Accelerated Solvent Extraction of Airborne Per- and Polyfluoroalkyl Substances from Styrene-Divinylbenzene Resin

Jason Hoisington

Summary

- PFAS in air analysis using styrene-divinylbenzene (OTM-45)
- Styrene-divinylbenzene/XAD-2
- Accelerated Solvent Extraction (ASE) parameters
- LC-MS/MS parameters and calibration
- Blank results
- Resin cleaning using ASE
- Spike recoveries

PFAS in Air – OTM-45

- Sample collection using XAD-2 (styrene-divinylbenzene resin) and liquid impingers
- Extraction by 36-hour shakeout using 5% ammonium hydroxide in methanol
- Concentration and reconstitution in either water or methanol
- Analysis by LC-MS/MS
- Extensive compound list (~50 PFAS compounds)

PFAS in Air – OTM-45

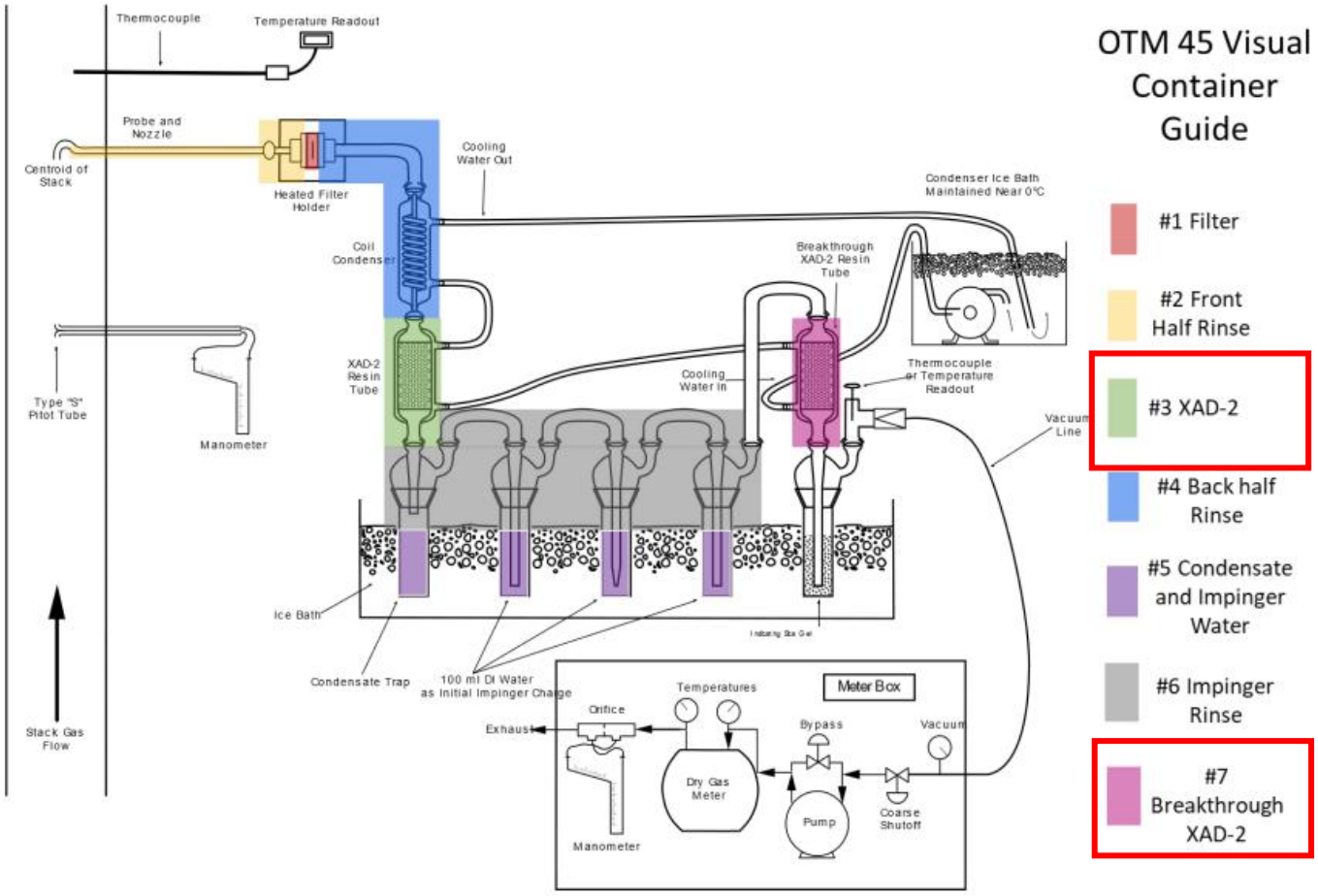


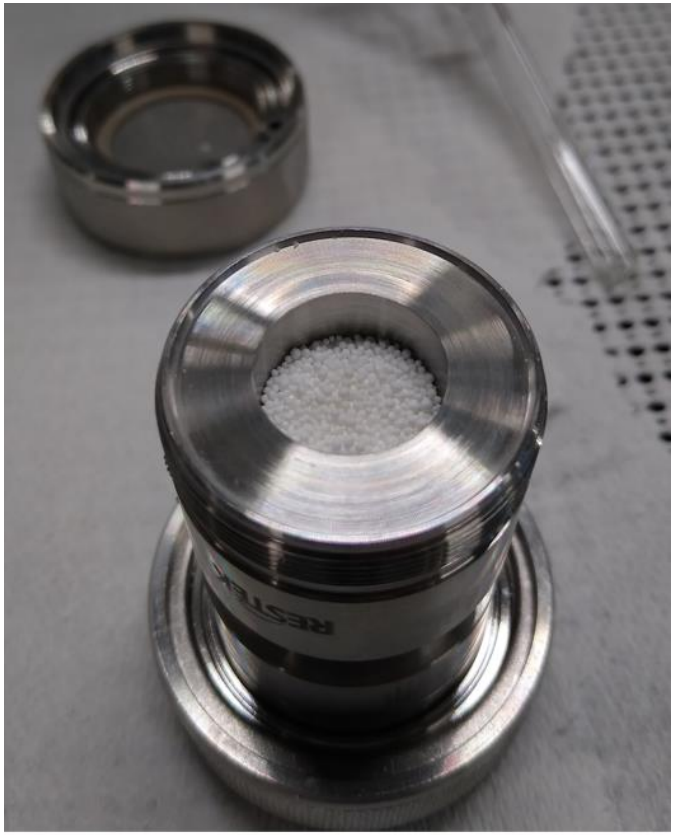
Figure OTM-45-1. Sampling Train

Styrene-Divinylbenzene Resin/ XAD-2

- Commonly used for collection of semi-volatiles in air, such as PAHs, PCBs, Dioxins

- Can be purchased pre-cleaned or processed and cleaned in-lab
  - Pre-cleaned resin may need further cleaning depending on background contamination

Styrene-Divinylbenzene Resin/ XAD-2



Restek Ultra Clean Resin

Pre-cleaned XAD-2

Accelerated Solvent Extraction vs. Shakeout

Advantages

- Faster – 45 minutes/sample
- Can be used to clean resin

Disadvantages

- More expensive
- Doesn’t incorporate back half rinse into extraction,
  - Can be added during concentration step

Accelerated Solvent Extraction

Dionex ASE 350 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**

Organomation N-Evap 111

- **Concentrated under nitrogen at 50°C, reconstituted using 80:20 Methanol:Water**

