A Semi-Automated Workflow for the Extraction and Analysis of 40 PFAS Targets in Biosolids

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EPA 1633, Revision A

Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS

Non-potable Water: WAX SPE → Carbon Clean-up

Soils & Solids: EDGE PFAS™ Solvent Extraction x3 → Carbon Clean-up → WAX SPE

Tissue: Solvent extraction & Incubation → Carbon Clean-up → WAX SPE

EDGE PFAS™: Automated Extraction

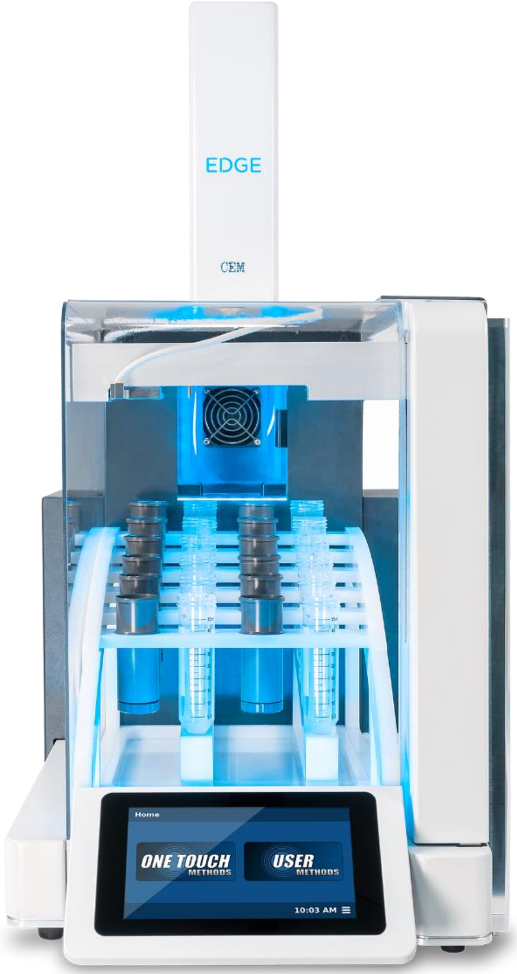
- Pressurized Fluid Extraction
- Sequential – automates 12 samples per rack
- Filtration step included

EDGE PFAS Sample Preparation

Layered in Q-Cup
Spike: Domestic Sludge at 25 ng/mL, Sand at 2 ng/mL
Sample: 0.5 g NIST SRM 2781 Domestic Sludge, 5 g Sand
Q-Disc® PFAS (filter)

CEM Agilent

Method Development



NIST SRM 2781

- Domestic Sludge
- Values for 6 PFAS Compounds

SRM 2781: Domestic Sludge Characteristics

Extract prior to SPE Dilution

Table 2.2 Typical chemical composition and properties of untreated/digested sludge.

Item/Sludge	Untreated Primary	Digested Primary	Reference
Total dry solids (TS), %	2.0–8.0	6.0–12.0	Metcalf & Eddy, 2003
Volatile solids (% of TS)	60–80	30–60	Metcalf & Eddy, 2003
Grease and fats (% of TS)			Metcalf & Eddy, 2003
Ether soluble	6–30	5–20	Metcalf & Eddy, 2003
Ether extract	7–35	—	Metcalf & Eddy, 2003
Protein (% of TS)	20–30	15–20	Metcalf & Eddy, 2003
Nitrogen (N, % of TS)	1.5–4	1.6–6.0	Metcalf & Eddy, 2003
Phosphorous (P_2O_5, % of TS)	0.8–2.8	1.5–4.0	Metcalf & Eddy, 2003
Potash (K_2O, % of TS)	0–1	0–3.0	Metcalf & Eddy, 2003
Cellulose (% of TS)	8.0–15.0	8.0–15.0	Metcalf & Eddy, 2003
Iron (not as sulfide)	2.0–4.0	3.0–8.0	Metcalf & Eddy, 2003
Silica (SiO_2, % of TS)	15.0–20.0	10.0–20.0	Metcalf & Eddy, 2003
Alkalinity (mg/L as $CaCO_3$)	500–1500	2500–3500	Metcalf & Eddy, 2003
Organic acids (mg/L as HAc)	200–2000	100–600	Metcalf & Eddy, 2003
Energy content	10,000–12,500	4000–6000	Metcalf & Eddy, 2003
pH	5.0–8.0	6.5–7.5	Metcalf & Eddy, 2003
Polymer			
Protein (sludge)	217–353		Jin et al., 2003, 2004
Protein (EPS)	28–56		Jin et al., 2003, 2004
Humic substances (Sludge)	73–195		Jin et al., 2003, 2004
Humic substances (EPS)	17–51		Jin et al., 2003, 2004
Carbohydrate (Sludge)	55–93		Jin et al., 2003, 2004
Carbohydrate (EPS)	5.7 – 40		Jin et al., 2003, 2004
Total extracted (EPS)	52 –119		Jin et al., 2003, 2004

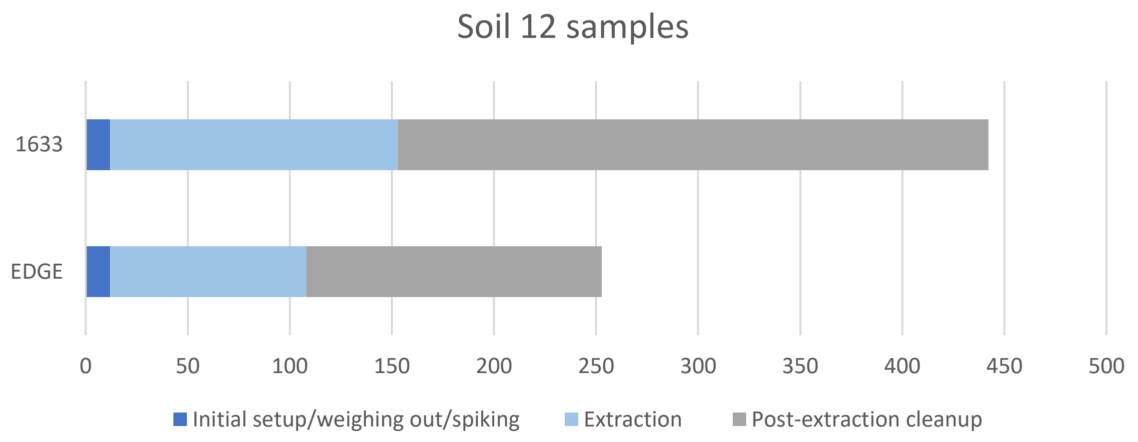
Yan, Shenshen & Sellamuthu, Balasubramanian & Tyagi, R. & Surampalli, Rao. (2009). Wastewater Sludge Characteristics. 10.1061/9780784410516.ch02.
Accessed:
https://www.researchgate.net/publication/283016984_Wastewater_Sludge_Characteristics

