Ambient and Indoor Air Sampling for PFAS

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PFAS in Air – Outline

- **PFAS Background**
  - Environmental PFAS testing
- **Source Air Sampling**
  - OTM-45 overview
  - ASE extraction
  - Resin Cleaning
- **Ambient and Indoor Air**
- **Future Work**

PFAS Background

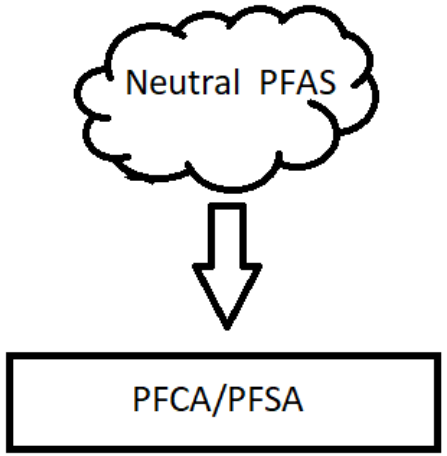
- PFAS (per- and polyfluoro alkyl substances) are a class of chemical compounds with many industrial and commercial applications, including non-stick surfaces, rain-repellent fabrics, electronics, and many others
- Linked to several human health problems, such as cancer, thyroid disease, and pregnancy issues
- Due to their inert nature, they are very stable in the environment and have the potential to bio-accumulate

State of Environmental PFAS Analysis

- **Water analysis, especially drinking water, well defined**
  - Several existing methods that have been in place for some time
- **Soil testing less well defined, but methods exist to cover it**
  - Modified water methods have been used, but newer methods have soil and solids included
- **Source air testing draft methods have been put out**
- **No methods for PFAS ambient or indoor air**

State of Environmental PFAS Analysis

- **Volatile PFAS are present in air**
  - Neutral PFAS such as fluorotelomer alcohols (FTOH), perfluorinated sulfonamides (FOSA) and sulfonamide ethanols (FOSE) are volatile and capable of long-range atmospheric transport
  - Neutral PFAS are precursors to ionic PFAS compounds such as perfluoroalkyl carboxylates (PFCA) and perfluoroalkane sulfonates (PFSA)



Annika Jahnke, Urs Berger, Trace analysis of per- and polyfluorinated alkyl substances in various matrices—How do current methods perform?, Journal of Chromatography A, Volume 1216, Issue 3, 2009, Pages 410-421

State of Environmental PFAS Analysis

- **Source emissions can spread volatile and semivolatile PFAS**
  - PFAS can be dispersed in vapor phase or on particulates

- **Combustion can create both short chain and large fluorinated molecules**
  - Combustion and incineration processes can create short chain PFAS such as trifluoroacetic acid (TFA) and carbon tetrafluoride (CF_4)
  - At ≤ 800°C fluorinated dioxins and furans can be created

