Emerging Per/Polyfluoroalkyl Substance (PFAS) Analysis in Water, Soil & Biota

NEMC Conference 2018

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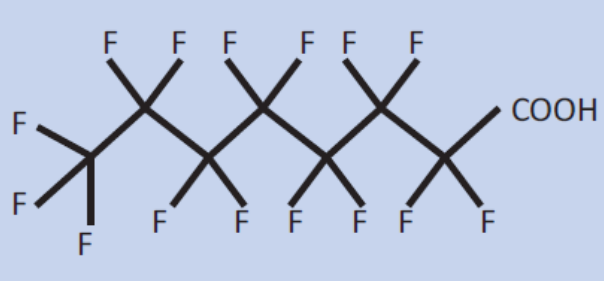
Trusted Answers

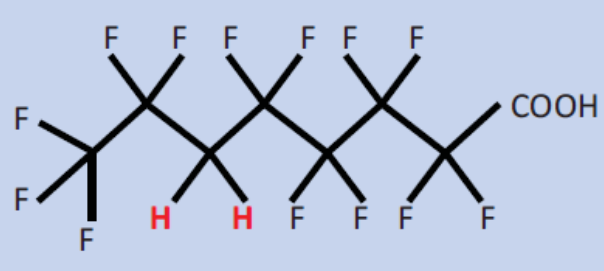
Terminology

Perfluoroalkyl substance



ALL H atoms linked to C in alkyl chain are substituted with F

Polyfluoroalkyl substance



SOME *(but not all)* H atoms linked to C in alkyl chain are substituted with F

Per/Polyfluoroalkyl substances
Unique Properties

- Thermal & Chemical stability: grease-proof food packaging, stain repellents
- Zwitterionic properties: surfactants
- Surface-tension lowering: fire-fighting foams




Contamination in Food and Water

Concern Grows Over Tainted Drinking Water

Vermont, New Hampshire and New York expand efforts to find out how much of a potentially toxic chemical is in drinking water

England since August 2014, when a resident of Hoosick Falls, N.Y., near the Vermont border, tested his drinking water and found high levels of the acid. The man was concerned because his father, a former employee of the town's plastics plant that used PFOA, died of cancer.

of PFOA contamination. The state in March sampled PFOA levels up to 620 parts per trillion in private Litchfield wells, well above the 100-parts-per-trillion level at which New Hampshire officials start to consider the amount unsafe. Tests in Merrimack measured as high as 1,600 parts per trillion.

environment

Williamtown water contamination highlights dangers of PFOS and PFOA

Qantas faces $180,000 fine over toxic foam spill at Brisbane Airport

21 April 2017 - 04:56pm First published 21 April 2017 - 11:02am
By Ruth McCosker

Qantas has been hit with an investigation notice while residents continue to be warned not to eat seafood following a toxic spill into Brisbane's waterways.

On Monday, April 10, 22,000 litres of a firefighting foam containing perfluorinated compounds was spilled from a Qantas hangar at Brisbane Airport.

c&en

Volume 94 Issue 20 | pp. 20-22
Issue Date: May 16, 2016 | Web Date: May 11, 2016

Perfluorinated chemicals taint drinking water

Are there toxins in your fast food packaging?

CBS NEWS

QLD News

Brisbane River seafood warning still in effect

Chris Honnery, The Courier-Mail
April 20, 2017 8:49pm

Regulatory Guidance for PFAS

Compound	Agency/State	Concentration (ng/L)	Year
PFOA + PFOS	EPA DWHA	70	2016
PFOA	MN	35	2017
PFOS	MN	27	2017
PFOA	NJ	14 (40)	2017 (2007)
GenX	NC	140	2017
PFOA/PFOS	UK	300 (Reg. 10)	2009
PFOS/PFHxS	AUS	70	2016
PFOS	VIC EPA	0.23	2016

Standard Methods

EPA Method 537

DRINKING WATER

EPA Document #: EPA/600/R-08/092

METHOD 537. DETERMINATION OF SELECTED PERFLUORINATED ALKYL ACIDS IN DRINKING WATER BY SOLID PHASE EXTRACTION AND LIQUID CHROMATOGRAPHY/TANDEM MASS SPECTROMETRY (LC/MS/MS)