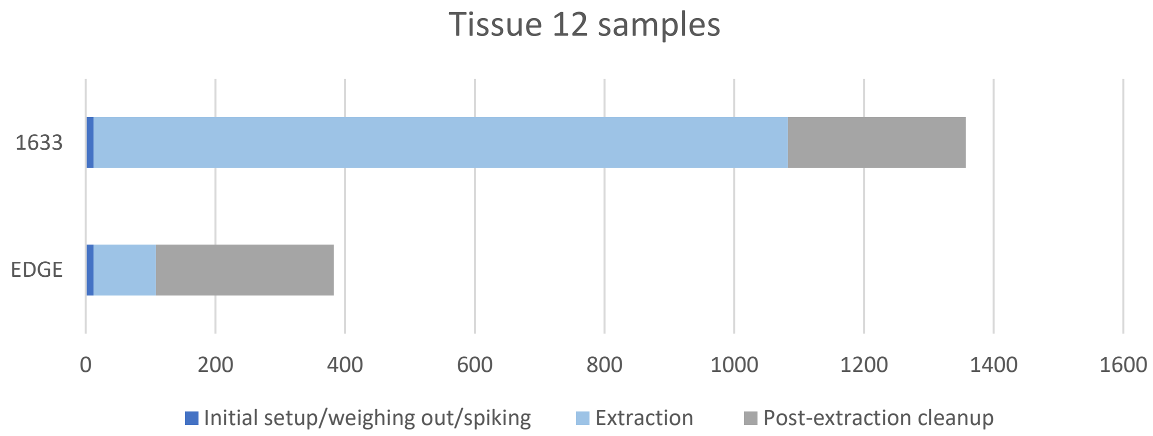
EDGE PFAS Biosolid/Soil Method

Cycle	Solvent	Top Add (mL)	Temp (°C)	Hold Time
1	0.3% M Methanolic Ammonium Hydroxide	10	65	3:00
2	0.3% M Methanolic Ammonium Hydroxide	15	65	3:00
3	0.3% M Methanolic Ammonium Hydroxide	5	--	--:--
Wash 1	Isopropanol	10	--	--:--
Wash 2	0.3% M Methanolic Ammonium Hydroxide	10	65	0:30
Wash 3	0.3% M Methanolic Ammonium Hydroxide	10	--	--:--

EDGE PFAS Advantages

Time Comparison (min) to EPA 1633A

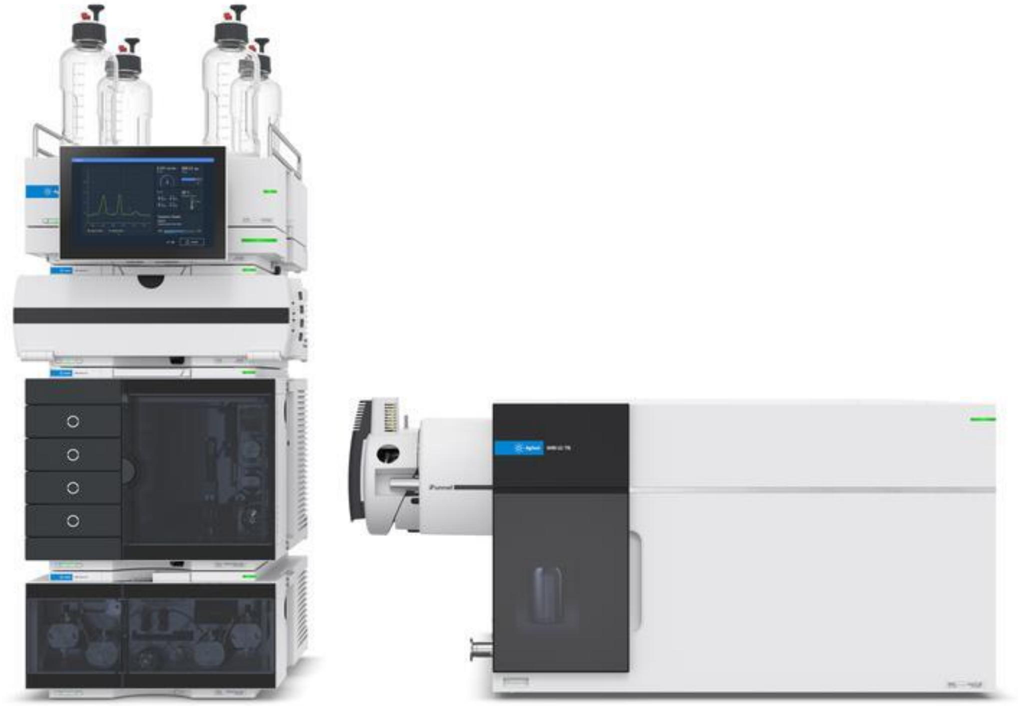




- Automation
- Improved repeatability
- Simple
- Applicable to many matrix types
- Safe

