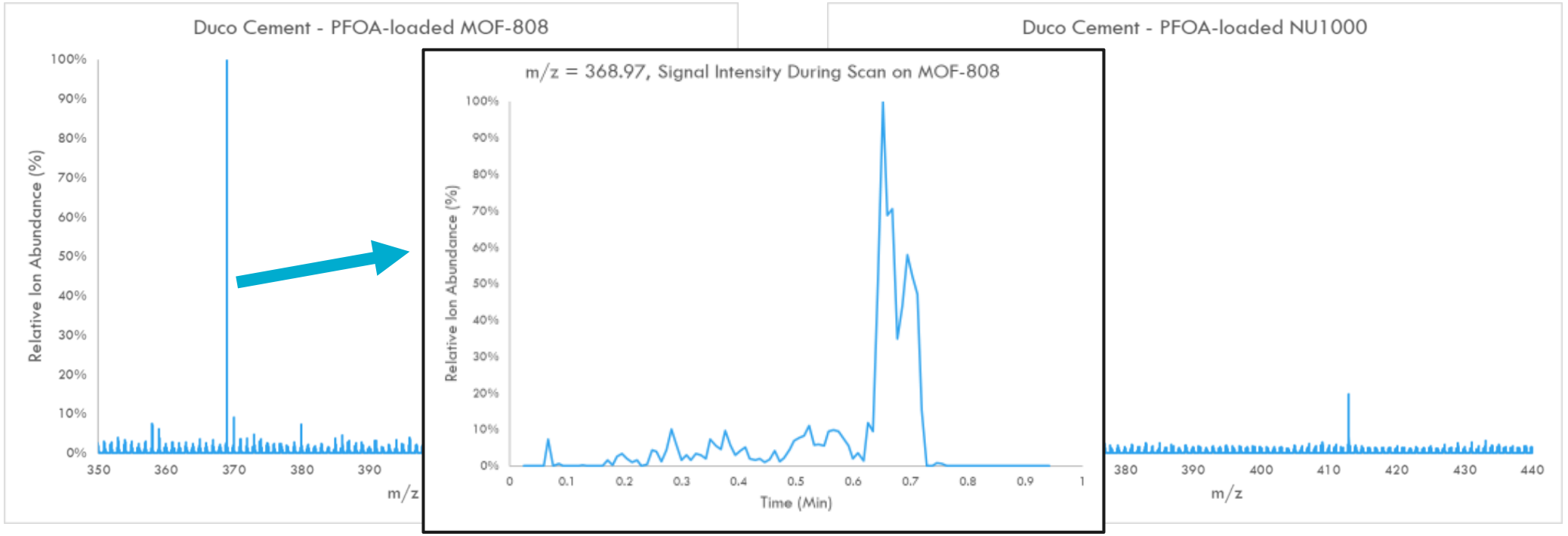
Still very inconsistent

MOF-808

100 PPM initial concentration PFOA

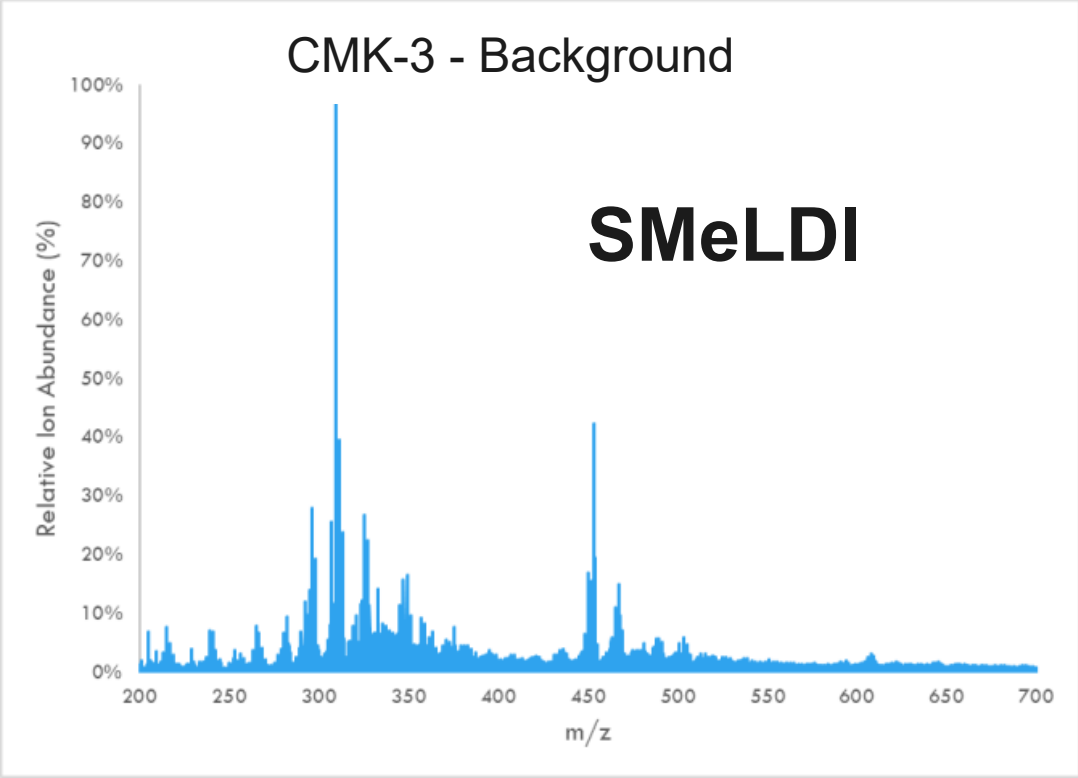
NU1000

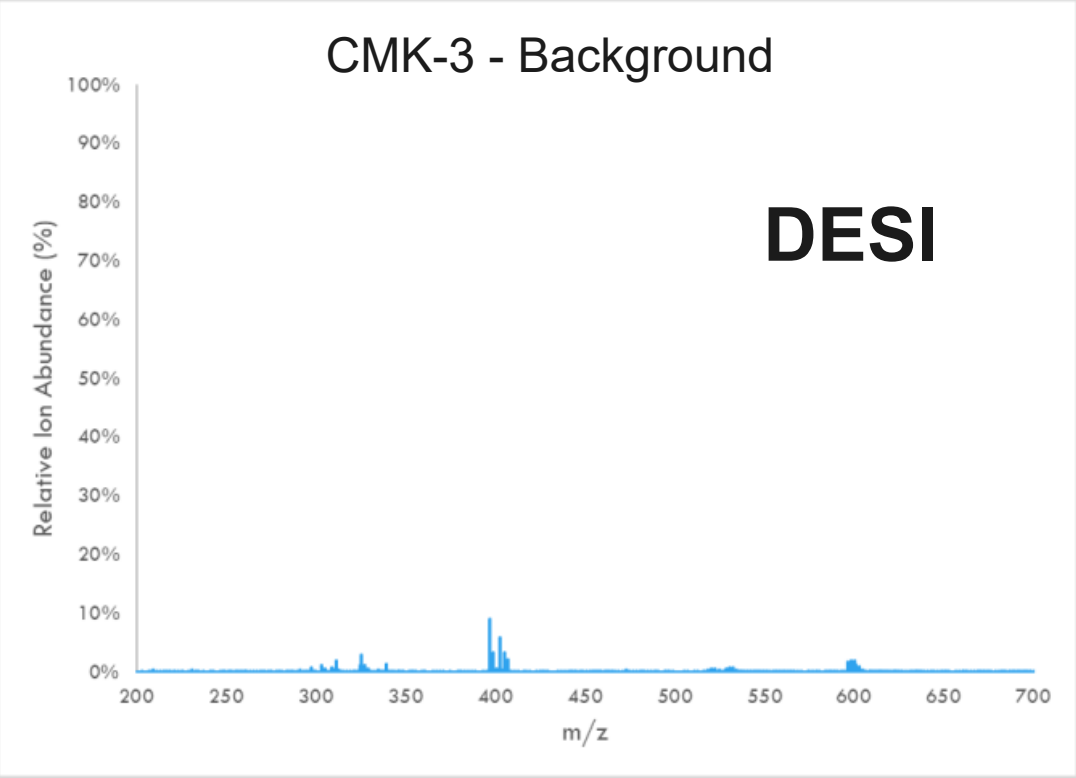
150 PPM initial concentration PFOA



DESI – DESORPTION ELECTROSPRAY IONIZATION