Version 1.1
September 2009

J.A. Shoemaker and D.R. Tettenhorst — US EPA, Office of Research and Development, National Exposure Research Laboratory

P.E. Grimmett — US EPA, Office of Research and Development, National Exposure Research Laboratory

B.K. Boutin — The National Council on Aging, Senior Environmental Employment Program

250 mL sample

Solid Phase Extraction

10 µL injection (96:4: MeOH/Water)

14 analytes

37 min run time

MDLs: 0.5 – 6.5 ng/L

ASTM Method 7979

Designation: D7979 – 17

SURFACE & WASTEWATER, SLUDGE

Standard Test Method for
Determination of Perfluorinated Compounds in Water, Sludge, Influent, Effluent and Wastewater by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)[1]

This standard is issued under the fixed designation D7979; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This procedure covers the determination of selected perfluorinated compounds (PFCs) in a water matrix using liquid chromatography (LC) and detection with tandem mass spectrometry (MS/MS). The target analytes are identified and quantitatively determined by this method. This method adheres to multiple reaction monitoring (MRM) mass spectrometry.

1.2 The Method Detection Limit (MDL)[2] and Reporting Range[3] for the target analytes are listed in Table 1.

1.3 The reporting limit in this test method is the minimum value below which data are normally documented as non-detects. Analyte detections between the method detection limit and the reporting limit are estimated concentrations and are not reported following this test method. In most cases, the reporting limit is the concentration of the Level 1 calibration standard as shown in Table 4 for the perfluorinated compounds after taking into account the sample aliquant, extract volume, and dilutions. At or above the Level 1 calibration concentration for PFOS, PFBS, FHEA and FOEA, these compounds can be identified at the Level 1 concentration but the standard deviation among replicates at this lower spike level resulted in a higher reporting limit.

1.4 Units—The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

priate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Referenced Documents

2.1 ASTM Standards:[4]
D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water
D3694 Practices for Preparation of Sample Containers and for Preservation of Organic Constituents
D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
E2554 Practice for Estimating and Monitoring the Uncertainty of Test Results of a Test Method Using Control Chart Techniques

2.2 *Other Standards:*[5]
EPA Publication SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods
Title 40 Code of Federal Regulations 40 CFR Part 136, Appendix B

5 mL sample

LLE with 5 mL MEOH + pH adjustment

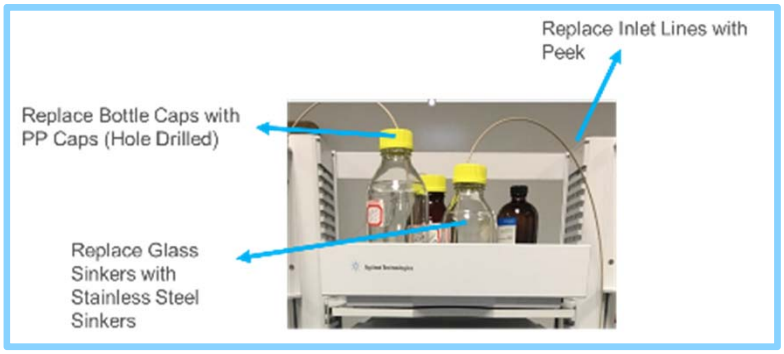
30 µL injection (50/50: MeOH/Water)

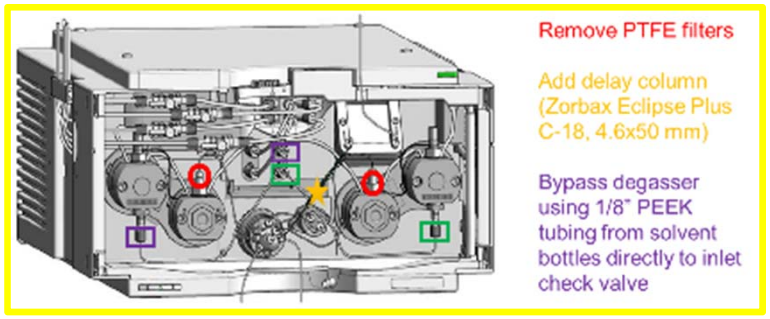
21 analytes

21 min run time

MDLs: 1.3 – 107 ng/L (13-11.6 ng/L for 537)