LC-MS/MS Analysis

Column

- Force C18 50mm x 2.1mm x 1.8µm
- PFAS delay 50mm x 2.1mm x 5µm

Mobile Phase

- A – Water, 50mM 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

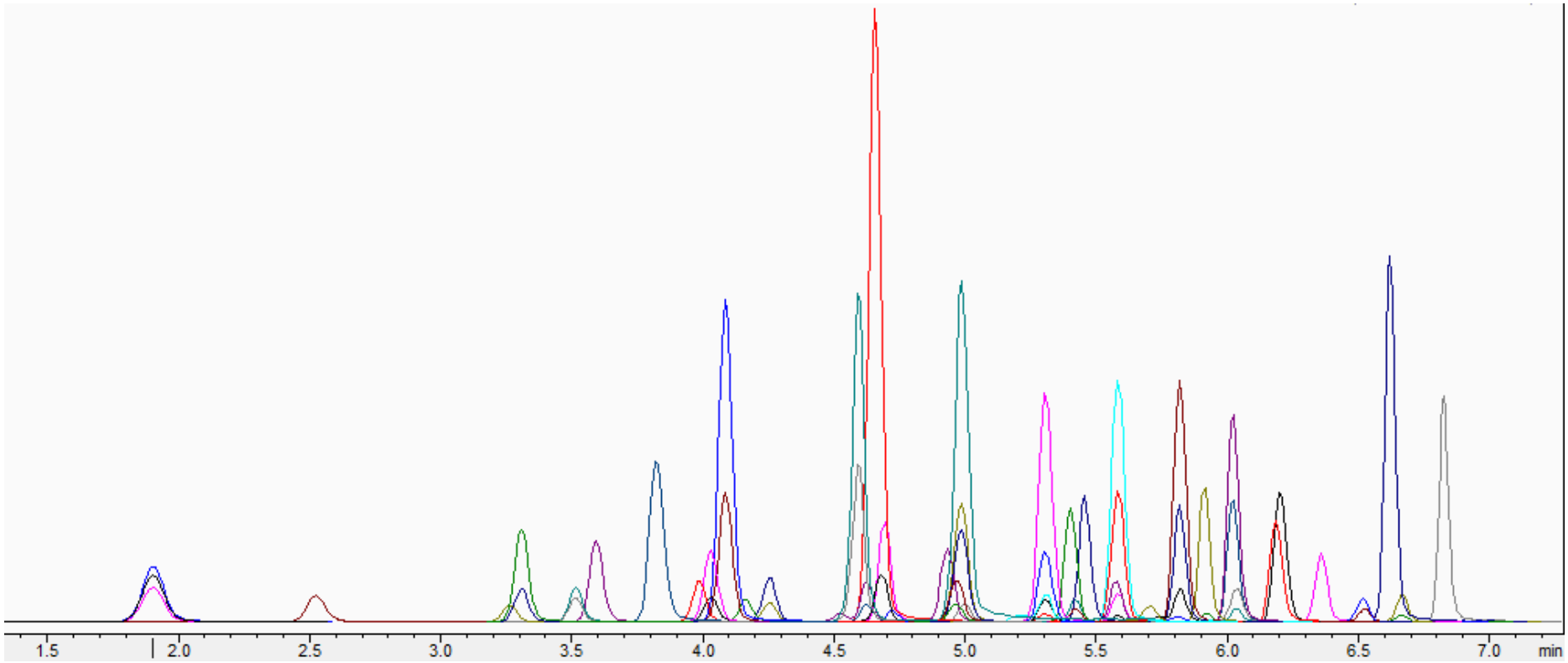
HPLC – Shimadzu Nexera X2

- Column Temp. – 40°C
- Autosampler Temp. – 5°C
- Injection volume – 3µL

Detector – Shimadzu 8045 MS/MS

- Nebulizing gas flow – 3 L/min
- Heating gas flow – 15 L/min
- Interface Temp. – 300°C
- DL Temp. – 200°C
- Heat Block Temp. – 200°C
- Drying gas flow – 5 L/min