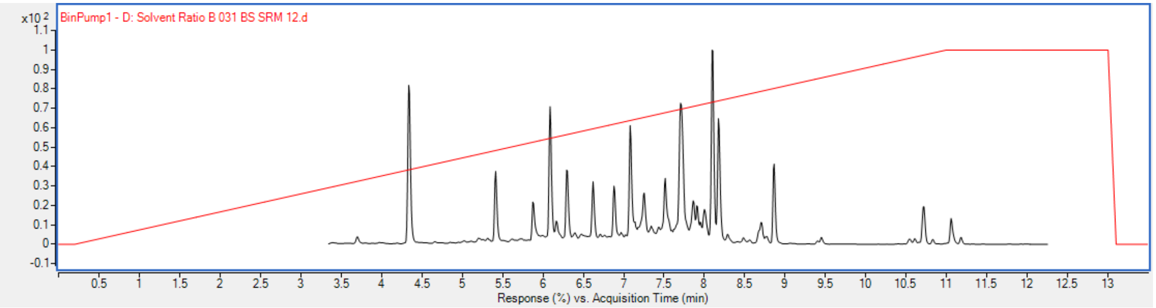
EPA 1633 SPE Extraction

Instrumental Analysis

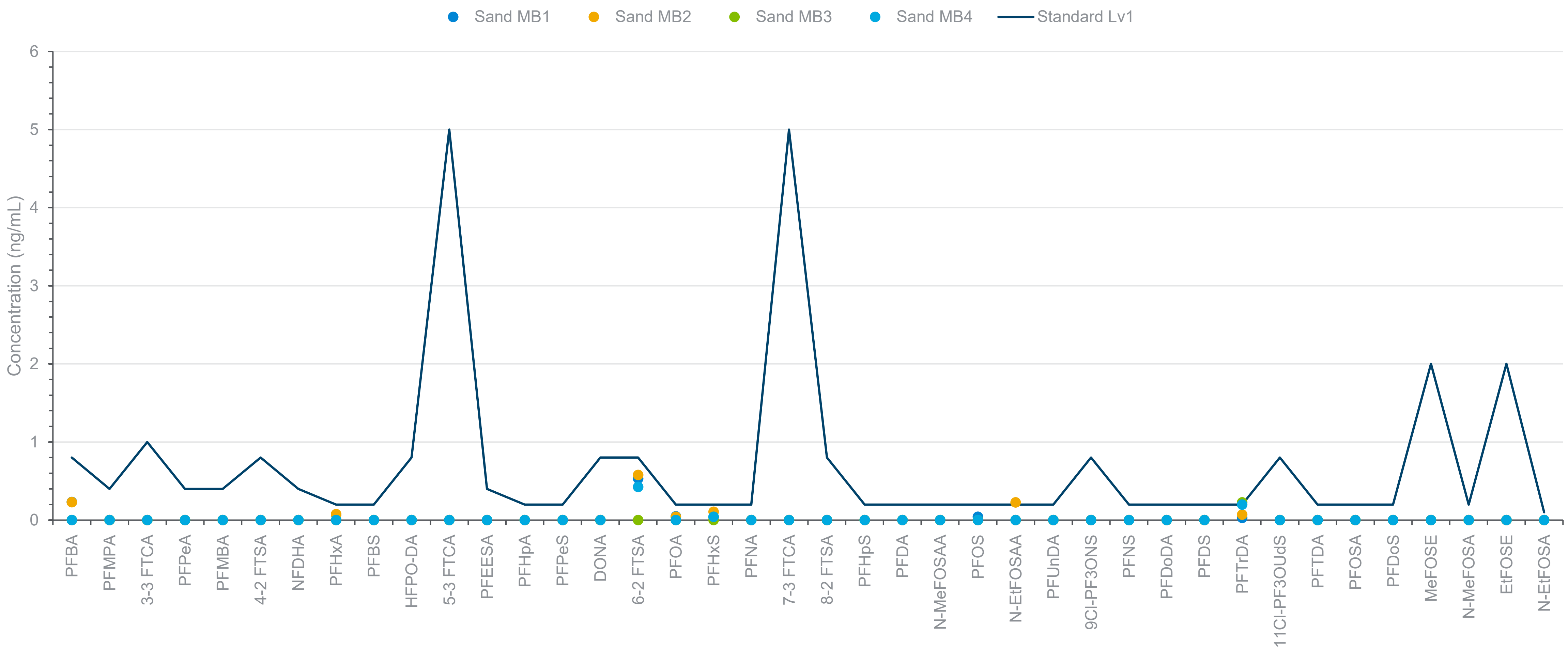


6495D TQ

Parameter	Value
Column	Poroshell AQ-C18, 2.1 x 100, 2.7 um
Injection volume	3 uL
Mobile phase	A: 2 mM Ammonium acetate in water B: 95: 5 Acetontitrile : Water
Runtime:	13.5 min (3 min posttime)
MS	PFAS MRM Database 2.0