PFAS Analysis – LC Instrument Setup
Eliminate Background Contamination





Potential Contamination Sources

- Solvents
- Filtration apparatus
- Teflon lined tubing

Anumol et al., Recommended Plumbing Configurations for Reduction in Per/Polyfluoroalkyl Substance Background with Agilent 1260/1290 Infinity (II) LC's, Agilent Application Note (5991-7863EN)

Extracting PFAS from matrix

Water

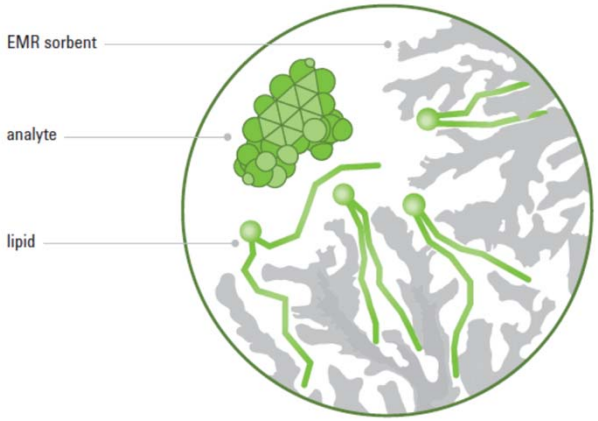
Weak Anion Exchange (WAX) Cartridge

WAX SPE with sorbent mass of 30, 60 and 150 mg available.

For PFAS in water, the 6 cc, 150 mg with 30 µm particle size is recommended.

Foods & Biologicals

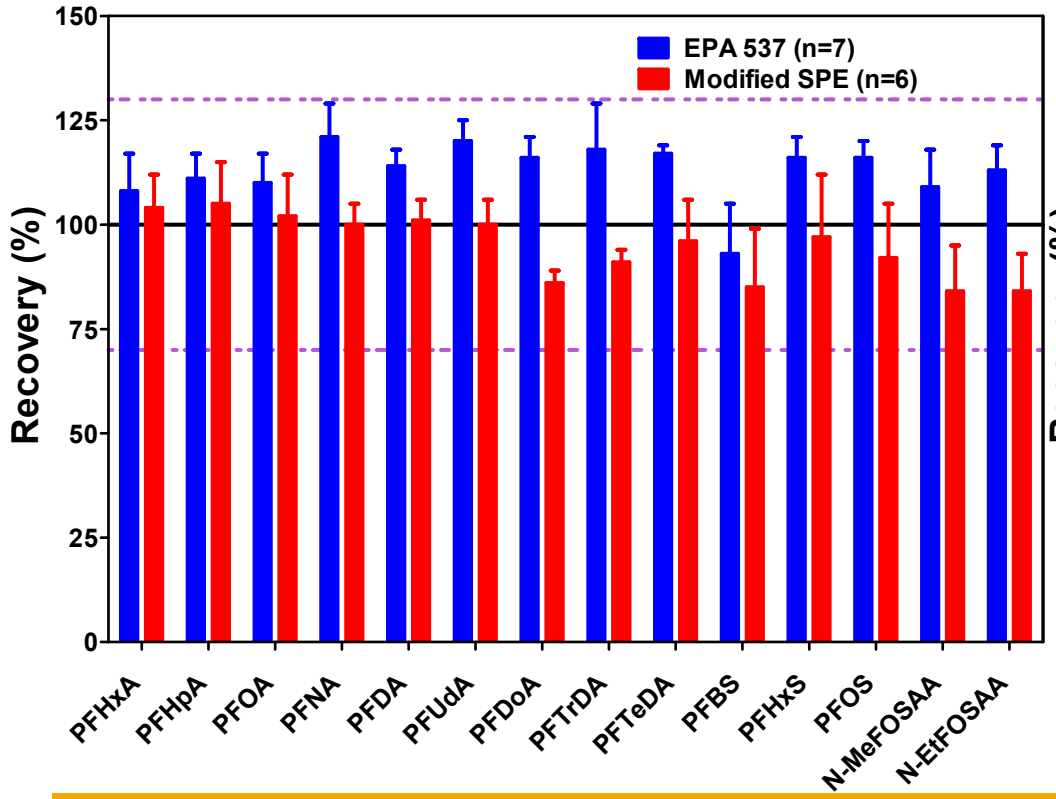
Enhanced Matrix Removal-Lipid (EMR-L)