- Electrospray on surface instead of laser ablation
  - Larger spot size than SMeLDI
  - Large flow rate (5x usual)
  - Less noise from *adsorbents*

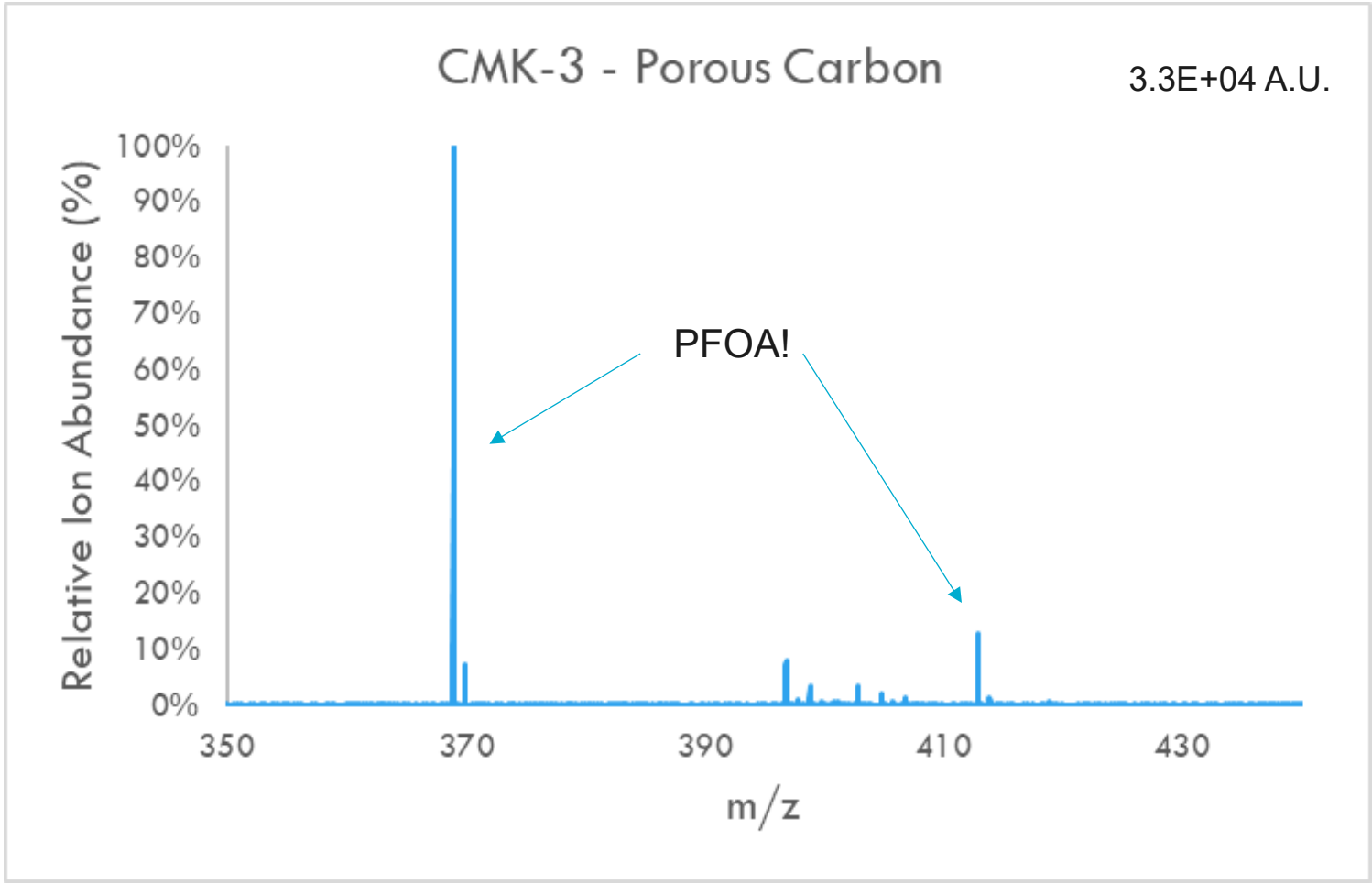




DESI – DOES IT WORK?

Does not ionize carbon or tape

Does it ionize PFOA?



Yes!