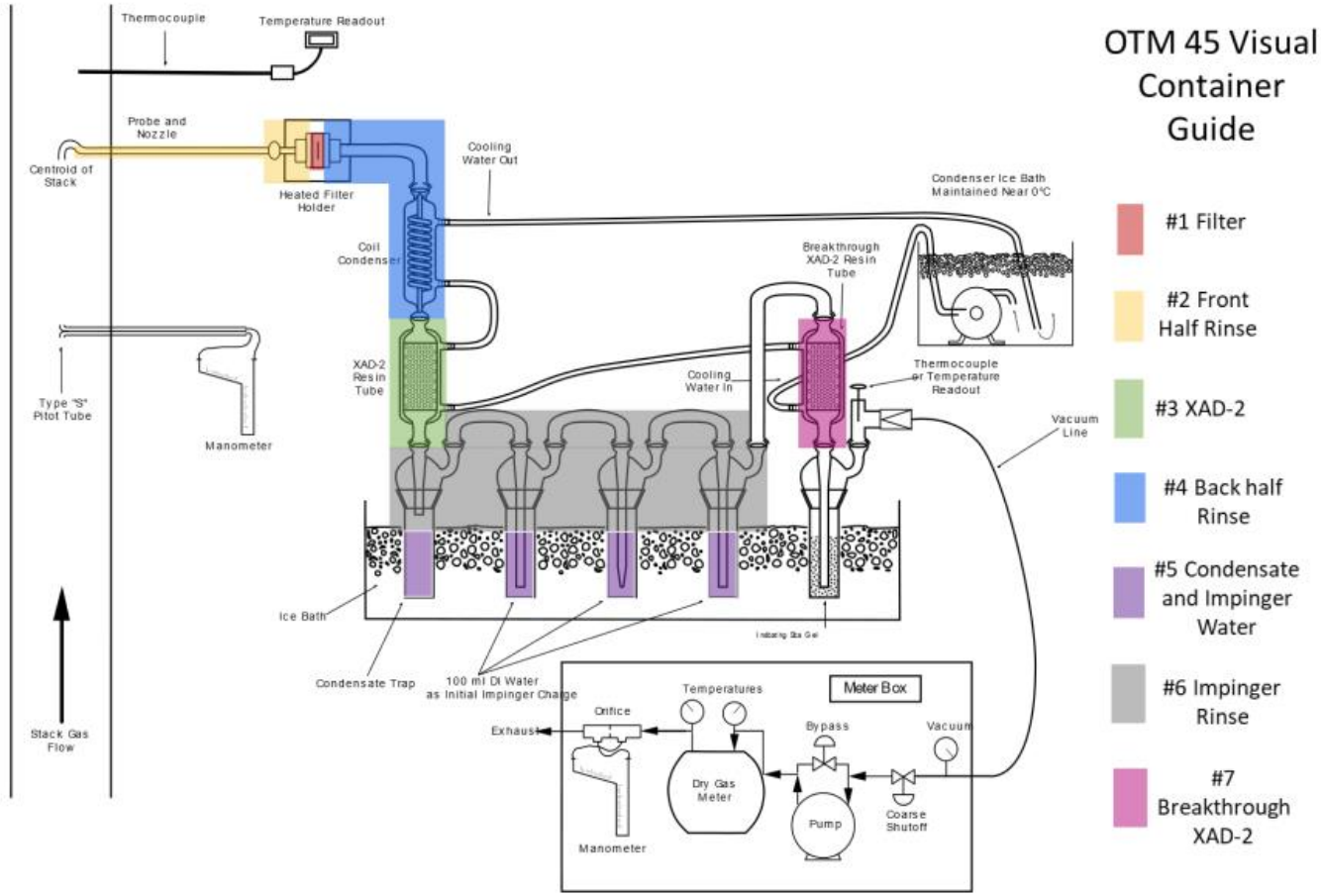
State of Environmental PFAS Analysis

- **PFAS can be present in indoor air**
  - Off gassing of volatile PFAS from consumer products
  - Airborne dust containing PFAS from product wear and tear

Kerstin Winkens et al,Perfluoroalkyl acids and their precursors in floor dust of children's bedrooms – Implications for indoor exposure, Environmental International, Volume 119, 2018, Pages 493-502

Source Air Sampling – OTM-45

- Combines filter, XAD-2, and liquid impingers
- Suitable for C_4 to C_{18} PFAS compounds
- Many different PFAS classes (PFCA, PFSA, FOSA, FOSE, etc.)



OTM-45 – Chromatography

- **OTM-45 provides a HPLC gradient method that is 35 minutes long**
  - No chromatogram or retention times given
- **Using a Restek Force C18 column a run time of 8.5 minutes can be achieved**
  - Over 4 times faster than the parameters in OTM-45