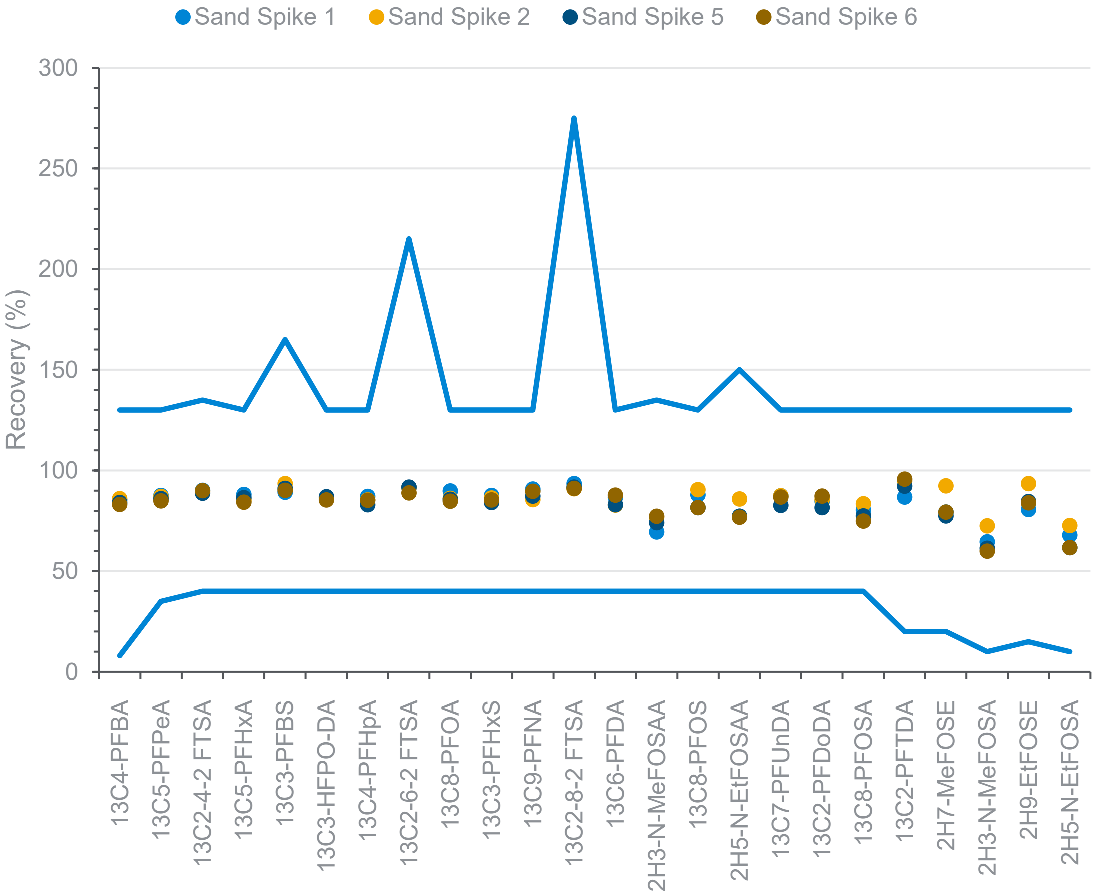
Sand Blanks



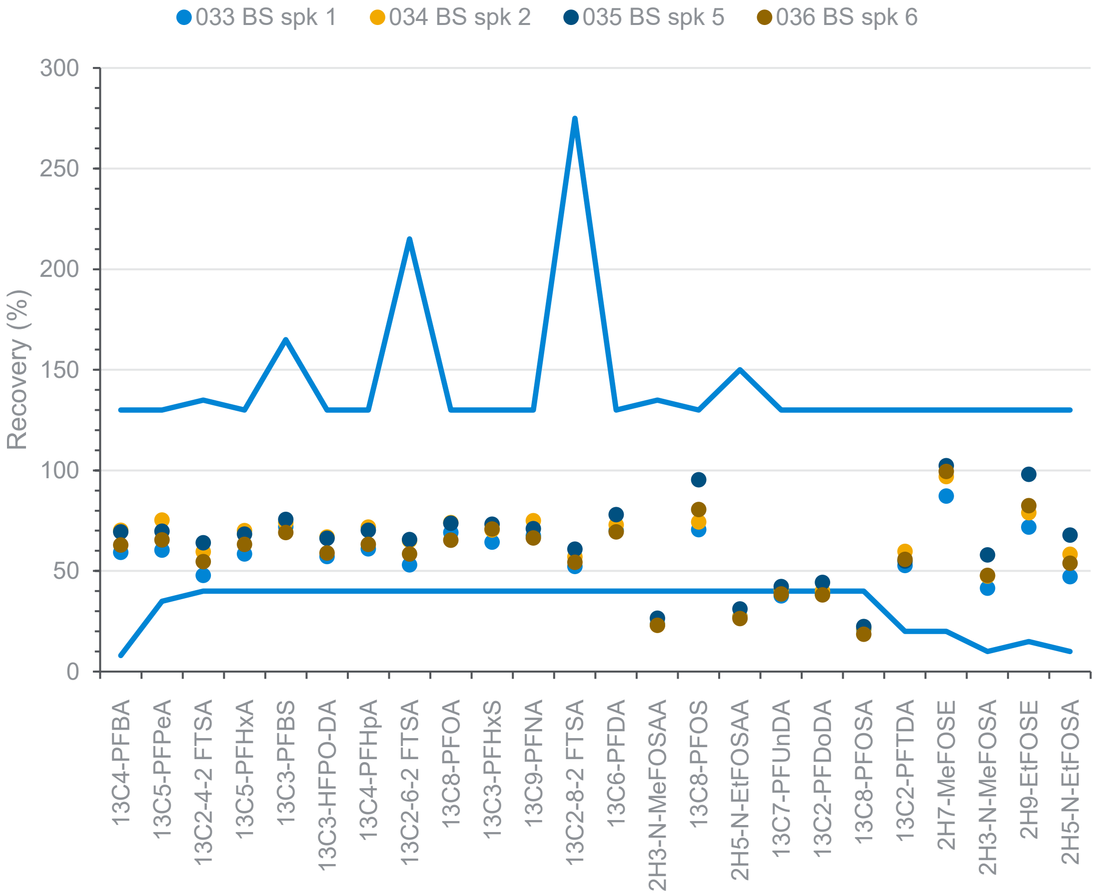
Sand MB1
Sand MB2
Sand MB3
Sand MB4
Standard Lv1
Concentration (ng/mL)
0
1
2
3
4
5
6
PFBA
PFMPA
3-3 FTCA
PFPeA
PFMBA
4-2 FTSA
NFDHA
PFHxA
PFBS
HFPO-DA
5-3 FTCA
PFEESA
PFHpA
PFPeS
DONA
6-2 FTSA
PFOA
PFHxS
PFNA
7-3 FTCA
8-2 FTSA
PFHpS
PFDA
N-MeFOSAA
PFOS
N-EtFOSAA
PFUnDA
9Cl-PF3ONS
PFNS
PFDoDA
PFDS
PFTrDA
11Cl-PF3OUdS
PFTDA
PFOSA
PFDoS
MeFOSE
N-MeFOSA
EtFOSE
N-EtFOSA