100 PPM initial conc. PFOA

- 50 mL solution
- 5 mg CMK-3

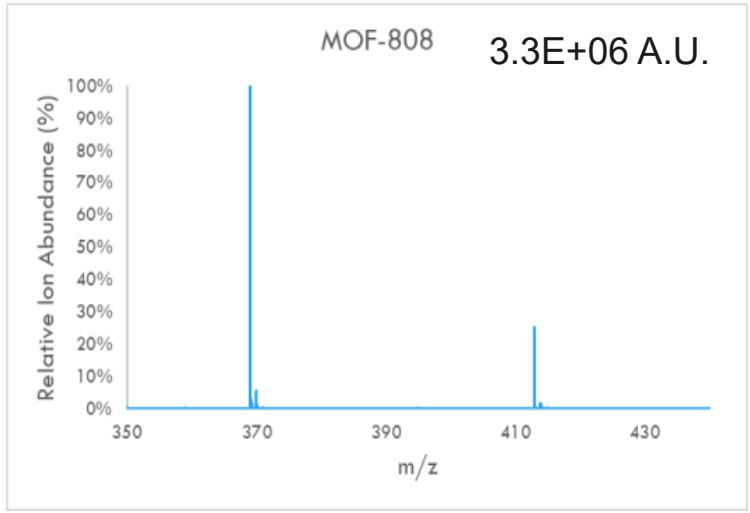
DESI – ADSORBENTS SURVEY

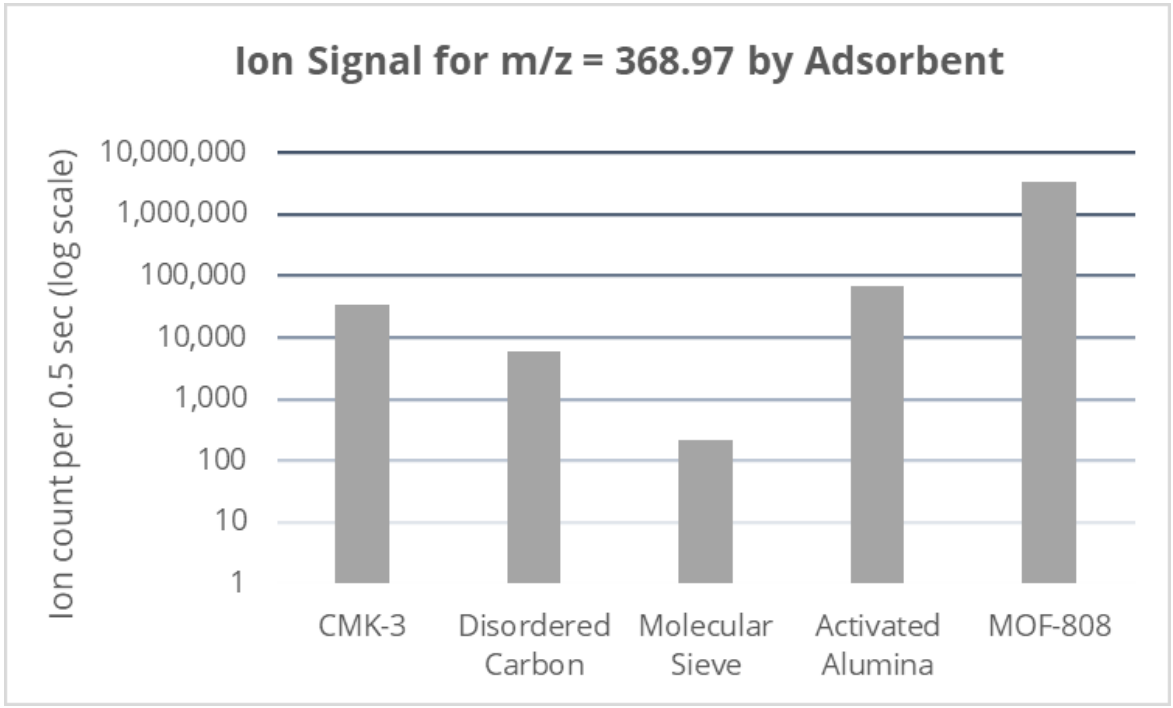
100 PPM PFOA

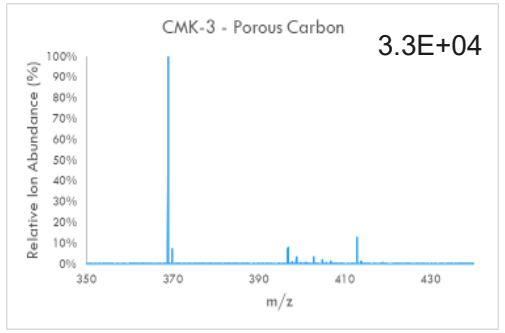
- 50 mL solution
- 5 mg adsorbent

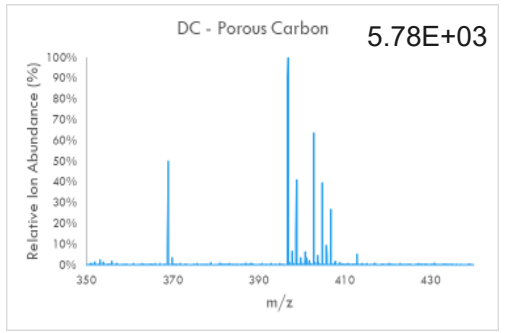
MOF-808 shows best signal

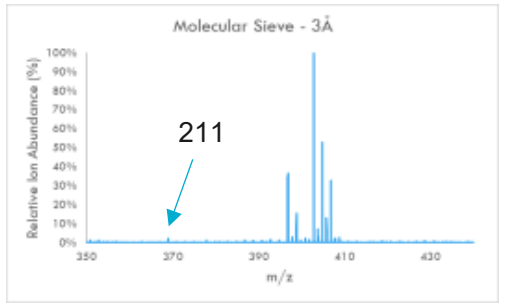
-Powder is difficult and slow to work with
-MOF-808 is expensive