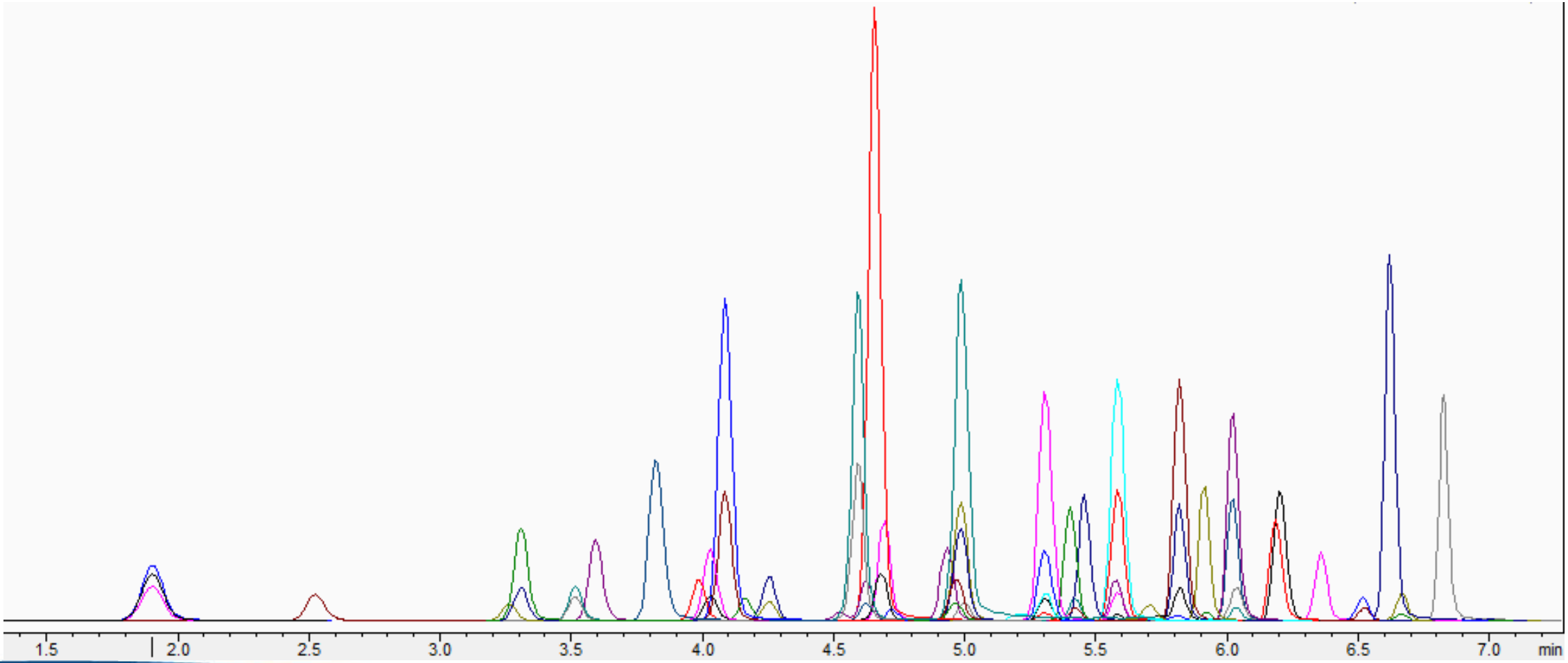
OTM-45 – Chromatography

- **Column**
  - Force C18 50mm x 2.1mm x 1.8µm
  - PFAS Delay 50mm x 2.1mm x 5µm
- **Mobile Phase**
  - A – Water, 5.0mM ammonium acetate
  - B – Methanol

Time (min)	Flow (mL/min)	%A	%B
0	0.4	80	20
6	0.4	5	95
6.01	0.4	5	95
7.5	0.4	5	95
7.51	0.4	80	20
8.5	0.4	80	20

- **HPLC – Shimadzu Nexera X2**
  - Column temperature – 40°C
  - Autosampler temperature – 5°C
  - Injection volume – 3µL
- **Detector – Shimadzu 8045 MS/MS**
  - Nebulizing gas flow – 3 L/min
  - Heating gas flow – 15 L/min
  - Interface temperature – 300°C
  - DL temperature – 200°C
  - Heat block temperature – 200°C
  - Drying gas flow – 5 L/min