Extraction Standard Recovery

Sand Spikes



Biosolid Spikes



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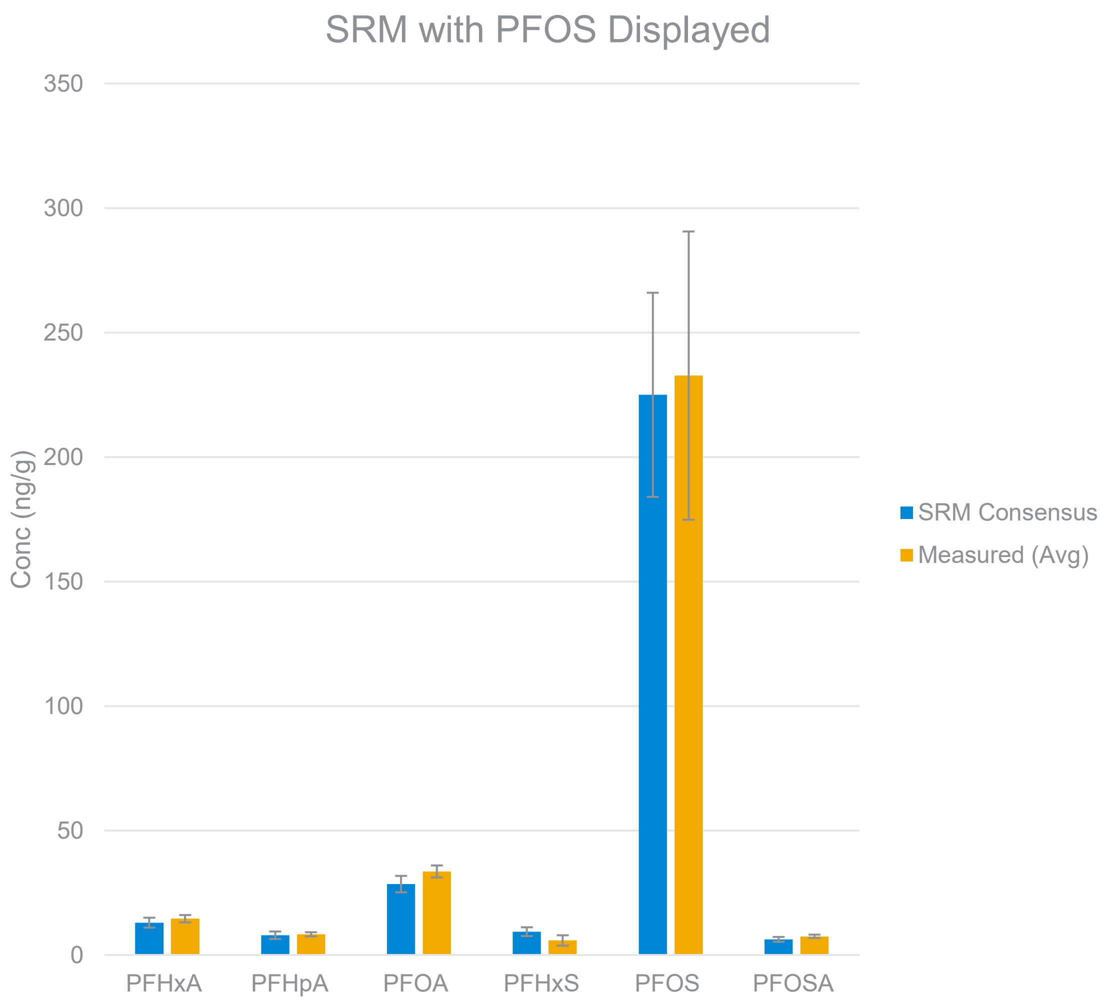
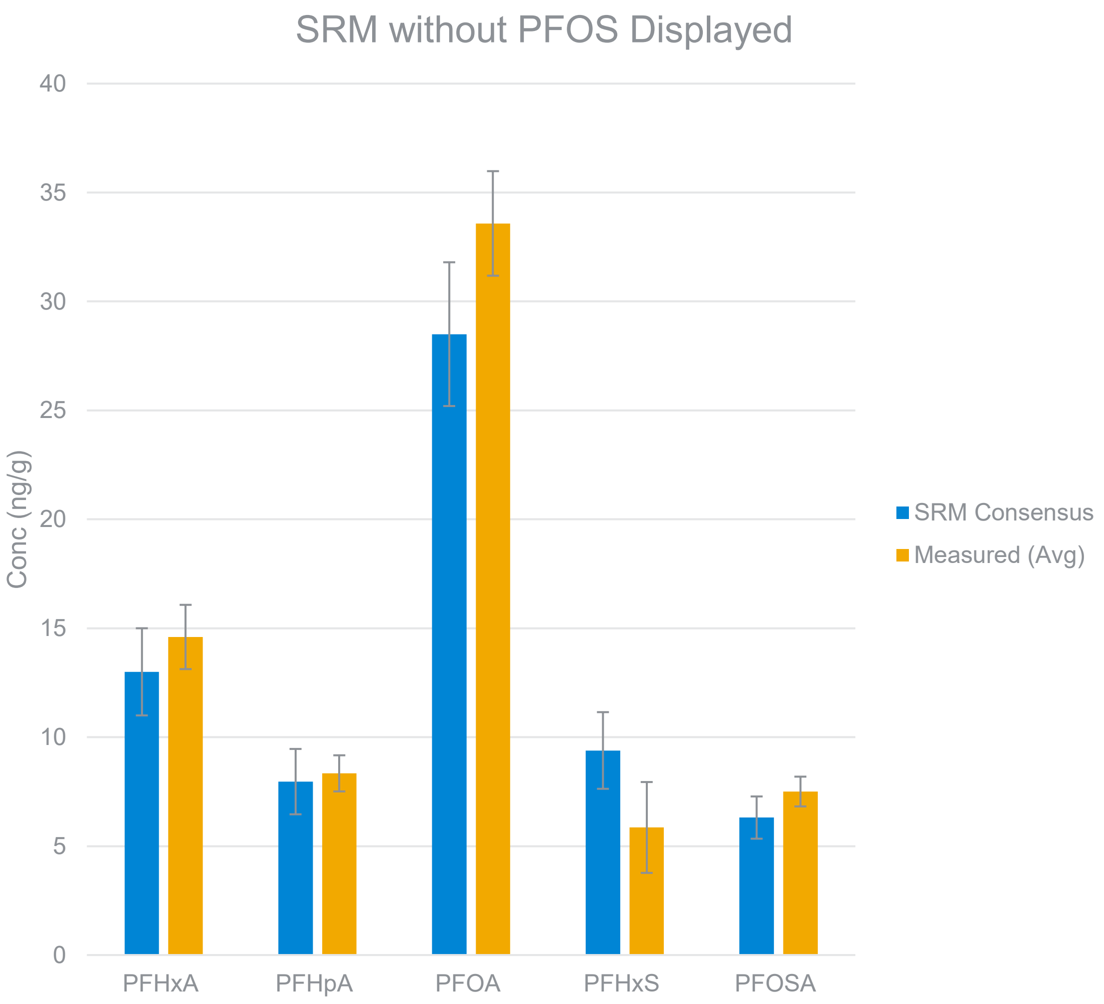
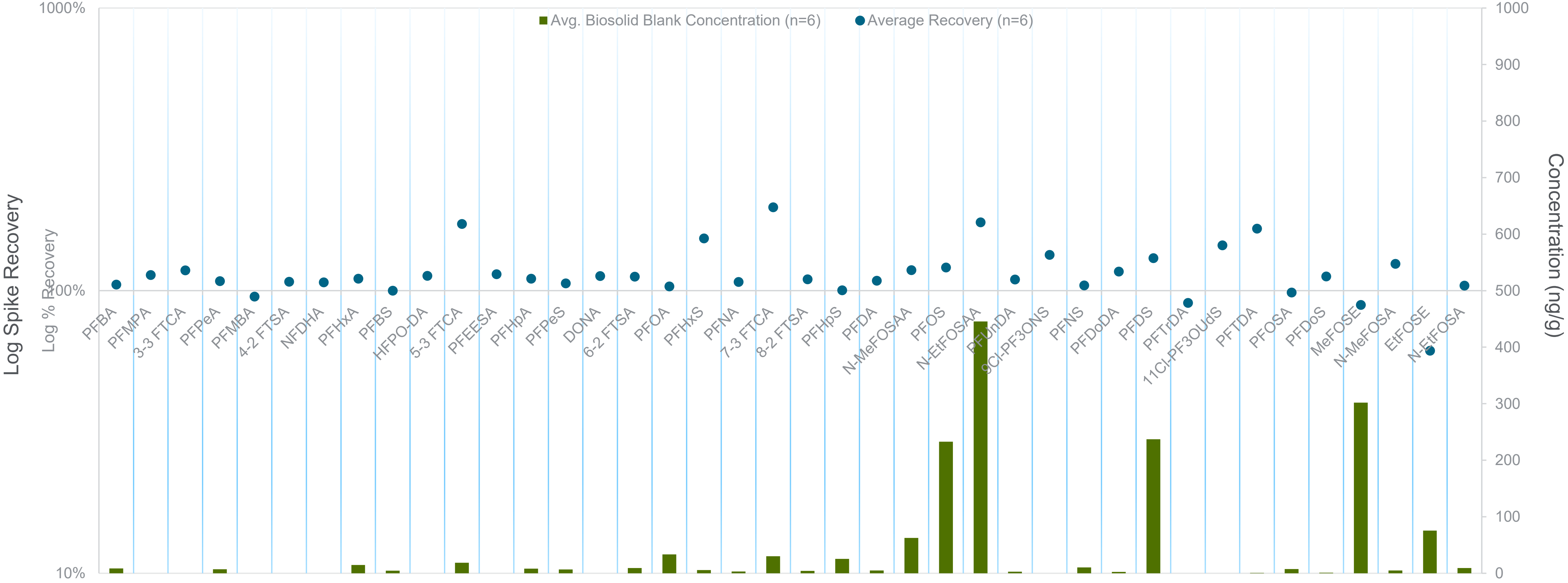
Comparison with Consensus Values