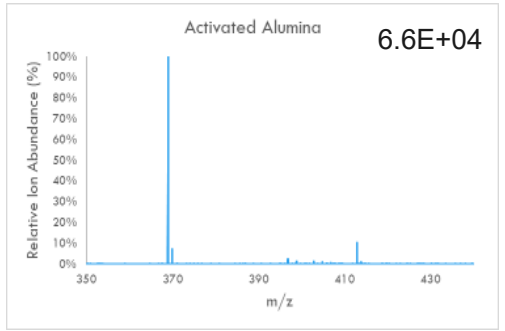






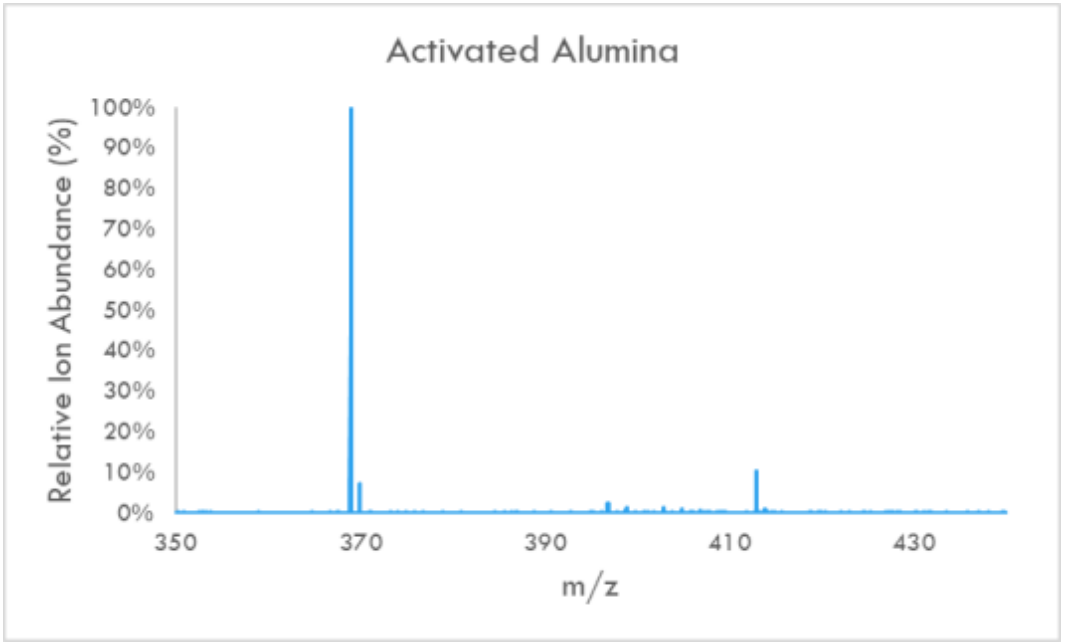


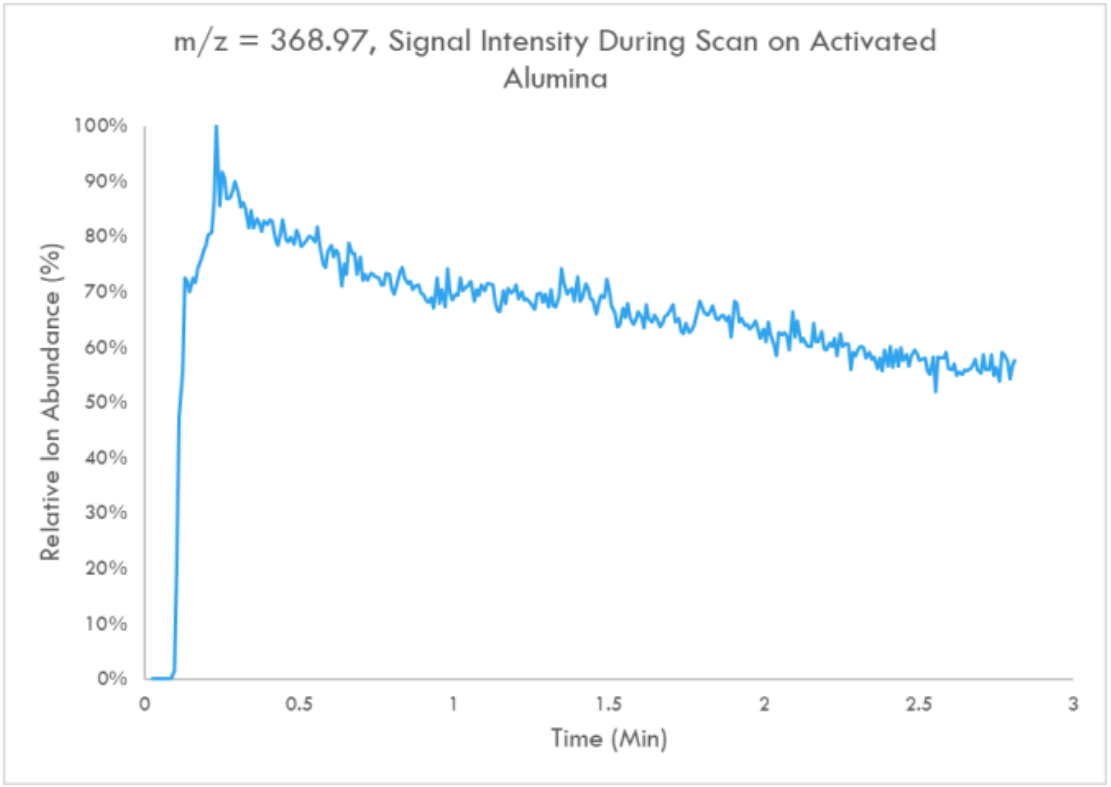




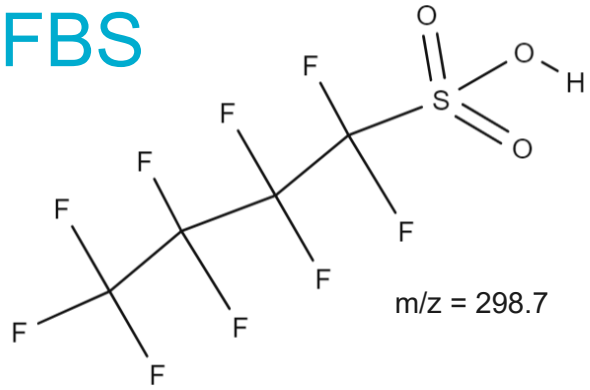
DESI – SIGNAL STABILITY

- Activated Alumina
- Cheap material, large on-hand supply
- Easy to handle, no need to dry
- Strong, stable signal