OTM-45 – Chromatography



OTM-45 – ASE Extraction

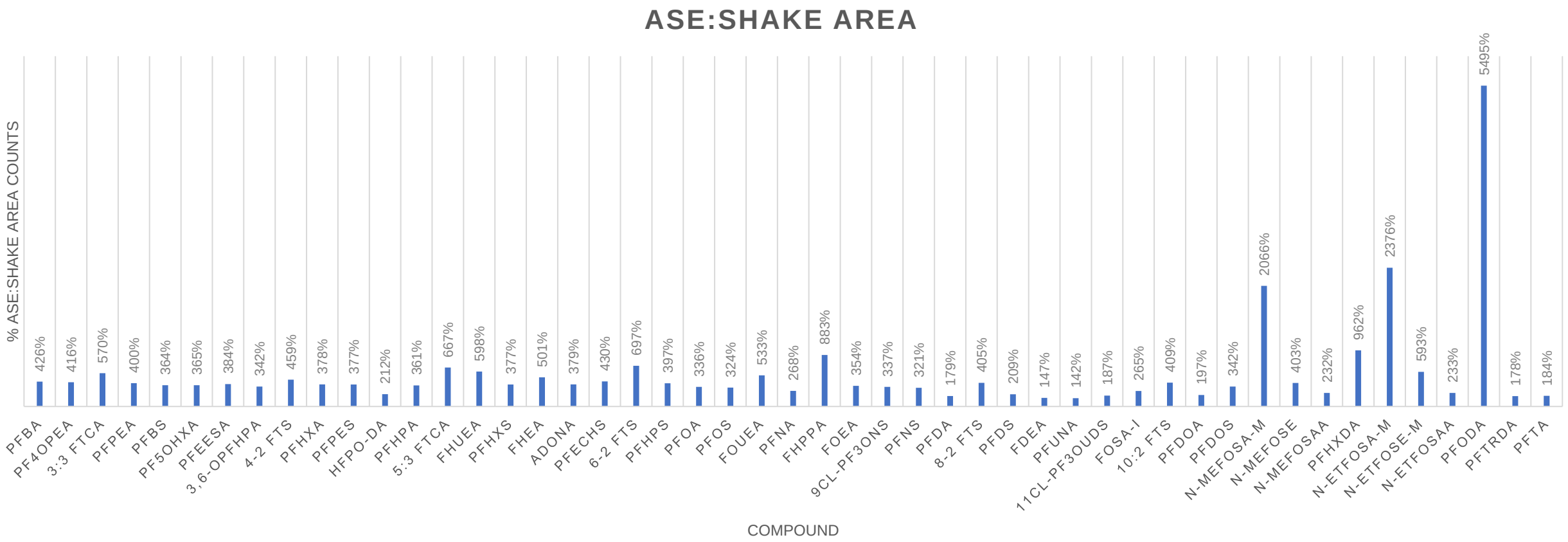
- **OTM-45 sample prep for XAD-2 fraction is two rounds of 16-hour shakeouts using 360 mL total solvent**
  - 32-hour extraction plus time for solvent blowdown

- **Accelerated Solvent Extraction (ASE) advantages**
  - Reduced time – ~45 minutes/sample
  - Reduced solvent use – <100mL solvent/sample
  - Higher extraction efficiency – 1.4 to 55 times more response on ASE

OTM-45 – ASE Extraction

- **Dionex ASE 350 Extraction Parameters**
  - Pressure – 1500 psi
  - Temperature – 120°C
  - Heating time – 6 minutes
  - Static time – 15 minutes
  - Cycles – 2
  - Rinse volume – 60%
  - Solvent – 4:1 Methanol:Acetonitrile

