Interlaboratory Study for PFAS Background Extracted from Multiple Pre-cleaned XAD-2 Adsorbent Lots

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Introduction

XAD®-2 is a macroporous, nonionic polymeric adsorbent resin composed of polystyrene cross-linked with divinylbenzene, developed in the early 1970s by Rohm and Haas for use in chromatographic and environmental applications. Characterized by a high surface area and a hydrophobic, aromatic matrix, XAD®-2 exhibits strong affinity for non-polar to moderately polar organic compounds.

Day 1	Soak with water 5 min, remove fines, soak w/water overnight
Day 2	Hot water, extract 8 hrs
Day 3	Methanol, extract 22 hr
Day 4	Methylene Chloride, extract 22 hr
Day 5	Ammonium hydroxide in methanol, extract 22 hr

Figure 1. Cleaning of XAD® -2 resin from OTM-45 Appendix.

There are 2x, 20-40 g cartridges of XAD®-2 specified by OTM-45 sampling train (**Figure 2**), highlighted in green (1) and pink (2).

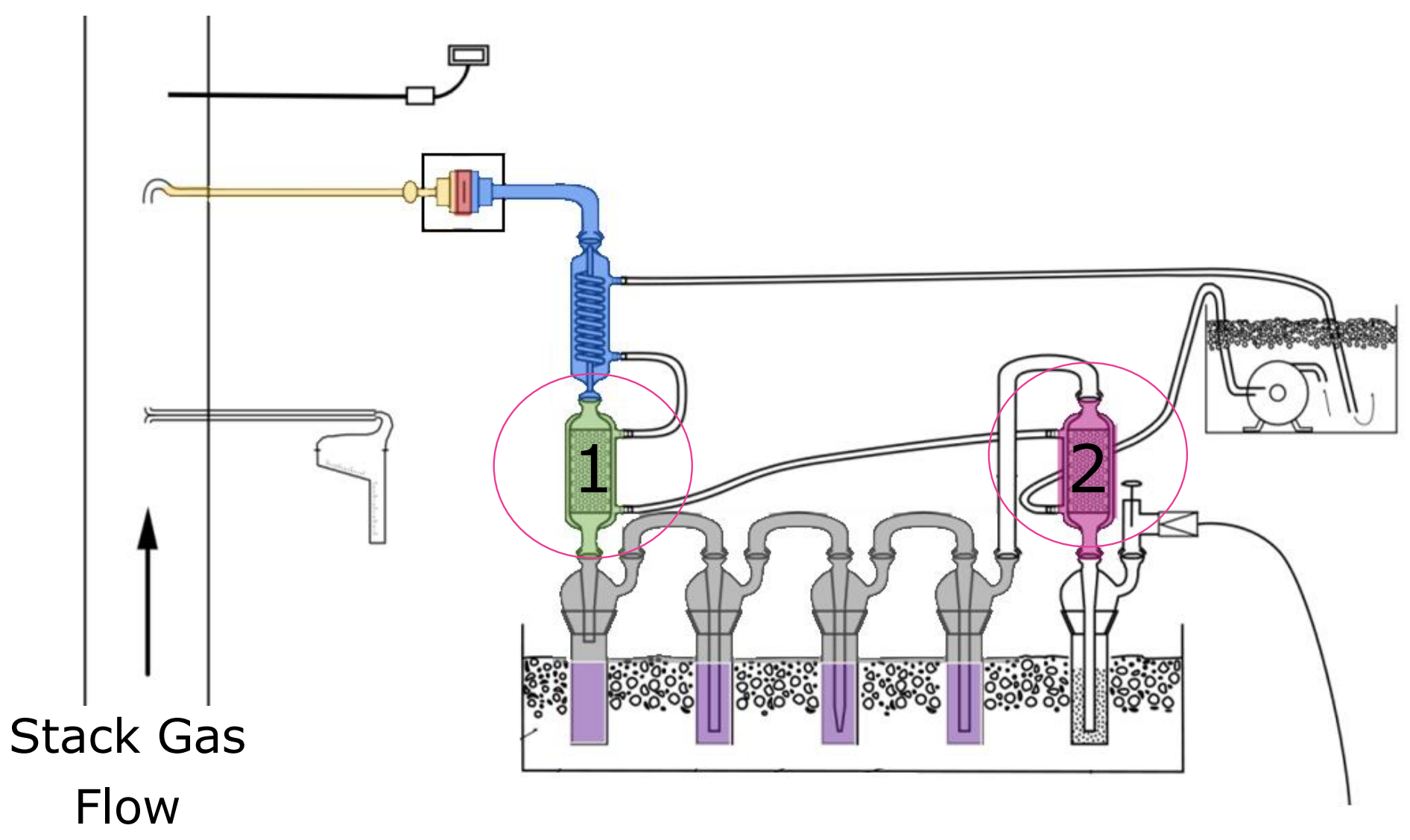

Figure 2. OTM-45 Sampling Train, Measurement of select per- and polyfluorinated alkyl substances from stationary sources.