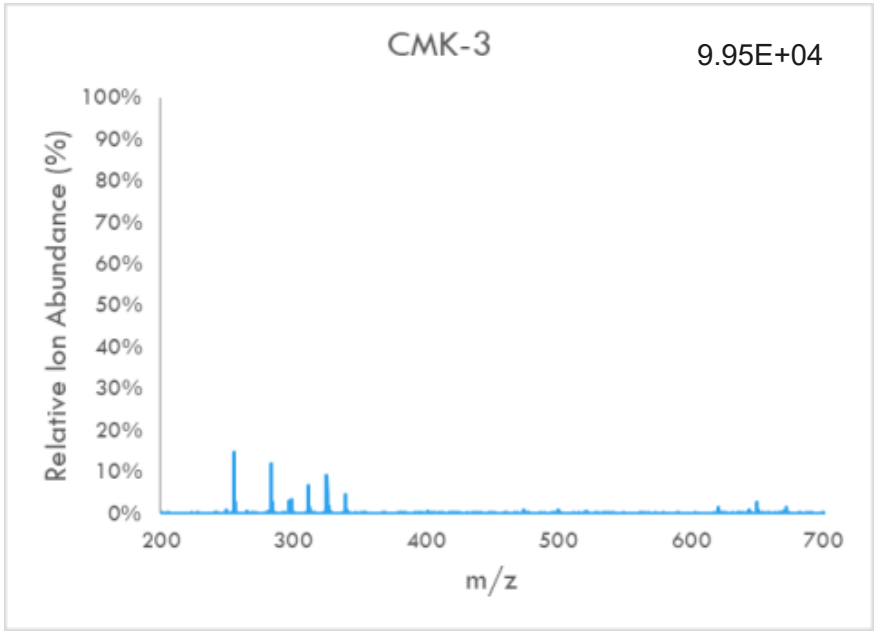


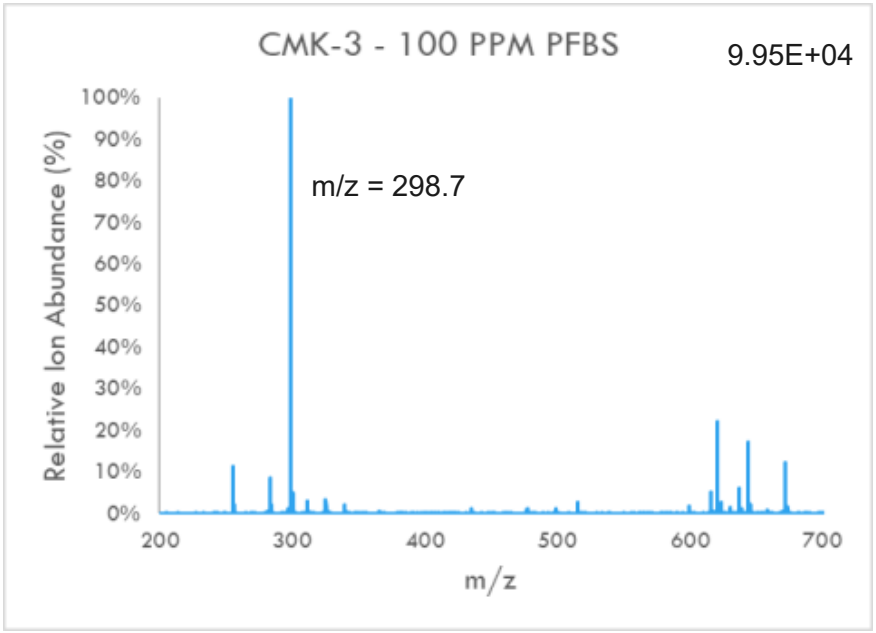


PERFLUOROBUTANESULFONIC ACID - PFBS



- Is this PFOA-specific?
  - No! ☺



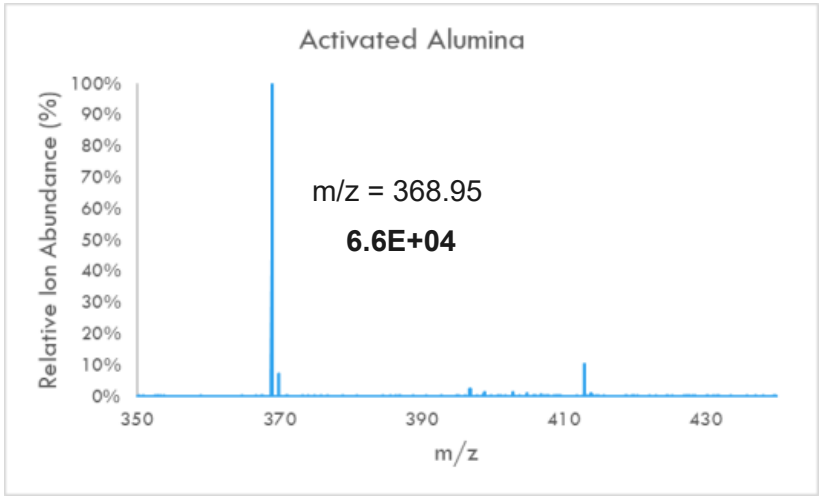


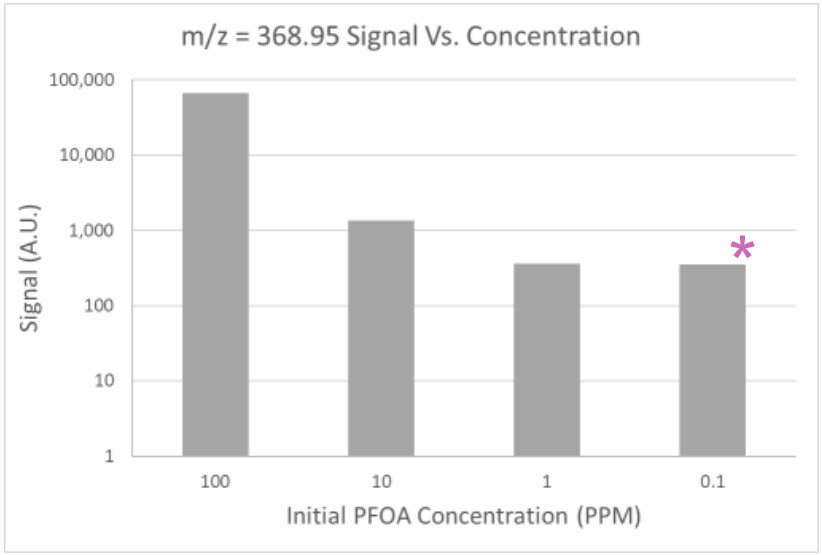
LOWERING CONCENTRATION – ACTIVATED ALUMINA

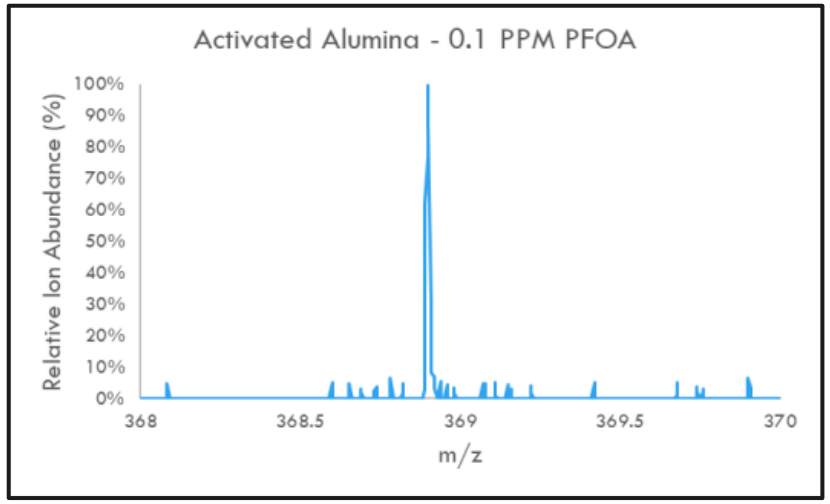
50 mL solution
5 mg of adsorbent

Most important question: **How low can we go?**