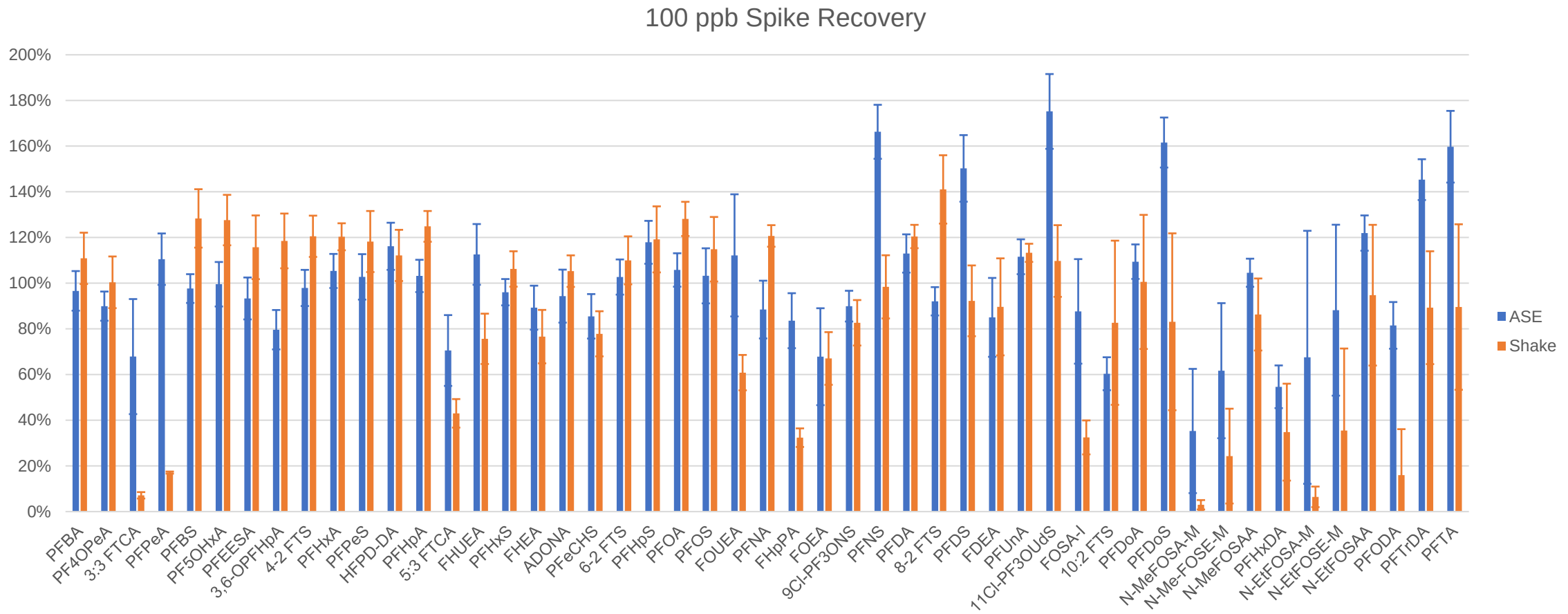
OTM-45 – ASE Extraction



OTM-45 - Accuracy

- **37 of 49 compounds met ±30% accuracy requirement when using ASE extraction**
- **34 of 49 compounds met ±30% accuracy requirement when using shakeout extraction**
- **Compounds that did not meet criteria were mostly those without exact isotope dilution standards**
  - Testing was done without the full list of isotope dilution standards listed in OTM-45