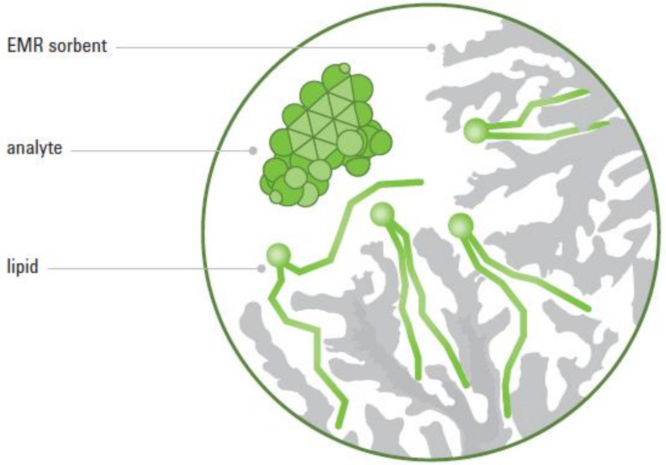


Biosolid Spikes



Enhanced Matrix Removal (EMR)

Passthrough Cleanup



EMR-Lipid

phospholipids

EMR-PFAS I

Fresh fruits, Vegetables, Baby Foods and Juice

EMR –PFAS II

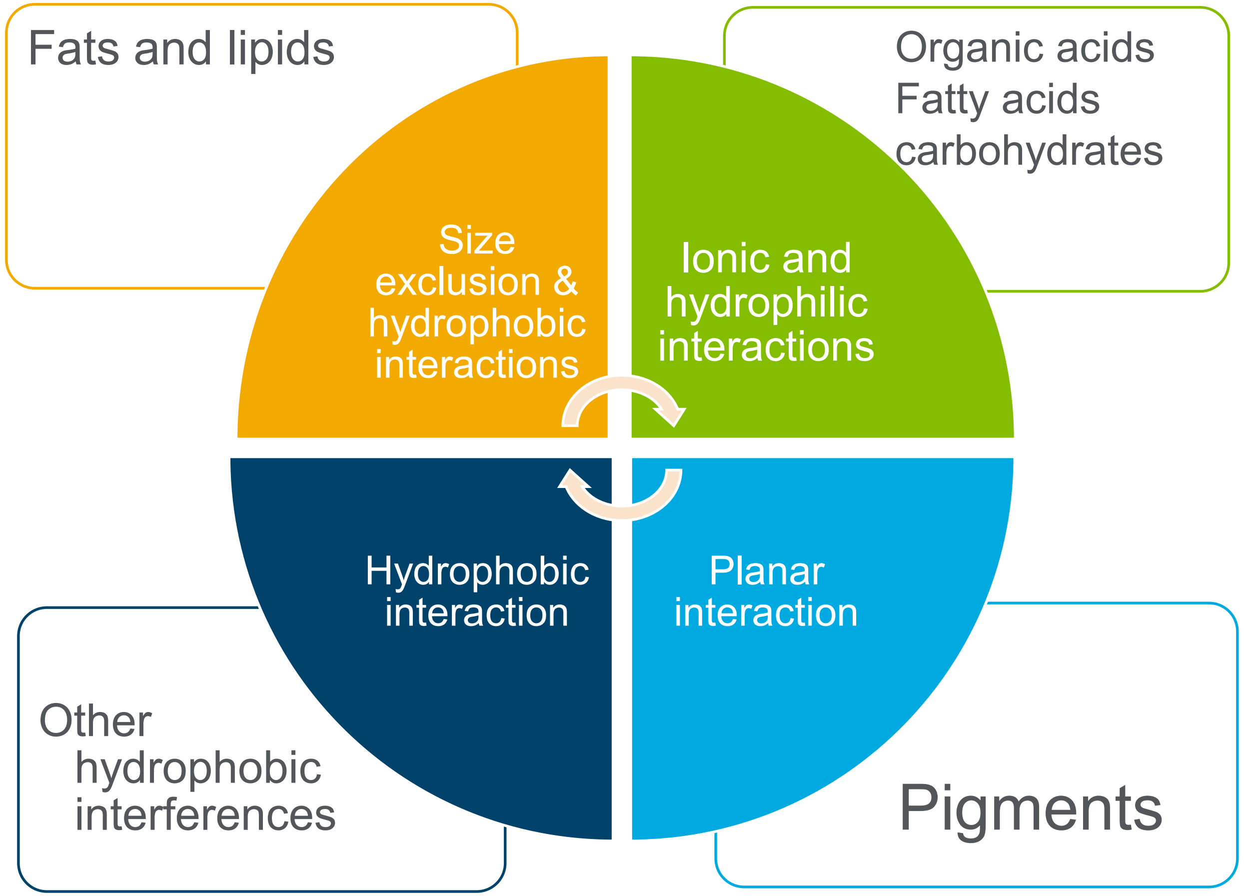
All animal origin food matrices

Complex plant origin dry matrices and oily matrices

Compatible with highly organic extract

EMR Mixed-mode Passthrough Cleanup

Comprehensive matrix co-extractives removal



Advantages

- ✓ Matrix co-extractives targeted chemical filtration mechanism
- ✓ Minimal impact on targets recovery
- ✓ Direct compatible with QuEChERS extraction
- ✓ One step cleanup
- ✓ Comprehensive and efficient matrix removal
- ✓ Higher sample volume (>90%)
- ✓ Saving time and effort

Captiva EMR PFAS Food I & II

Captiva EMR PFAS Food I

- Simpler sorbents and formula
- Applicable for fresh produce and processed plant-origin food
- Used after QuEChERS extraction
- Removes sugars, salts, organic acids, pigments and other hydrophilic & hydrophobic interferences from food matrix
- Two formats provide flexible sample crude extract loading capacity