Initial PFOA Conc. – 100 PPM



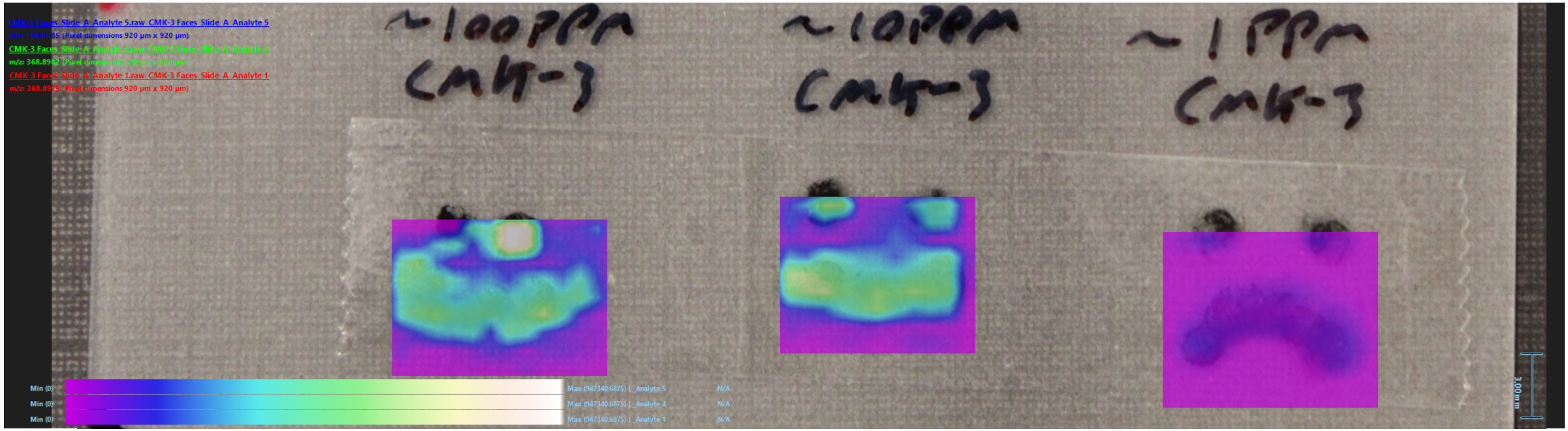




* Short-lived signal

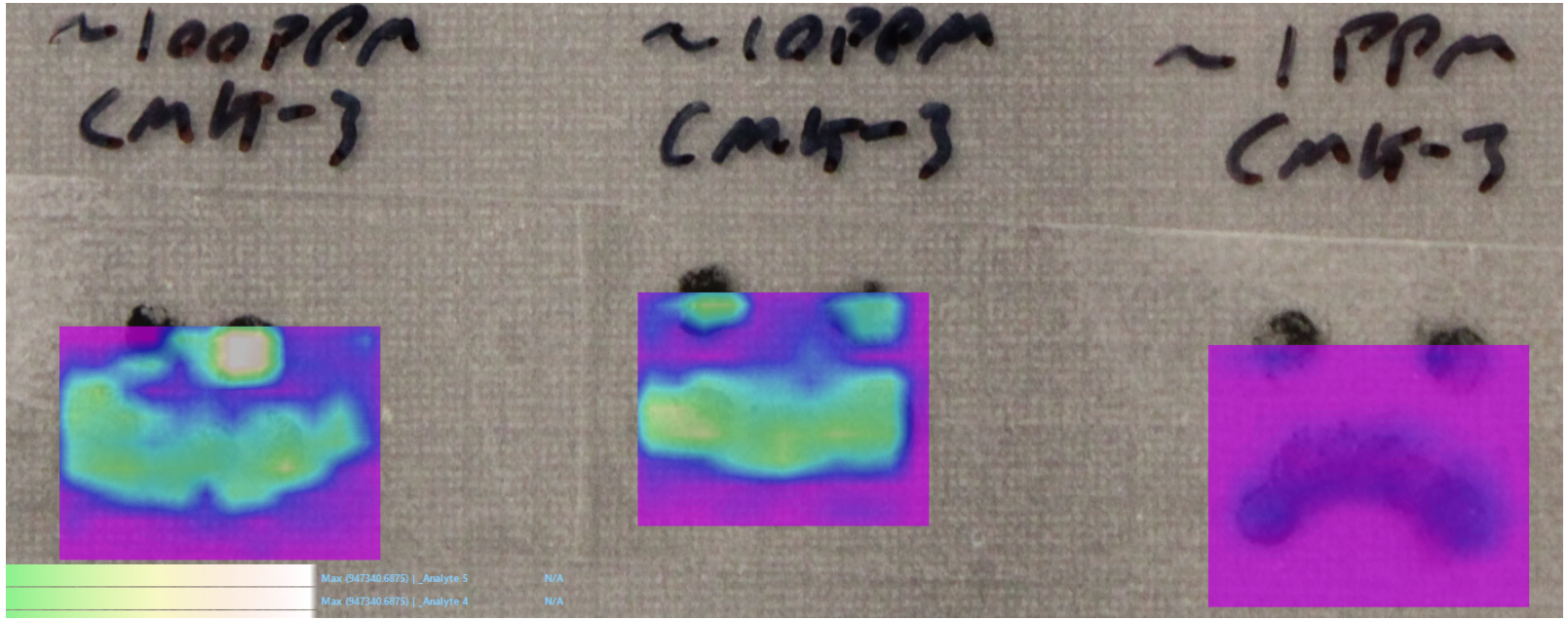
LOWERING CONCENTRATION – CMK-3 (POROUS CARBON)

- 100, 10, 1 PPM solutions



CONCLUSION

- We are developing a new, rapid method for detecting PFOA and other contaminants
  - Direct analysis of solid adsorbent
  - Rapid throughput without sacrificing MS information
    - Can still ID individual PFAS