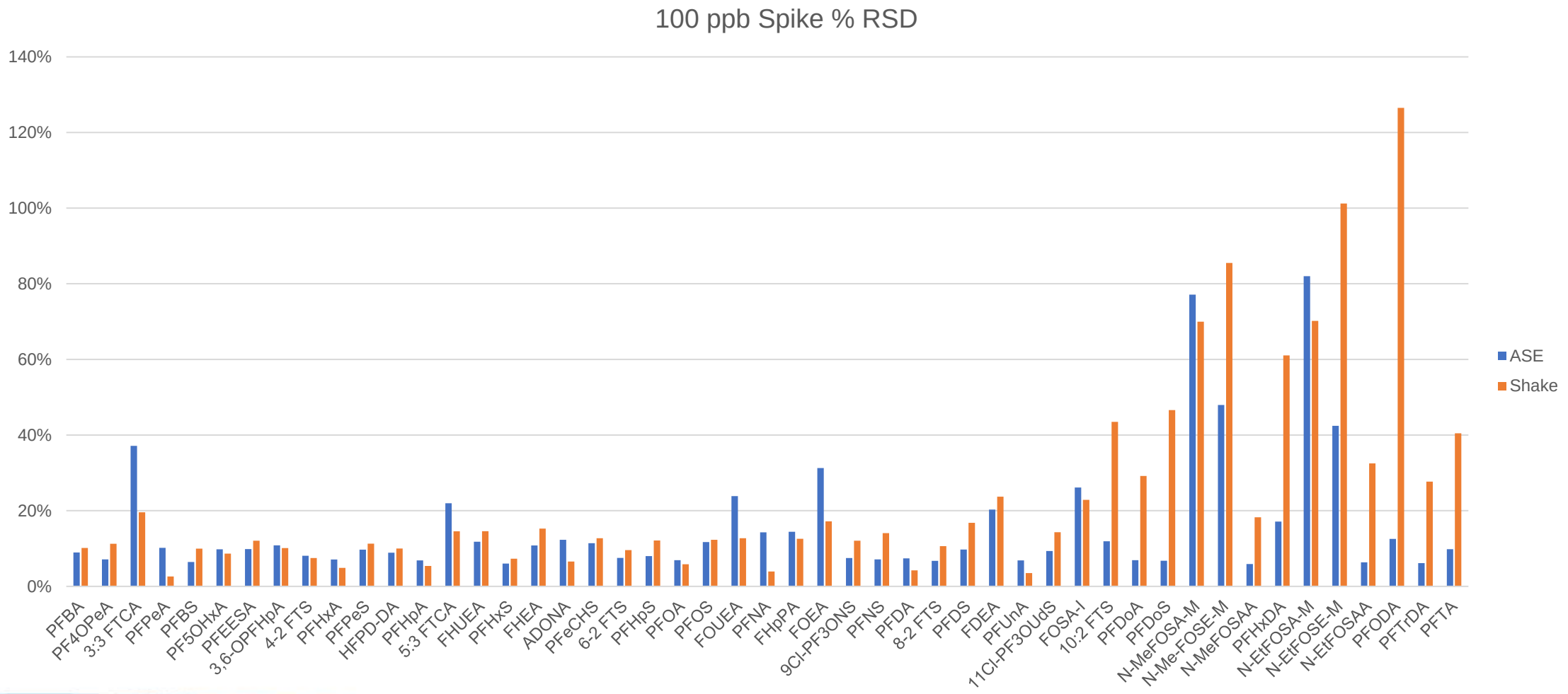
OTM-45 - Accuracy



OTM-45 - Precision

- 40 of 49 compounds met ≤ 20% RSD requirement when using ASE extraction
- 35 of 49 compounds met ≤ 20% RSD requirement when using shakeout extraction
- % RSD for last eluting compounds much higher by shakeout

OTM-45 - Precision



OTM-45 - MDL

- OTM-45 does not give Method Detection Limit (MDL) values for all 49 compounds
- MDL values are calculated with a nominal 3 m^3 sampling volume
- Calculated MDL values from ASE extraction meet or are below OTM-45 values with 2 exceptions

OTM-45 – MDL

Name	OTM-45 MDL	Restek MDL	Name	OTM-45 MDL	Restek MDL	Name	OTM-45 MDL	Restek MDL
PFBA	2.08	0.06	FHEA		0.09	FDEA		0.07
PF4OPeA		0.02	ADONA	0.14	0.02	PFUnA	0.33	0.08
3:3 FTCA		0.05	PFeCHS		0.03	11Cl-PF3OUdS	0.18	0.04
PFPeA	0.2	0.03	6-2 FTS	0.29	0.02	FOSA-I	0.27	0.13
PFBS	0.17	0.07	PFHpS	0.08	0.03	10:2 FTS		0.04
PF5OHxA		0.01	PFOA	0.43	0.22	PFDoA	0.12	0.10
PFEESA		0.01	PFOS	0.35	0.04	PFDoS		0.06
3,6-OPFHpA		0.02	FOUEA		0.07	N-MeFOSA-M		0.07
4-2 FTS	0.20	0.02	PFNA	0.15	0.06	N-Me-FOSE-M		0.07
PFHxA	0.31	0.02	FHpPA		0.14	N-MeFOSAA	0.4	0.05
PFPeS	0.14	0.02	FOEA		0.18	PFHxDA		0.05
HFPO-DA	2.77	0.22	9Cl-PF3ONS	0.17	0.03	N-EtFOSA-M		0.17
PFHpA	0.21	0.10	PFNS	0.14	0.18	N-EtFOSE-M		0.05
5:3 FTCA		0.07	PFDA	0.13	0.05	N-EtFOSAA	0.39	0.08
FHUEA		0.06	8-2 FTS	0.27	0.07	PFODA		0.05
PFHxS	0.17	0.06	PFDS	0.17	0.32	PFTrDA	0.12	0.8
MDL values in ng/m3 air						PFTA	0.19	0.05

Restek's Work with PFAS in Air OTM-45 – Resin Cleaning

- **Modified extraction method used to better clean Ultra-Clean Resin**

- **Dionex ASE 350 Cleaning Parameters**
  - Pressure – 1500 psi
  - Temperature – 120°C
  - Heating time – 6 minutes
  - Static time – 15 minutes
  - Cycles – 2
  - Rinse volume – 60%
  - Solvent – 1:1 Methanol:Methylene Chloride