Supelpak™-2SVM is a clean version of XAD®-2 ready for analysis of semi-volatiles for various methods including *EPA 10 – Semivolitiles in Stationary Source Emissions, EPA TO-13A PAHs in Ambient Air*, *EPA 23 – Dioxins in Stationary Source Emission*, and *ASTM D6209 – PAHs in Ambient Air*. However, background levels of PFAS containments were not low enough to meet the requirements of the environmental labs.

Method

To prepare the XAD®-2 resin for use for PFAS analysis, we first pre-cleaned it using a more sustainable process compared to OTM-45 appendix described, and then immediately analyzed the cleaned batches using the extraction procedures outlined in Method OTM-45. Batches that showed low background levels of PFAS were then sent out to multiple certified PFAS-testing laboratories for confirmation of cleanliness.

Figure 4. Supelpak™-2 4PFAS, a ready-to-use cleaned XAD®-2 resin for PFAS analysis

Sample Preparation

The exact method to extract PFAS from XAD®-2 was not held constant between laboratories. Each lab did use a verified method. The general method outlined in OTM-45 Rev 1 is listed below (key differences are highlighted in **Table 1**).

1. 2x Extraction of XAD®-2 resin with MeOH+NH_4OH (1.5% v/v)
2. Combine fractions, use 90 mL of extract, neutralize and bring up to 1 L w/ water
3. Concentrate to <10 mL, then <2 mL (not dryness)
4. SPE with WAX and GCB
5. Analysis by LC-MS/MS

Table 1. Overview of methods utilized by the various laboratories.

	Overview of Laboratories Parameters					
	L1	L2	L3	L4	L5a	L5b
Mass resin (g)	30	20	30	20	20	
Method	OTM-45 v1	OTM-45 v1	OTM-45 v1	OTM-45 v0	OTM-45 v0	
Enrichment	SPE	SPE	SPE	Evaporate	Evaporate	ASE

Table 2. LC-MS conditions utilized by one of the laboratories for analysis.

LC-MS Conditions	
Instrument:	Agilent Infinity Series II & SCIEX Triple Quad 6500+
Column:	Ascentis® Express 90 Å PFAS, 2.7 µm, 100 x 2.1 mm I.D.
Delay Column:	Ascentis® Express 160 Å PFAS, 2.7 µm, 50 x 3.0 mm I.D.
Detector:	MS/MS, MRM, ESI(-)
Injection:	5 µL
Other parameters available upon request	