Captiva EMR PFAS Food II

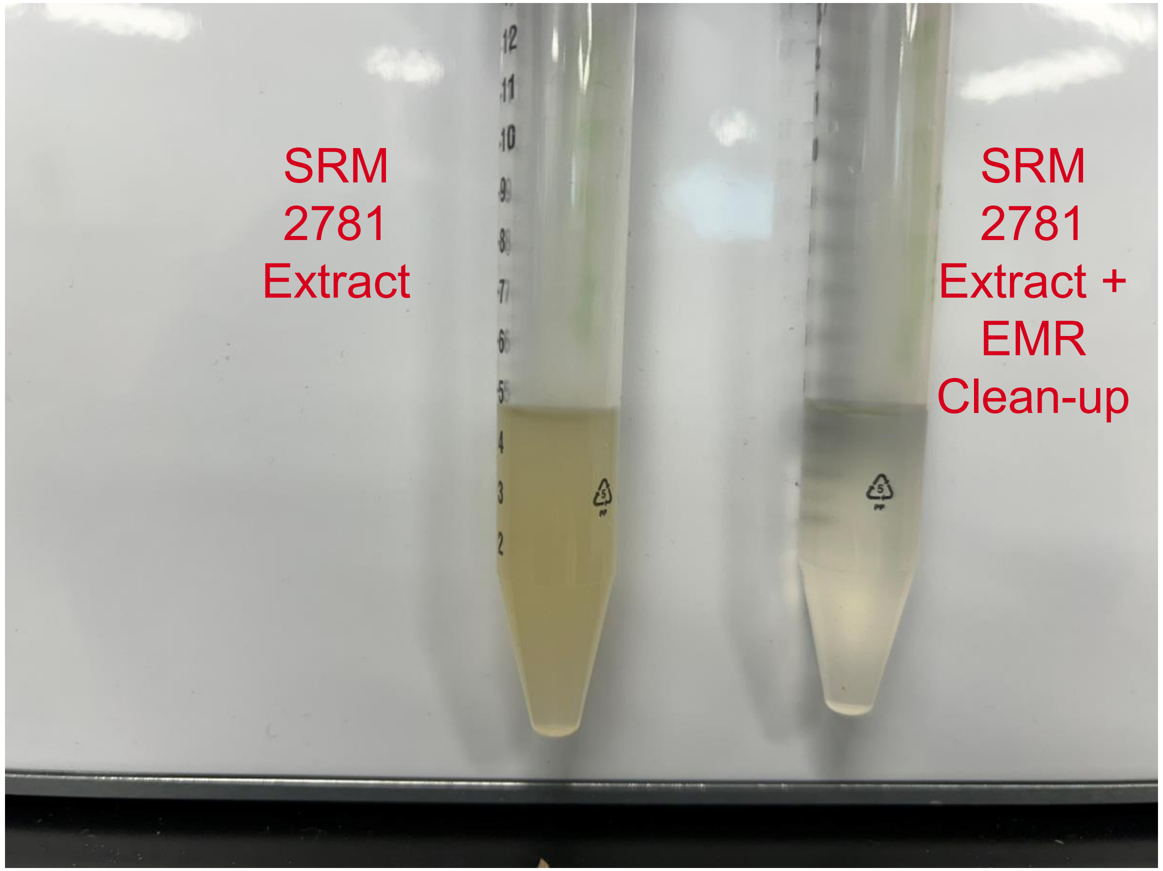
- More comprehensive sorbents and formula
- Applicable for animal origin food and complex dry food.
- Used after QuEChERS extraction
- Removes sugars, salts, organic acids, fats and lipids, pigments and other hydrophobic interferences from food matrices.
- One format for generic use in multiple matrices