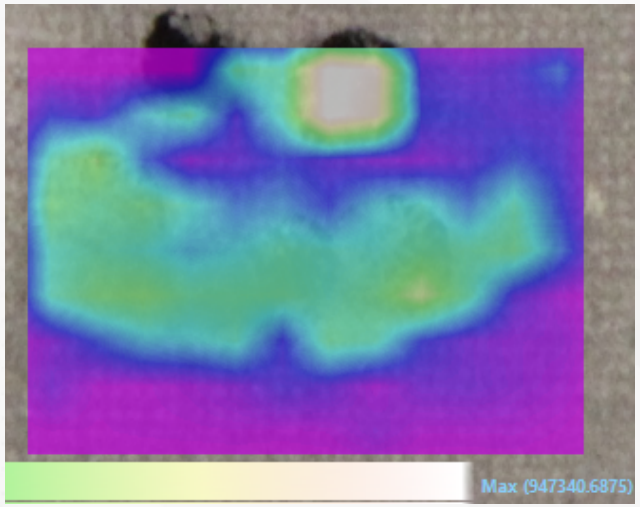
ACKNOWLEDGEMENTS

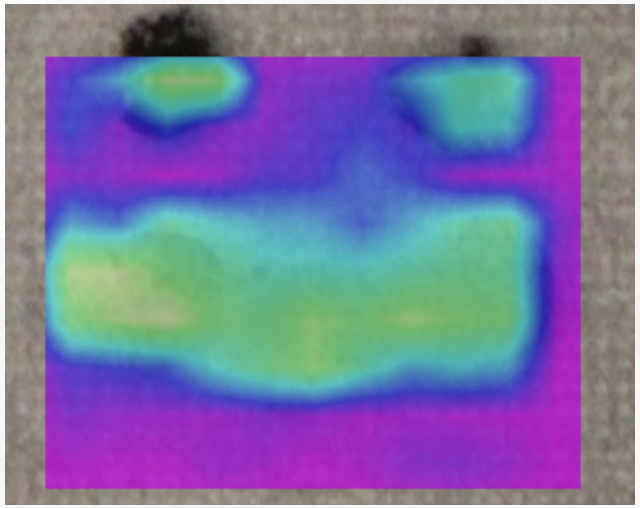
- Postdoctoral Mentors – Ryan D. Davis and Jessica K. Román-Kustas
- Fellow postdocs Mohammed Shohel and Samantha M. Kruse
- Lab members Andre Benally and David Schafer
- Ph.D. intern Jessica A. Lafond

- Sandia National Laboratories
- Department of Energy
- LDRD program

THANK YOU FOR YOUR TIME

QUESTIONS?

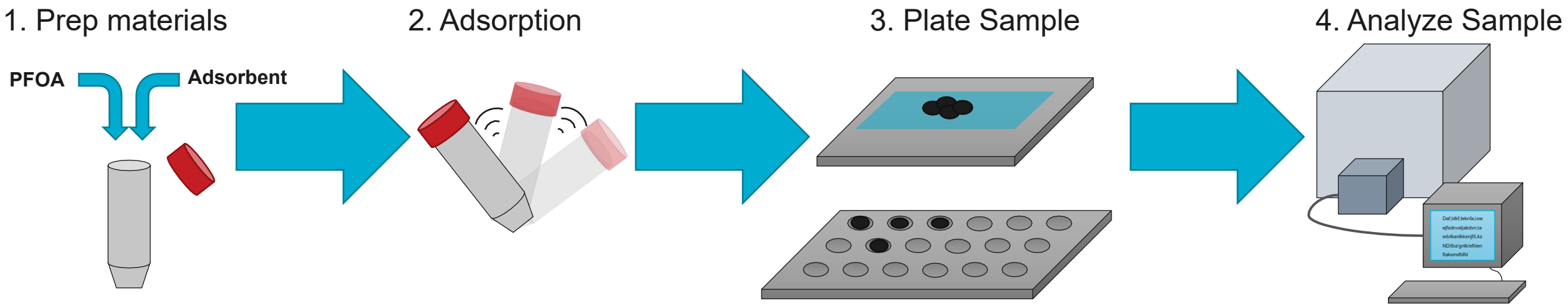




SUPPLEMENTARY

EXPERIMENTAL SETUP

1. Prepare synthetic solutions
2. Adsorption process – typically excessive (i.e., 1 or 24 hours with agitation)
3. Plate sample
4. Analyze sample using MALDI- or DESI-MS



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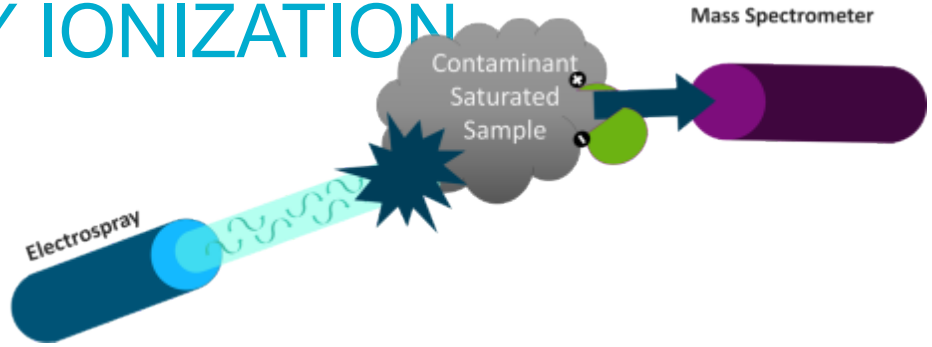
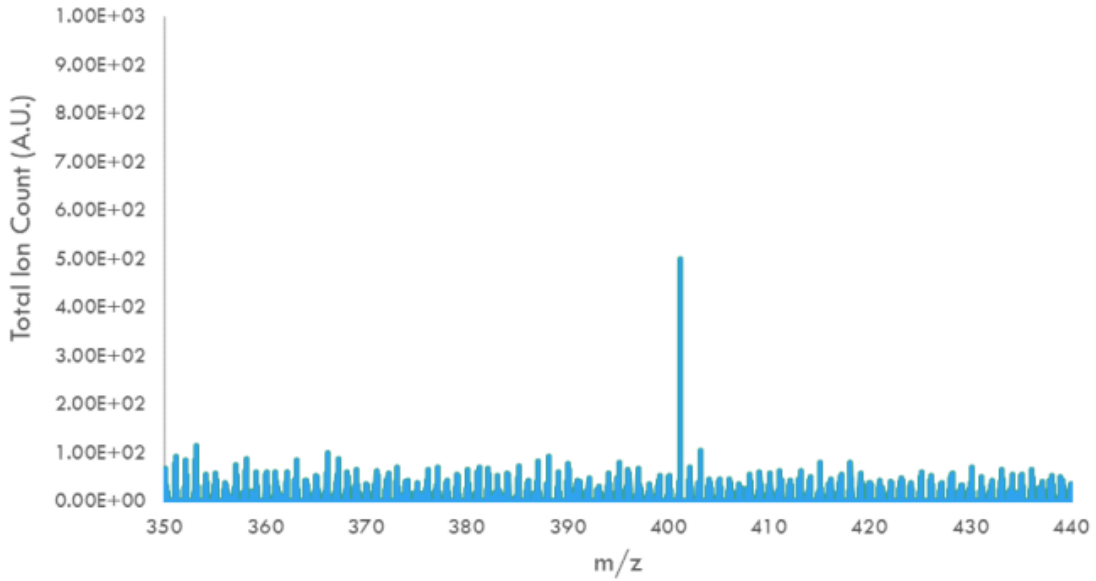
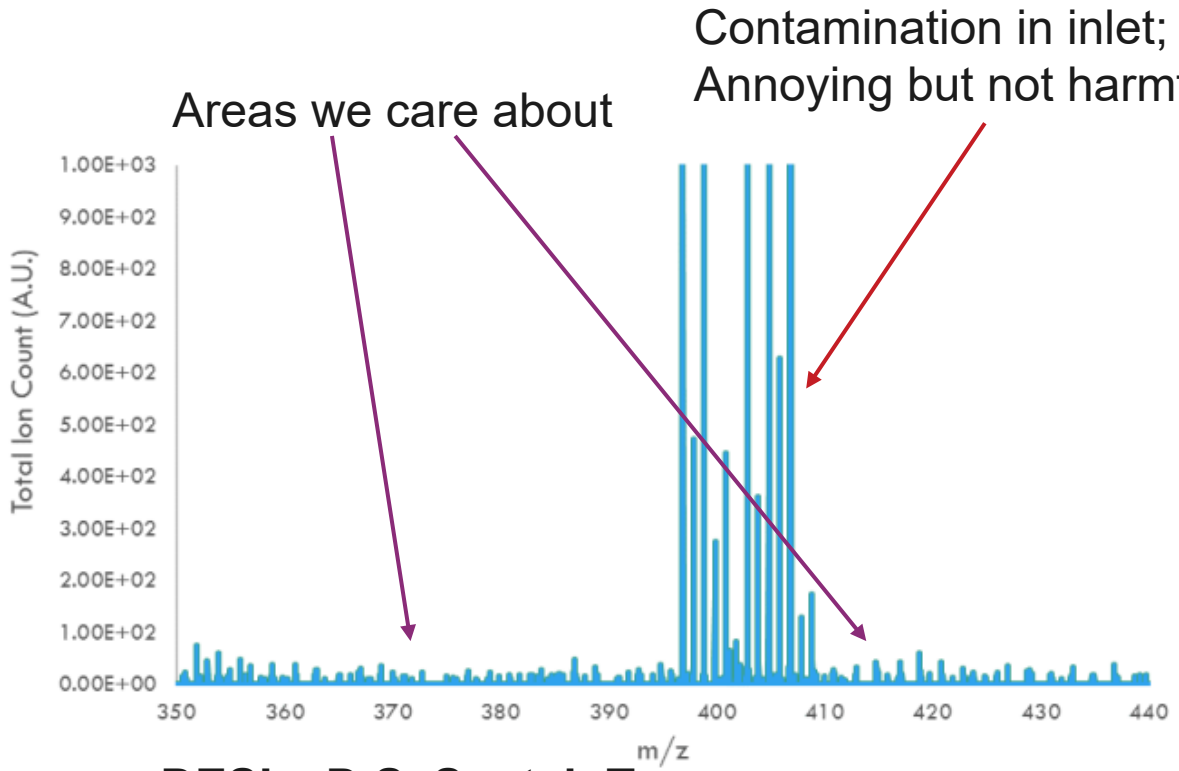


