Wastewater, Fish Tissue and Biosolids - An Analytical Evaluation of EPA Draft Method 1633

Megumi Shimizu[1], Kendra Adams[1], Sam Lodge[2], Phil Bassignani[3], Craig Butt[1], Matthew Noestheden[1], Karl Oetjen[1]

[1] SCIEX, [2] Phenomenex, [3] Alpha Analytical

Introduction

EPA draft method 1633 covers the extraction and analysis of 40 per- and polyfluoroalkyl substances (PFAS) in a variety of environmentally relevant matrices. As a method not yet promulgated, the test method procedure and method performance requirements are not part of the clean water act, but it is currently be offered by many commercial laboratories. Here we evaluate the performance of the draft method procedure in wastewater, fish tissue and biosolids. Full initial demonstration of capability (IDC) data are provided including method detection limits and precision in each matrix evaluated. The full test method was applied to the analysis of real-world samples and the resulting data are presented.

SCIEX Triple Quad 5500+ LC-MS/MS System

Bile acid separation

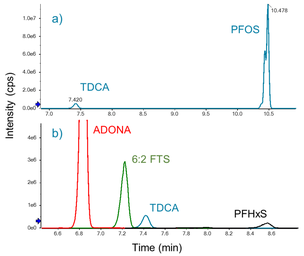

Figure 1. Separation of bile acid (TDCA) from PFOS > 1 min (as specified in EPA Draft Method 1633) and separation from other target analytes were achieved using a Phenomenex Luna Polar C18 100x2.1 mm 3 µm.

Method

Sample preparation: Methods follow those outlined in the EPA Draft Method 1633 document. Samples were extracted and concentrated using 500 mg Phenomenex Strata™-X-AW SPE cartridges. The final eluent was spiked with the non-extracted internal standard mix.

Chromatography: The SCIEX ExionLC™ system was used and chromatographic separation was achieved using a Phenomenex Luna Polar C18 (100 x 2.1mm, 3um particle size) at column temperature 40 C. A delay column was used to separate the instrument PFAS contamination from the analyte peak. Injection volume was 2 µL.

Mass spectrometry: Analysis was performed on the SCIEX 5500+ System with the Turbo V™ Ion Source using an electrospray ionization (ESI) probe in negative ion mode. Data were collected using the Scheduled MRM™ Algorithm using compound-specific parameters. The ESI source and parameters were also optimized.

The performance you need in real-world samples

Difficult, dirty matrices – no problem!

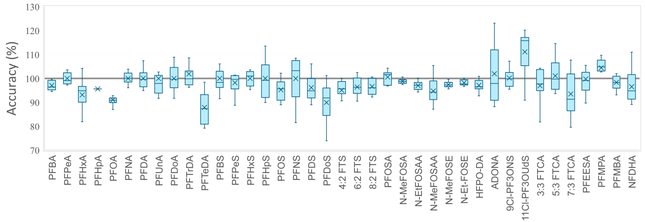

Figure 2. Box and whisker plot showing the accuracy and precision of a Continuous Calibration Verification (Cal level 4: 2.5 – 62.5 ng/mL) throughout a 41-hour, 125-injection sequence of water, soil, biosolid, and fish tissue samples. The accuracy of CCVs must be within 70 – 130% according to EPA method performance standards.

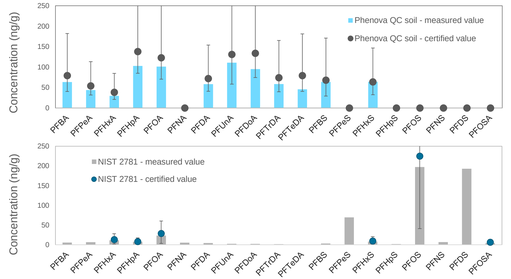

Figure 3. Comparisons of measured concentrations (bars) and certified concentrations (dots) in Phenova QC soil (top) and NIST 2781 domestic sludge samples (bottom). The error bars represent uncertainties of the certified values.

Quantitation in fish tissue, sludge, and water

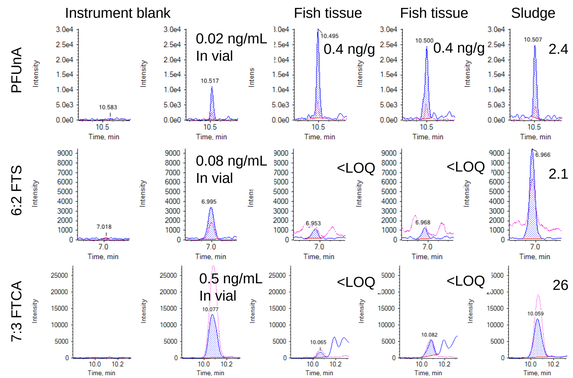

Figure 4. Extracted ion chromatograms of PFUnA, 6:2 FTS and 7:3 FTC in the lowest calibration level, in un-spiked fish tissue (2 g) and sludge samples (0.5 g).