EMR Pass Through Cleanup

Filtration Post WAX SPE Cleanup

Captiva EMR-Lipid

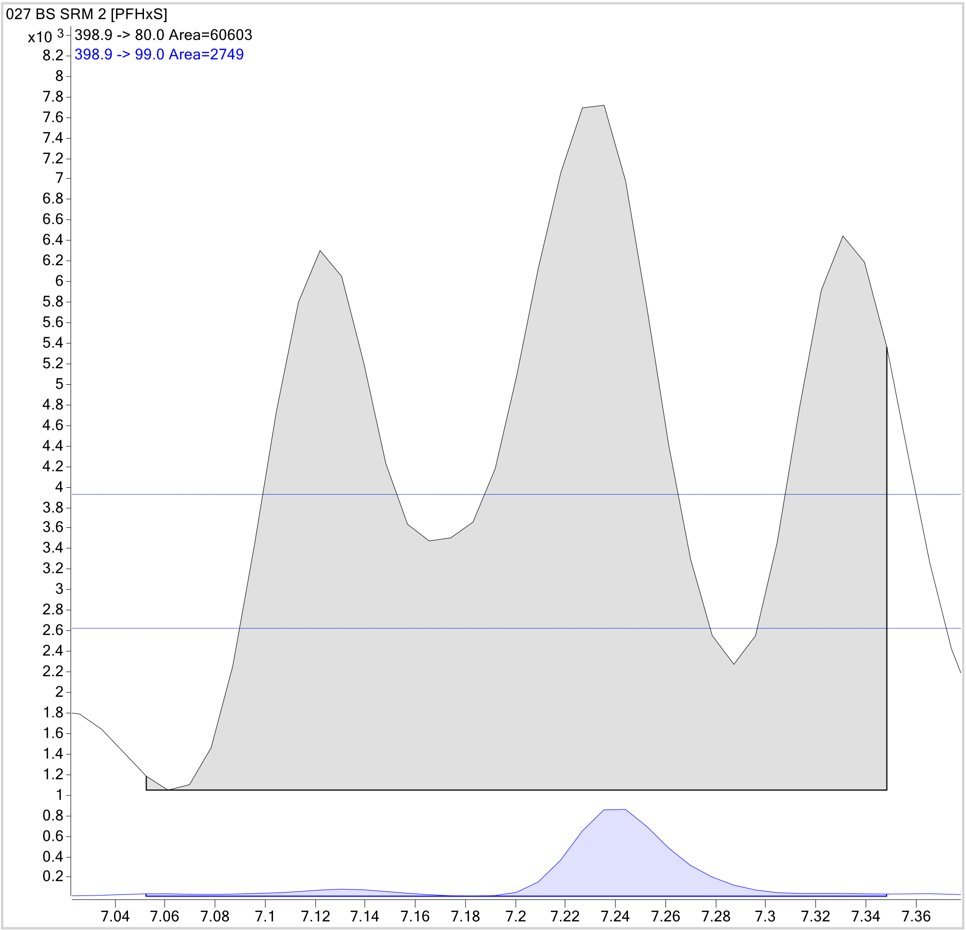
Captiva EMR PFAS Food II



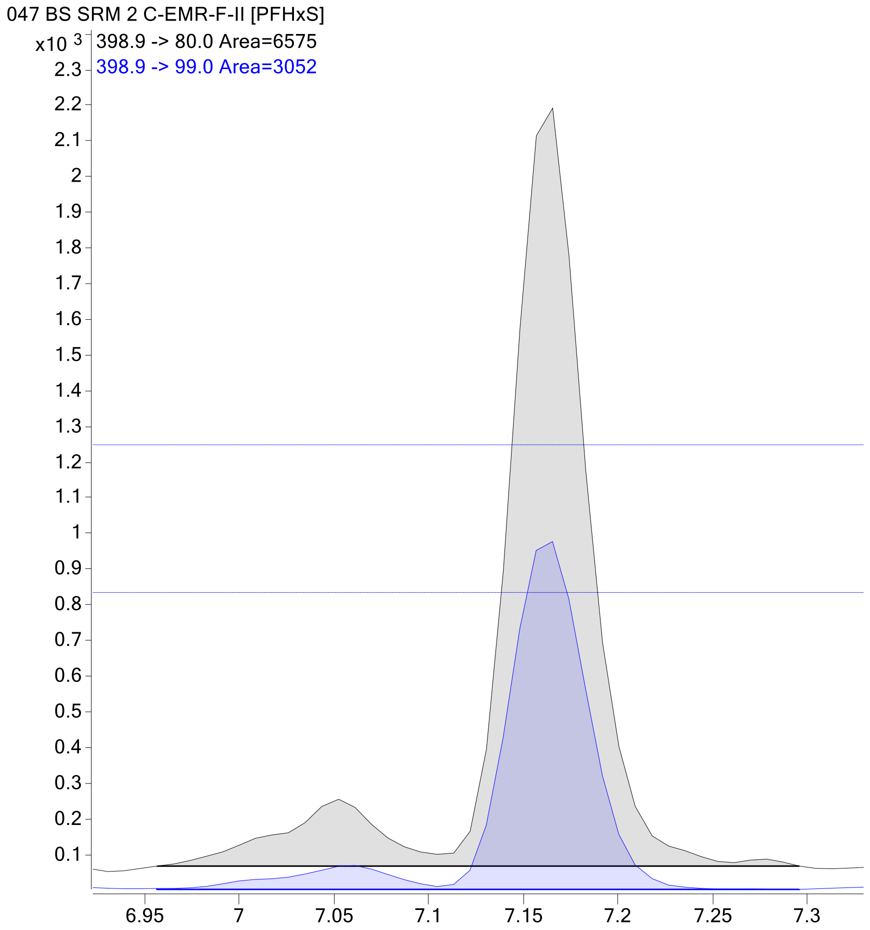
PFHxS in SRM 2871

EMR – PFAS Type II

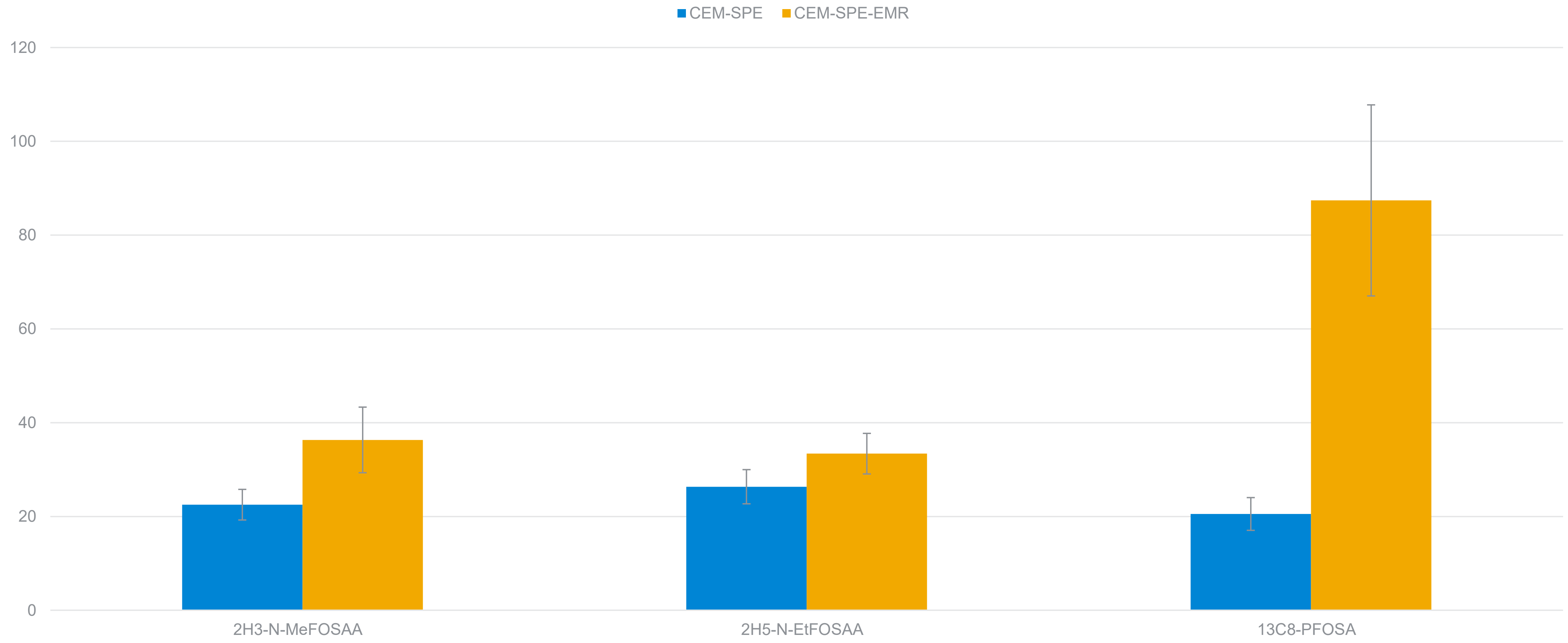
CEM – Carbon - WAX SPE



CEM – Carbon– WAX SPE – EMR PFAS II



EIS Recovery Comparison



Conclusions

- Initial results from semi-automated extraction protocol consistent with EPA 1633 for analysis of domestic sludge
- Reduced extraction mass would improve results quality
- Post extraction filtration step with EMR offers improved clean-up

Automation & Innovation for Sample Preparation Session
Thursday at 11:00

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Trusted Answers