- Electrospray on surface instead of laser ablation
  - Larger spot size than SMELDI
  - Large flow rate (5x usual)
- Similar background noise from *adhesives*



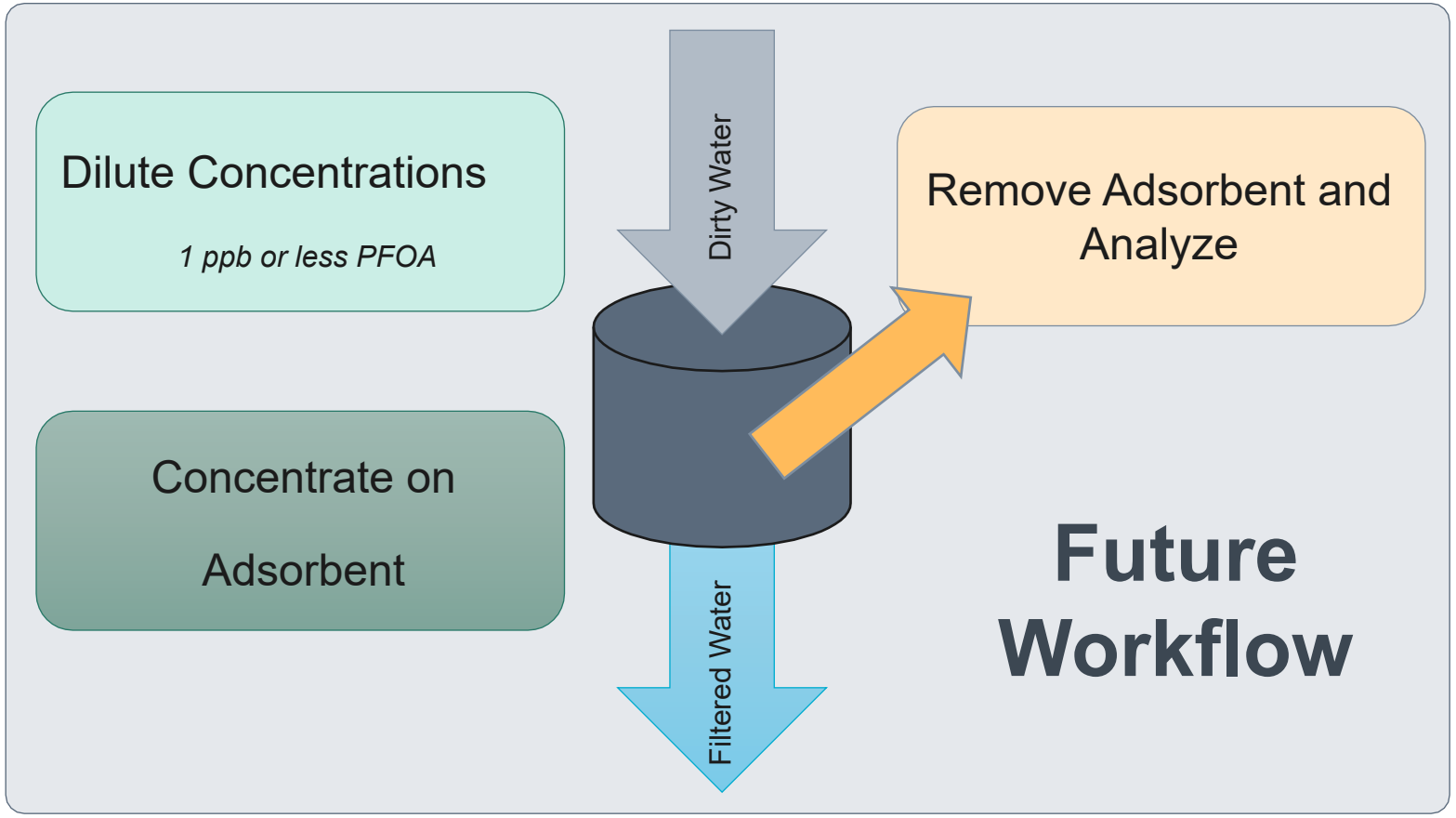
SMeLDI – D.S. Scotch Tape



DESI – D.S. Scotch Tape

FUTURE WORK

- Tie up loose ends
  - E.g., MOF-808
- Pre-concentration work
- Other PFAS (or pollutants)



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