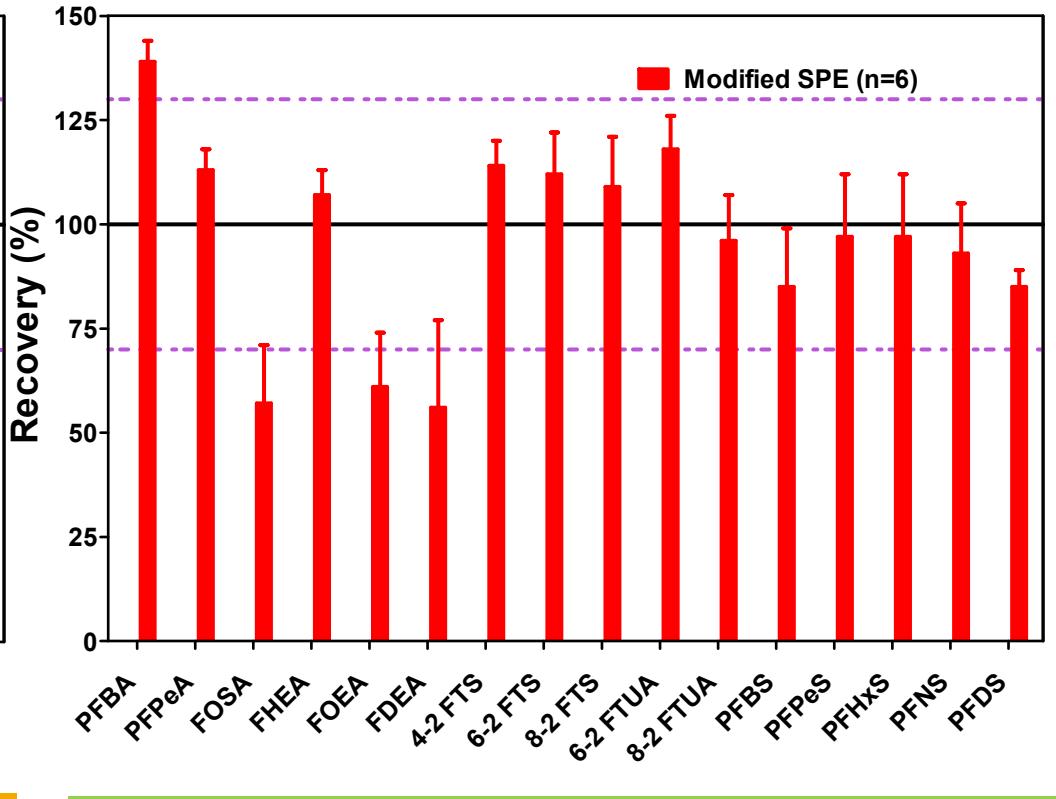
EMR-L specifically retains lipids while letting PFAS pass through

Available in powder and flow-through cartridge (1, 3 and 6 cc) format

Solid Phase Extraction
USEPA 537 vs Modified



EPA 537 Analytes



Additional PFAS including ASTM

Experimental:
Procedure: Phospholipid Removal Evaluation:

Protein Precipitation:

Add 400 µL of Acetonitrile with 1% Formic Acid into a test tube

↓

Add 100 µL of blank plasma, pre-spun

↓

Vortex on a Heidolph Multi Reax® at 800-1000 rpm, 5 minutes

↓

Centrifuge at 5000 rpm, 5 min

↓

Pipette the supernant to an autosampler vial for analysis

↓

Inject directly into LC/MSMS

Captiva EMR-Lipid:

Add 400 µL of Acetonitrile with 1% Formic Acid to **Captiva EMR-Lipid 1 mL cartridge**

↓

Add 100 µL of blank plasma, pre-spun

↓

In-well mixing. Allow PPT.