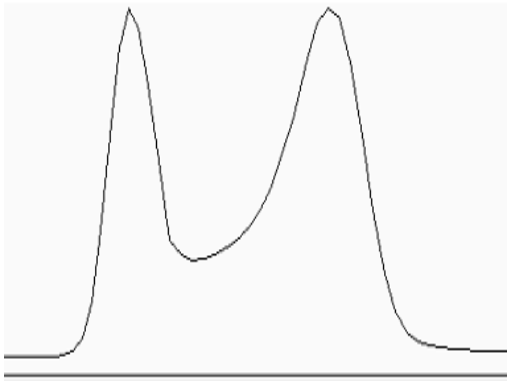
LC-MS/MS Analysis



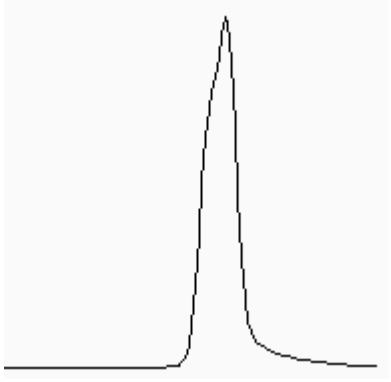
LC-MS/MS Analysis

#	Name	RT (min)	#	Name	RT (min)	#	Name	RT (min)	#	Name	RT (min)
1	M4PFBA	1.793	19	M3HFPO-DA	4.254	36	PFNA	5.336	54	M7PFUnA	5.857
2	M3PFBA	1.794	20	M4PFHpA	4.605	37	PFOS	5.340	55	N-EtFOSAA	5.860
3	PFBA	1.795	21	PFHpA	4.606	38	M8PFOS	5.341	56	11Cl-PF3OUdS	5.954
4	PF4OPeA	2.414	22	M3PFHxS	4.644	39	13C4-PFOS	5.341	57	FDEA	5.962
5	3:3 FTCA/FPrPA	3.196	23	PFHxS	4.645	40	FOUEA	5.428	58	FOSA-I	6.042
6	M5PFPeA	3.250	24	ADONA	4.663	41	FHpPA	5.445	59	PFDoA	6.064
7	PFPeA	3.251	25	5:3 FTCA/FPePA	4.689	42	FOEA	5.451	60	M2PFDoA	6.065
8	M3PFBS	3.487	26	FHUEA	4.705	43	9Cl-PF3ONS	5.494	61	10:2 FTS	6.075
9	PFBS	3.488	27	FHEA	4.735	44	L-PFNS	5.612	62	L-PFDoS	6.232
10	PF5OHxA	3.555	28	PFeCHS	4.965	45	PFDA	5.619	63	PFTrDA	6.247
11	PFEESA	3.807	29	6-2 FTS	4.987	46	M6PFDA	5.619	64	PFTA	6.402
12	3,6-OPFHpA	3.969	30	M2 6-2 FTS	4.989	47	8-2 FTS	5.620	65	N-MeFOSA-M	6.521
13	M2 4-2FTS	4.021	31	M8PFOA	5.009	48	M2 8-2 FTS	5.620	66	N-MeFOSE-M	6.531
14	4-2 FTS	4.022	32	13C2-PFOA	5.010	49	N-MeFOSAA	5.742	67	PFHxDA	6.657
15	M5PFHxA	4.078	33	PFOA	5.010	50	d3-NMeFOSAA	5.750	68	N-EtFOSE-M	6.666
16	PFHxA	4.079	34	PFHpS	5.029	51	L-PFDS	5.848	69	N-EtFOSA-M	6.668
17	PFPeS	4.172	35	M9PFNA	5.335	52	d5-NEtFOSAA	5.854	70	PFODA	6.853
18	HFPO-DA	4.253				53	PFUnA	5.857			

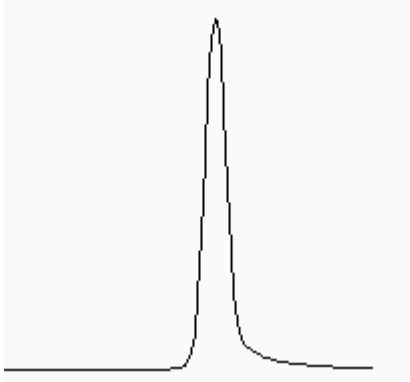
LC-MS/MS Analysis – Solvent



PFBA
5uL injection
100% MeOH



PFBA
5uL injection
80:20 MeOH:Water



PFBA
3uL injection
80:20 MeOH:Water

LC-MS/MS Analysis – Calibration

OTM-45 Calibration

- **Isotope dilution**
  - **Not all target compounds have isotopes easily available**
- **Linear or quadratic fits**
- **Weighting and forced 0 allowed**
- **Calibration points should be ±10% of true value**
- **No r^2 requirement**

LC-MS/MS Analysis – Calibration

Compound	0.25 ppb	0.5ppb	1 ppb	2.5 ppb	5 ppb	20 ppb	100 ppb
PFBA	-3.8%	-7.4%	-0.3%	-9.8%	4.8%	9.2%	-1.8%
ADONA	-9.5%	-10.2%	17.4%	8.4%	5.0%	4.0%	-1.3%
PFODA	3.5%	-18.2%	-1.2%	-3.7%	10.6%	-1.9%	0.0%
PFTrDA	-10.1%	-19.7%	-10.8%	0.5%	3.7%	0.4%	-11.1%

