P#33 Global Inter-Laboratory Evaluation of PFAS Detection Consistency Using Precleaned Polystyrene/Divinylbenzene Resin

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Abstract

Per- and polyfluoroalkyl substances (PFAS) pose significant environmental concerns due to their persistence. This study evaluates the reliability of PFAS detection through a global inter-laboratory assessment, focusing on background contamination of a polystyrene/divinylbenzene resin, XAD-2, as listed in EPA method OTM-45. Multiple laboratories participated in measuring PFAS using identical lots of precleaned resin.

This analysis aims to assess the reproducibility of PFAS detection among international laboratories and to underscore the standardization of the sample preparation and analytical conditions to enhance result consistency. Key findings will demonstrate the critical role of pre-cleaned XAD-2 resin in effectively monitoring and quantifying PFAS and other air pollutants. By incorporating a standardized pre-cleaned XAD-2 for analysis, this study seeks to improve the accuracy and reliability of PFAS analyses, thereby supporting regulatory compliance and environmental assessments.

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.

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

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

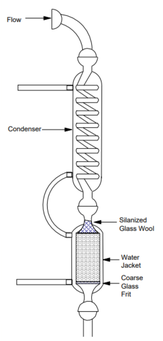
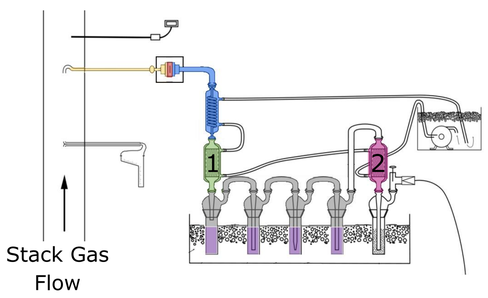


Fig 2. OTM-45 Sampling Train, *Measurement of select per- and polyfluorinated alkyl substances from stationary sources.*

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



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, we first pre-cleaned it using a sustainable and environmentally friendly process, 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.

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 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	
Liquid Chromatography	Agilent Infinity Series II
Injection volume	5 µL
Delay Column	Ascentis® Express 90 Å PFAS 50 mm x 3.0 mm, 2.7 µm
Analytical Column	Ascentis® Express 90 Å PFAS 100 mm x 2.1 mm, 2.7 µm
Mass Spectrometer	SCIEX Triple Quad 6500+
Detector Mode	Negative
Other parameters available upon request	

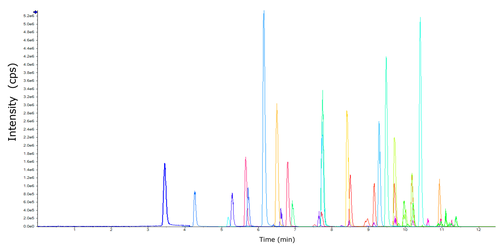


Fig 3. Representative Extracted PFAS chromatogram (MRM) example.

Results

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

Table 3. Highlighted PFAS compounds above Reporting Limit for Lab 4.

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

Table 4. Reporting Limits 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	-

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

Results Continued

Also considered was the recovery of isotope dilution standards as outlined within OTM-45. Shared below are the recoveries from Lab 1, showing two samples from each lot.

Table 5. Isotope Dilution Standards Recoveries for Lab 1

Isotope Dilutions	Recovery %				
	L1	L2	L3	L5A	L5B
13C-Perfluorobutanoic acid	87	92	73	90	73
13C-Perfluoropentanoic acid	85	85	77	86	72
13C-Perfluorohexanoic acid	82	87	69	92	70
13C-Perfluoroheptanoic acid	81	83	68	56	57
13C-Perfluorooctanoic acid	88	87	74	88	67
13C-Perfluorononanoic acid	85	94	78	94	68
13C-Perfluorodecanoic acid	60	72	74	92	69
13C-Perfluoroundecanoic acid	58	59	48	86	72
13C-Perfluorododecanoic acid	116	51	55	84	74
13C-Perfluorotetradecanoic acid	25	56	-	71	65
13C-Perfluorobutanesulfonate	71	86	75	94	57
13C-Perfluorohexanesulfonate	72	87	69	86	72
13C-Perfluorooctanesulfonate	60	67	77	92	75
13C-Hexafluoropropylene oxide	69	88	48	88	60
d3-N-Methyl-PFOS-amidoacetic acid	85	99	-	98	73
d5-N-Ethyl-PFOS-amidoacetic acid	76	102	-	105	66
13C-Perfluorooctanesulfonamide	64	89	-	99	73
d5-N-ethyl PFOS-amide	29	52	-	19	26
d7-N-methyl-PFOS-amido ethanol	39	47	-	12	34
d9-N-ethyl PFOS-amido ethanol	41	65	-	42	35
13C-Perfluorooctanesulfonamide	30	61	-	43	37
13C-4:2 Fluorotelomer sulfonate	116	113	95	103	108
13C-6:2 Fluorotelomer sulfonate	120	120	71	136	96
13C-8:2 Fluorotelomer sulfonate	118	144	78	110	109

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 varied across laboratories. These differences in detection sensitivity could reflect variations in instrumentation, methodology nuances, or lab-specific protocols.

Significance for PFAS Analysis

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.