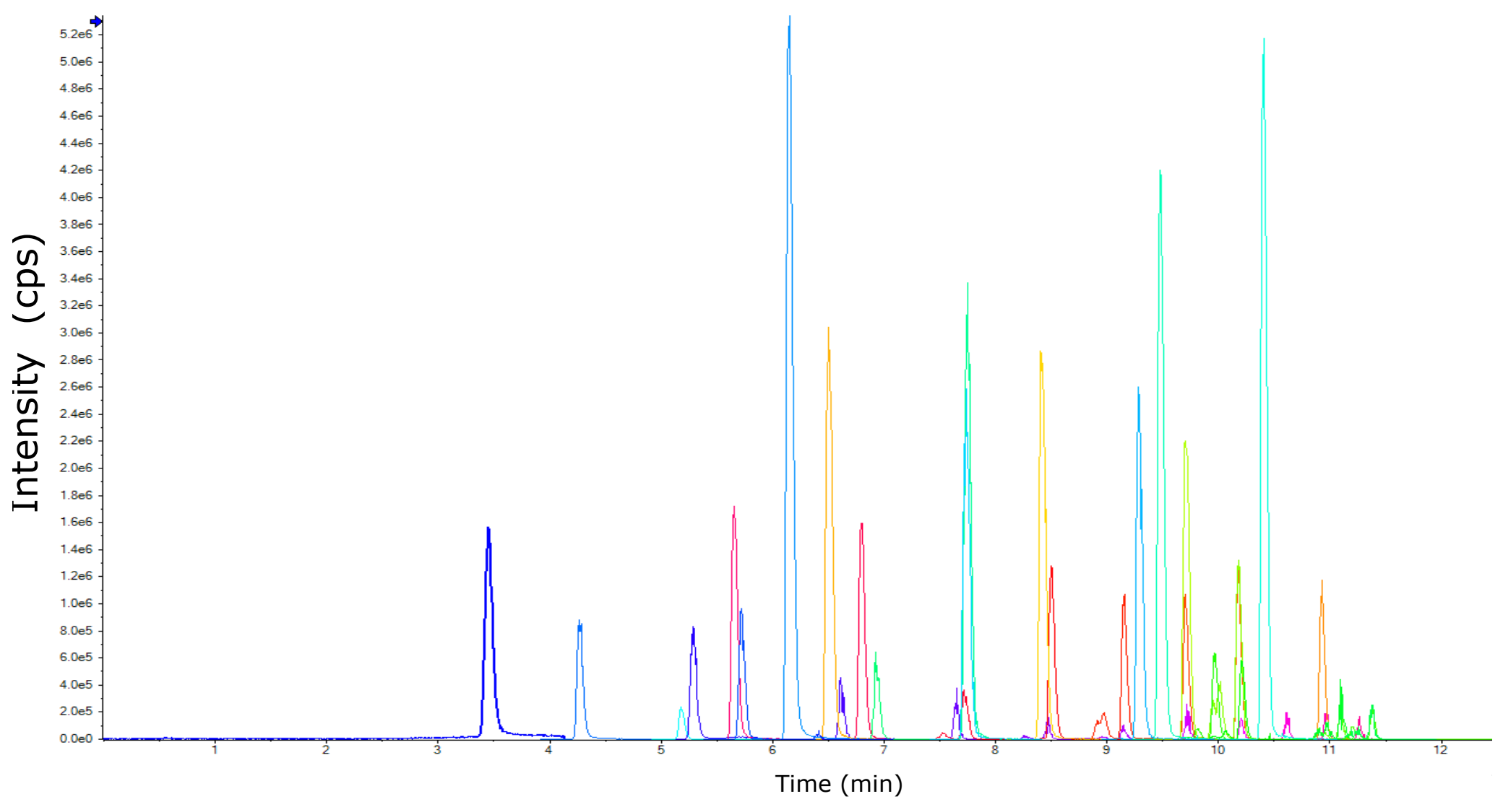

Figure 3. Representative extracted PFAS chromatogram (MRM).

Results

Four of the five laboratories reported non-detect for all the targeted PFAS compounds outlined. One laboratory (Lab 4), detected two analytes slightly above their report limits (**Table 3**).

Table 3. Highlighted PFAS compounds above reporting limit for Lab 4.

	Concentration (pg/g)		
	Sample 1	Sample 2	Reporting Limit
PFHxA	<RL	26.12	25
PFOA	<RL	27.18	25
All other analytes	<RL	<RL	25

Discussion

Four of the five laboratories that participated in this study reported non-detects for the targeted PFAS analytes specified. While this outcome strongly supports the effectiveness of the pre-cleaning process and indicates a very low background contamination level in the cleaned XAD®-2 resin, it's worth noting that the reporting limits (**Table 4**) as well as isotope standard recoveries (**Table 5**) varied across laboratories. These differences in detection sensitivity could reflect variations in instrumentation, methodology nuances, or lab-specific protocols.