- **38/50 compounds met ±10% criteria for all calibration points**
- **48/50 compounds were within ±20% for all calibration points**
- **2/50 compounds were >20% for one calibration point**

Resin Blanks and Background

Compound	ASE Blank (ng/g)	XAD-2 (ng/g)	XAD-2 (ng/g)	XAD-2 (ng/g)	Avg. (ng/g)	Ultra Clean Resin (ng/g)	Ultra Clean Resin (ng/g)	Ultra Clean Resin (ng/g)	Avg. (ppb)
PFBA	0.05	0.54	0.51	0.60	**0.55**	0.43	0.35	0.43	**0.40**
PF4OPeA	0.09	0.10	0.11	0.10	**0.10**	0.63	0.45	0.53	**0.54**
ADONA	<0.04	0.05	0.05	0.11	**0.71**	0.06	0.04	0.05	**0.05**

- **3g of resin extracted and concentrated to 0.5mL for XAD-2 and Ultra Clean Resin**
- **ASE blank run using empty ASE cell and concentrated to 0.5mL**
- **All other compounds <0.04 ng/g**

Cleaned Resin Blanks and Background

Compound	XAD-2 (ng/g)	XAD-2 (ng/g)	XAD-2 (ng/g)	Avg. (ng/g)	Ultra Clean Resin (ng/g)	Ultra Clean Resin (ng/g)	Ultra Clean Resin (ng/g)	Avg. (ng/g)
PFBA	0.29	0.24	0.28	**0.27**	0.12	0.18	0.10	**0.13**
PF4OPeA	0.37	0.29	0.24	**0.30**	0.06	0.09	0.10	**0.08**
ADONA	0.71	0.25	0.30	**0.42**	0.05	0.08	0.04	**0.06**

- XAD-2 and Ultra Clean Resin run through one cycle of ASE extraction
- 3 g of cleaned resin was extracted and concentrated to 0.5mL

- XAD-2 results suggest that the extraction/cleaning may not be complete compared to Ultra Clean Resin
- Eurofins presented data showing similar constant or rising blank results after MeOH cleaning for some PFAS for XAD-2

Spike Recoveries

	XAD-2	XAD-2	XAD-2	Avg.	Ultra Clean Resin	Ultra Clean Resin	Ultra Clean Resin	Avg.
PFBA	35%	47%	71%	51%	109%	96%	97%	101%
PF4OPeA	33%	46%	69%	49%	116%	93%	99%	103%
ADONA	48%	65%	78%	63%	123%	106%	118%	116%
HFPO-DA	127%	112%	101%	113%	102%	83%	94%	93%
PFHpS	42%	54%	70%	55%	127%	129%	121%	126%
10:2 FTS	35%	33%	30%	33%	60%	58%	55%	58%
PFODA	24%	22%	20%	22%	39%	34%	30%	34%

- % Recoveries on 50/100 ppb spike. OTM-45 recovery recommendations 70-130%
- Many compounds without isotopically labeled ISTDs had <70% recovery
- OTM-45 provides no data for spike recoveries from method development
- Pre-extraction ISTDs recovery limits 20-130%
- Low XAD-2 results further suggest incomplete extraction for some compounds compared to Ultra Clean Resin

Future Work

- Expand collection of isotopically labeled standards to improve calibration and recoveries
- Improve ASE blank levels to reduce background contamination
- Test more lots of resin to better understand cleanliness, resin cleaning needs, and extraction requirements
- Investigate low level accuracy and perform MDL study

Conclusions

- Restek Ultra-Clean resin can be used for the collection of PFAS compounds in air
- Accelerated solvent extraction can provide faster extractions for OTM-45 while maintaining recoveries
- Accelerated solvent extraction offers an alternative method to cleaning Ultra-Clean Resin
- Precleaned XAD-2 seems to have incomplete extraction compared to Ultra-Clean Resin using same ASE parameters
- Using 80:20 methanol:water during concentration provides better peak shape for PFBA than 100% methanol

Questions?