↓

Pull low vacuum, 2-4 psi, 1 drop/3-5 sec

↓

Collect in polypropylene test tubes

↓

Inject directly into LC/MSMS, using polypropylene* autosampler vials

* Polypropylene collection tubes and autosampler vials are recommended since PFASs will stick to glass

Results and Discussion:
Recovery and RSD

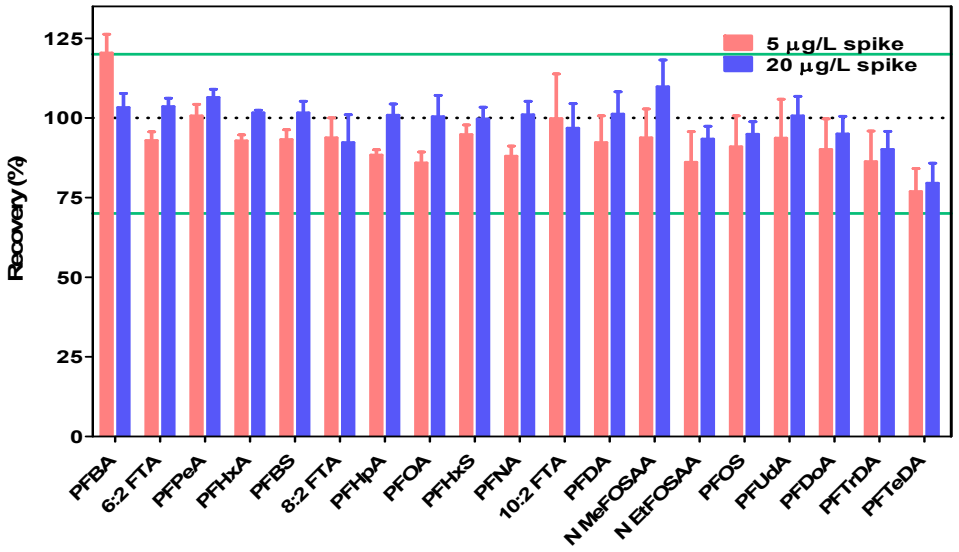


Figure 3. Recovery and RSD for the PFASs evaluated in the study at 5 and 20 ng/mL

The recovery and relative standard deviation for the 22 PFASs were determined at 5 and 20 ng/mL shown in Figure 3. The overall recovery was between 75-125% for both 5 and 20 ng/mL. Relative standard deviation was 0.8-14% for 5 and 20 ng/mL.

Results and Discussion:

Phospholipid Removal by Captiva EMR-Lipid versus Protein Precipitation:

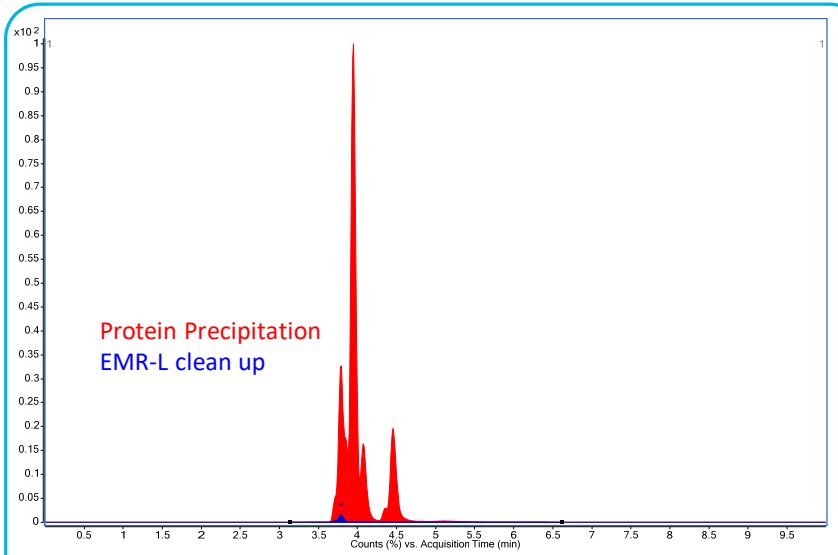
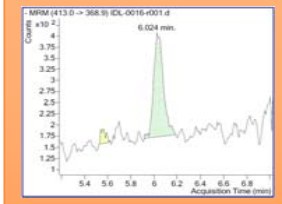
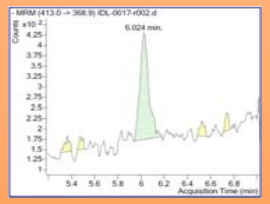
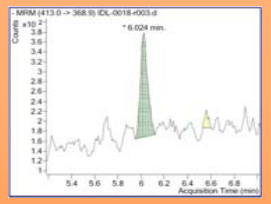
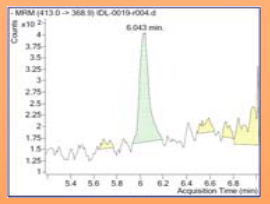
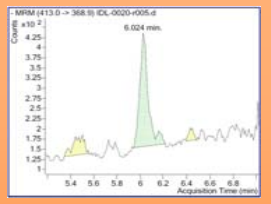
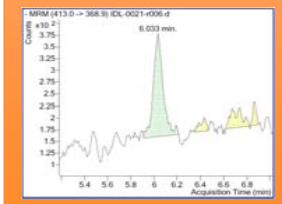
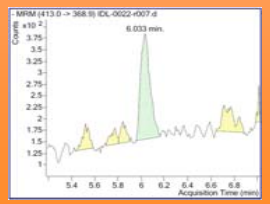
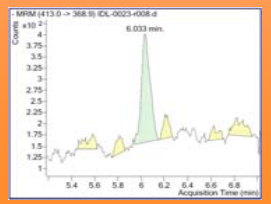
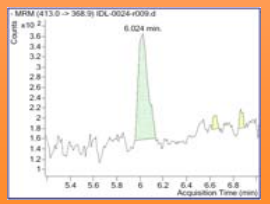
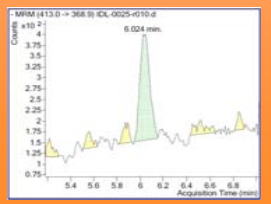


Figure 4. Overlay of the MRM chromatogram after protein precipitation and Captiva EMR-Lipid clean-up, evaluation of 11 phospholipids

- Captiva EMR-Lipid, a novel phospholipid removing sorbent available in a SPE cartridge format allows for in-situ protein precipitation and phospholipid removal as the extract passes through the sorbent during elution.
- Figure 4 shows the overall phospholipid removal of Captiva EMR-Lipid when compared to protein precipitation, overlay.

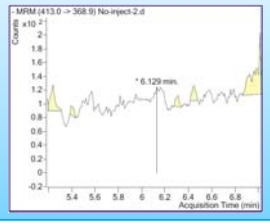
- Captiva EMR-Lipid removes ~99% of the phospholipids based on peak area determined from the LC/MSMS MRM method for 11 phospholipids.