Table 4. Reporting limits (RL) for various PFAS analytes by lab

	Reporting Limit (pg/g)						Reporting Limit (pg/g)				
Analyte	L1	L2	L3	L4	L5	Analyte	L1	L2	L3	L4	L5
PFBA	333	13.3	4.4	25	200	N-MeFOSAA	33	3.3	1.1	25	300
PFPeA	33	6.7	0.6	25	200	N-EtFOSE	33	33	0.6	25	10
PFHxA	100	3.3	1.1	25	200	4:2 FTS	33	13	0.6	25	200
PFHpA	33	3.3	0.6	25	200	6:2 FTS	33	13	2.2	25	200
PFOA	33	3.3	0.6	25	200	8:2 FTS	33	13	1.1	25	200
PFNA	33	3.3	0.6	25	200	10:2 FTS	33	-	1.1	25	-
PFDA	33	3.3	0.6	25	200	ADONA	100	13	0.6	25	200
PFUnA	33	3.3	0.6	25	200	HFPO-DA	166	13	0.6	25	500
PFDoA	33	3.3	1.1	25	300	9Cl-PF3ONS	33	13	0.6	25	500
PFTrA	33	3.3	1.1	25	200	11Cl-PF3OUdS	33	13	0.6	25	500
PFTeDA	33	3.3	1.1	25	200	NFDHA	33	6.7	0.6	25	3
PFHxDA	33	-	0.6	25	-	PFEESA	33	6.7	0.6	25	3
PFODA	33	-	1.1	25	-	PFMBA	33	6.7	0.6	25	3
PFBS	33	3.3	0.6	25	200	PFMPA	33	6.7	0.6	25	3
PFPeS	33	3.3	0.6	25	200	PFECHS	33	-	0.6	25	-
PFHxS	33	3.3	0.6	25	200	6:2 FTUCA	33	-	2.2	25	-
PFHpS	33	3.3	0.6	25	200	8:2 FTUCA	33	-	2.2	25	-
PFOS	33	3.3	0.6	25	200	10:2 FTUCA	33	-	2.2	25	-
PFNS	33	3.3	0.6	25	300	3:3 FTCA	33	17	2.2	25	3
PFDS	33	3.3	0.6	25	300	5:3 FTCA	33	83	1.1	25	3
PFDoS	33	3.3	1.1	25	300	7:3 FTCA	33	83	1.1	25	3
FOSA	33	3.3	0.6	25	200	6:2 FTCA	33	-	4.4	25	-
N-MeFOSA	33	3.3	1.1	25	20	8:2 FTCA	33	-	4.4	25	-
N-EtFOSA	33	3.3	1.1	25	20	10:2 FTCA	33	-	4.4	25	-

Also considered was the recovery of isotope dilution standards as outlined within OTM-45. Shared below are the averaged recoveries from two samples being sent to each lab.

Table 5. Isotope dilution standards recoveries

Isotope Standard	Recovery %				
	L1	L2	L3	L5A	L5B
^{13}C-Perfluorobutanoic acid	87	92	73	90	73
^{13}C-Perfluoropentanoic acid	85	85	77	86	72
^{13}C-Perfluorohexanoic acid	82	87	69	92	70
^{13}C-Perfluoroheptanoic acid	81	83	68	56	57
^{13}C-Perfluorooctanoic acid	88	87	74	88	67
^{13}C-Perfluorononanoic acid	85	94	78	94	68
^{13}C-Perfluorodecanoic acid	60	72	74	92	69
^{13}C-Perfluoroundecanoic acid	58	59	48	86	72
^{13}C-Perfluorododecanoic acid	116	51	55	84	74
^{13}C-Perfluorotetradecanoic acid	25	56	-	71	65
^{13}C-Perfluorobutanesulfonate	71	86	75	94	57
^{13}C-Perfluorohexanesulfonate	72	87	69	86	72
^{13}C-Perfluorooctanesulfonate	60	67	77	92	75
^{13}C-Hexafluoropropylene oxide	69	88	48	88	60
d_3-N-Methyl-PFOS-amidoacetic acid	85	99	-	98	73
d_5-N-Ethyl-PFOS-amidoacetic acid	76	102	-	105	66
^{13}C-Perfluorooctanesulfonamide	64	89	-	99	73
d_5-N-ethyl PFOS-amide	29	52	-	19	26
d_7-N-methyl-PFOS-amido ethanol	39	47	-	12	34
d_9-N-ethyl PFOS-amido ethanol	41	65	-	42	35
^{13}C-Perfluorooctanesulfonamide	30	61	-	43	37
^{13}C-4:2 Fluorotelomer sulfonate	116	113	95	103	108
^{13}C-6:2 Fluorotelomer sulfonate	120	120	71	136	96
^{13}C-8:2 Fluorotelomer sulfonate	118	144	78	110	109

Conclusions

Validation of Resin Cleanliness:

Consistent non-detect results across multiple independent labs suggest that the cleaned XAD®-2 material is ***suitable for use in ultra-trace PFAS air sampling applications***, without further purification reducing false positives due to background contamination.

The CoA for this cleaned XAD®-2 product, Supelpak™-2 4PFAS will provide the reporting limits and contaminant level for each PFAS analyte listed within OTM-45.

Enhanced Confidence in Field Deployments:

When validated, such low-background sorbents could streamline sampling logistics by minimizing the need for extensive pre-treatment or post-collection sample screening.

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