OTM-45 – Resin Cleaning

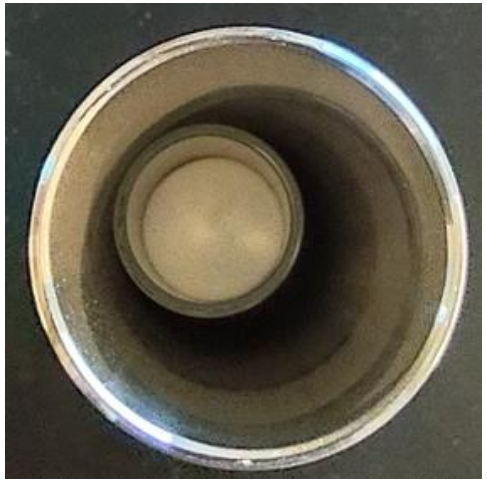
Name	Blank	Restek MDL	Name	Blank	Restek MDL	Name	Blank	Restek MDL
PFBA	<MDL	0.06	FHEA	<MDL	0.09	FDEA	<MDL	0.07
PF4OPeA	<MDL	0.02	ADONA	<MDL	0.02	PFUnA	<MDL	0.08
3:3 FTCA	<MDL	0.05	PFeCHS	<MDL	0.03	11Cl-PF3OUdS	<MDL	0.04
PFPeA	<MDL	0.03	6-2 FTS	<MDL	0.02	FOSA-I	<MDL	0.13
PFBS	<MDL	0.07	PFHpS	<MDL	0.03	10:2 FTS	<MDL	0.04
PF5OHxA	<MDL	0.01	PFOA	<MDL	0.22	PFDoA	<MDL	0.10
PFEESA	<MDL	0.01	PFOS	<MDL	0.04	PFDoS	<MDL	0.06
3,6-OPFHpA	<MDL	0.02	FOUEA	<MDL	0.07	N-MeFOSA-M	<MDL	0.07
4-2 FTS	<MDL	0.02	PFNA	<MDL	0.06	N-Me-FOSE-M	<MDL	0.07
PFHxA	<MDL	0.02	FHpPA	<MDL	0.14	N-MeFOSAA	<MDL	0.05
PFPeS	<MDL	0.02	FOEA	<MDL	0.18	PFHxDA	<MDL	0.05
HFPO-DA	<MDL	0.22	9Cl-PF3ONS	<MDL	0.03	N-EtFOSA-M	<MDL	0.17
PFHpA	<MDL	0.10	PFNS	<MDL	0.18	N-EtFOSE-M	<MDL	0.05
5:3 FTCA	<MDL	0.07	PFDA	0.07	0.05	N-EtFOSAA	<MDL	0.08
FHUEA	<MDL	0.06	8-2 FTS	<MDL	0.07	PFODA	<MDL	0.05
PFHxS	<MDL	0.06	PFDS	<MDL	0.32	PFTrDA	<MDL	0.08
MDL and blank values in ng PFAS/g resin						PFTA	<MDL	0.05

Ambient and Indoor Air Sampling

- Resin sampling from OTM-45 can be adapted to ambient and indoor air
- 8 g of Ultra-Clean Resin was packed into a small volume air sampler
- 20 µm frit to catch particulates
- TD tube used to catch any potential breakthrough compounds

Ambient and Indoor Air Sampling

- **Small volume sampler can be fit into a 100 mL ASE cell for cleaning and extraction**
- **Removes the need to separately clean and extract resin, frits, and glass holder**



Ambient and Indoor Air Sampling

- Initial testing shows no breakthrough for OTM-45 compounds
- FTOH also tested and showed no breakthrough
- Sample taken for 16.5 hours at 30 mL/min = 29.7 L of air sampled

Ambient and Indoor Air Sampling

- More work planned with resin sampling for ambient and indoor air
- Recovery, precision and MDL data using small volume Ultra-Clean Resin samplers
- Gather more data on PFAS breakthrough on Ultra-Clean Resin
- Collect real samples of ambient and indoor air

Questions?

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