PFOA – 1 µL injection of 24 fg/µL

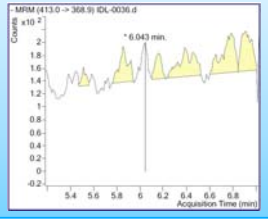











RSD = 9%

IDL = 6.4 fg

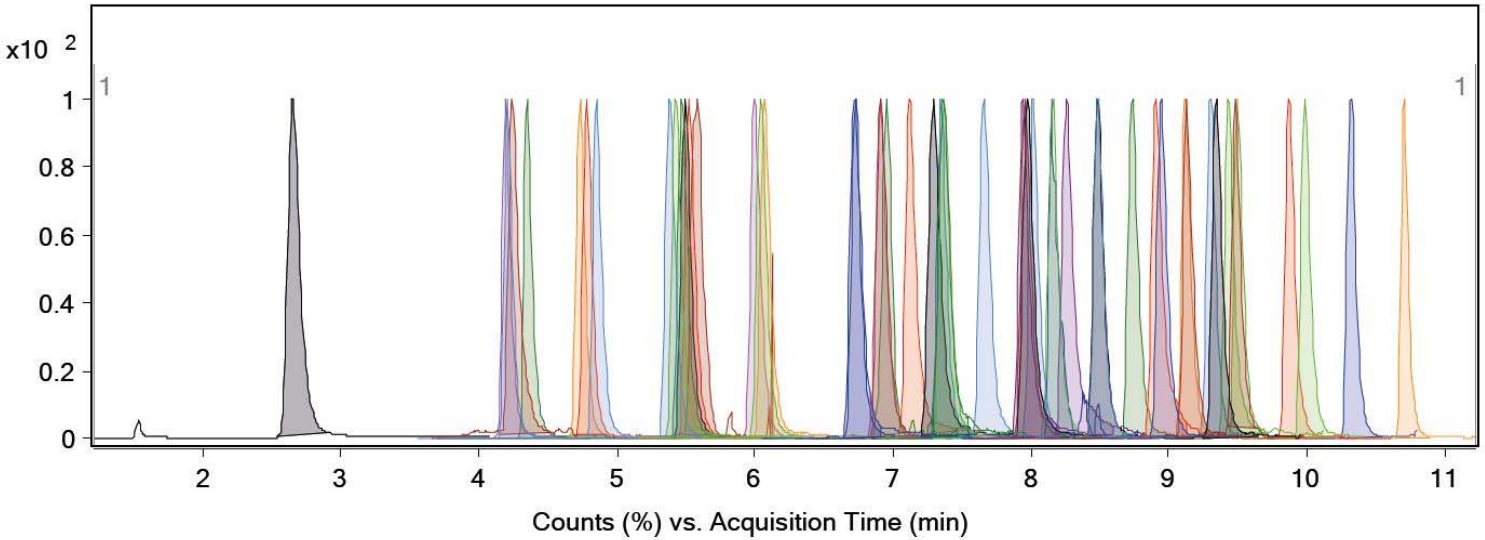


No inject



Methanol blank

52 PFAS in one LC-MS/MS method (5 ng/mL chromatogram)



Compound classes:

PFCAs

PFSAs

ADONA

PFPAs

n:2 FTS

FASAs

FASAAs

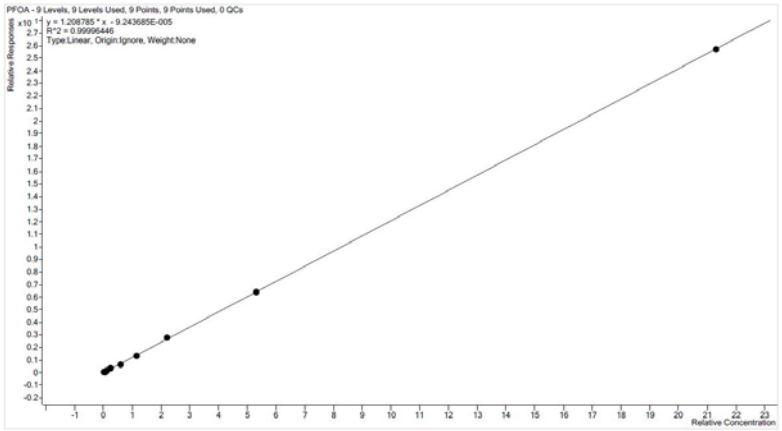
FASEs

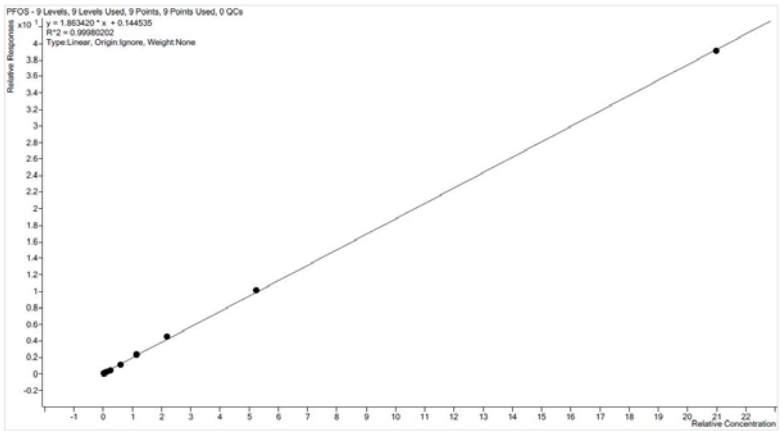
diPAPs

diSAmPAP

PFPis

Calibration curves PFOA and PFOS





PFOA:

2 μL injection in MeOH

linear (r^2 = 0.999)

Range 0.1 to 100 ng/mL

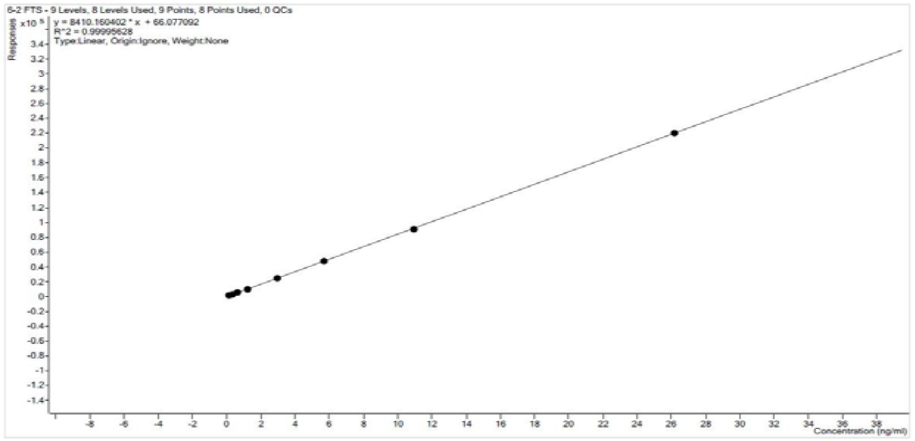
PFOS:

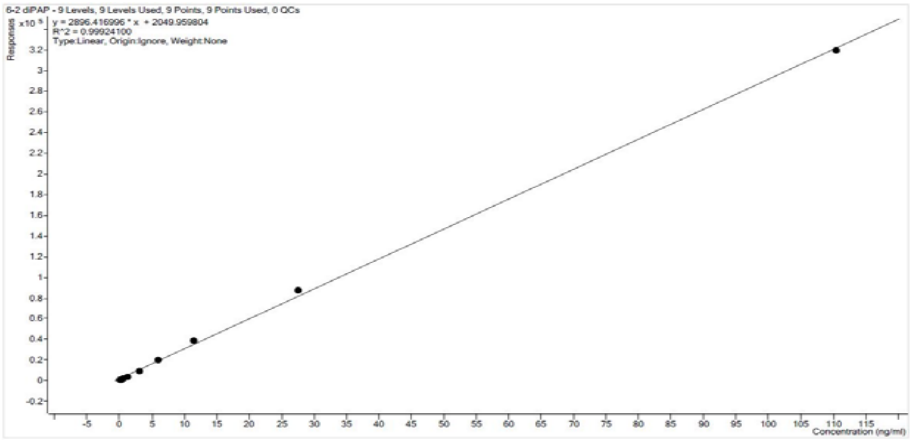
2 μL injection in MeOH

linear (r^2 = 0.999)

Range 0.1 to 100 ng/mL

Calibration curves 6:2 FTS and 6:2 diPAP





6:2 FTS:

2 μL injection in MeOH

linear (r^2 = 0.999)

Range 0.1 to 25 ng/mL

6:2 diPAP:

2 μL injection in MeOH

linear (r^2 = 0.999)

Range 0.1 to 100 ng/mL

Fish Extract Recovery & Data

Fish Extract Recovery & Data

Acknowledgements

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