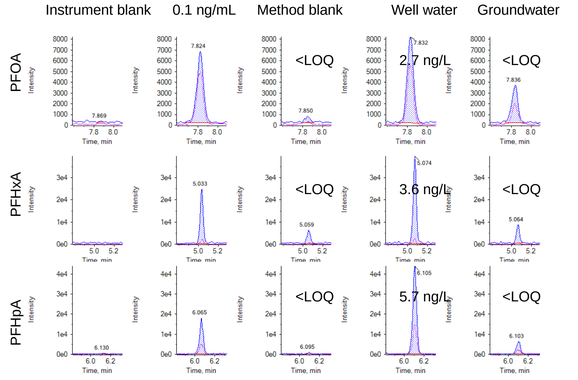

Figure 5. Extracted ion chromatograms of PFOA, PFHxA, and PFHpA in the lowest calibration point (0.1 ng/mL), method blank, un-spiked monitoring well (420 mL) and municipal groundwater (500 mL) samples.

1633 Matrix performance summary

Table 1. Method detection limit (MDL) and minimum level of quantitation (ML) in water, soil, and tissue matrices. The ML values in this table were derived from the concentrations of the lowest calibration standard (LOQ) using the 500 mL sample volume (aqueous), 2 g (tissue), or 5 g (soil) sample weight.

		Water (ng/L)		Soil (ng/g)		Tissue (ng/g)	
	LOQ (ng/mL in vial)	MDL	ML	MDL	ML	MDL	ML
PFBA	0.4	0.49	1.60	0.22	0.32	0.15	0.80
PFPeA	0.04	0.23	0.16	0.10	0.03	0.05	0.08
PFHxA	0.1	0.13	0.40	0.05	0.08	0.09	0.20
PFHpA	0.1	0.11	0.40	0.05	0.08	0.03	0.20
PFOA	0.1	0.08	0.40	0.05	0.08	0.06	0.20
PFNA	0.02	0.07	0.08	0.04	0.02	0.16	0.04
PFDA	0.02	0.05	0.08	0.06	0.02	0.27	0.04
PFUnA	0.02	0.04	0.08	0.05	0.02	0.61	0.04
PFDoA	0.02	0.06	0.08	0.05	0.02	0.06	0.04
PFTrDA	0.02	0.06	0.08	0.05	0.02	0.12	0.04
PFTeDA	0.1	0.10	0.40	0.10	0.08	0.04	0.20
PFBS	0.02	0.07	0.08	0.06	0.02	0.04	0.04
PFPeS	0.1	0.04	0.40	0.06	0.08	0.32	0.00
PFHxS	0.2	0.09	0.80	0.05	0.16	0.04	0.40
PFHpS	0.1	0.10	0.40	0.04	0.08	0.08	0.20
PFOS	0.1	0.11	0.40	0.05	0.08	0.11	0.20
PFNS	0.02	0.06	0.08	0.05	0.02	0.14	0.04
PFDS	0.1	0.04	0.40	0.04	0.08	0.44	0.20
PFDoS	0.1	0.08	0.40	0.06	0.08	0.16	0.20
4:2 FTS	0.08	0.14	0.32	0.20	0.06	0.11	0.16
6:2 FTS	0.08	0.12	0.32	0.21	0.06	1.10	0.16
8:2 FTS	0.08	0.19	0.32	0.18	0.06	0.24	0.16
PFOSA	0.2	0.03	0.80	0.07	0.16	0.03	0.40
N-MeFOSA	0.02	0.05	0.08	0.06	0.02	0.04	0.04
N-EtFOSAA	0.02	0.12	0.08	0.06	0.02	0.04	0.04
N-MeFOSAA	0.02	0.04	0.08	0.08	0.02	0.09	0.04
N-EtFOSAA	0.02	0.05	0.08	0.06	0.02	0.09	0.04
N-MeFOSE	0.2	0.29	0.80	0.54	0.16	0.20	0.40
N-Et-FOSE	0.2	0.35	0.80	0.55	0.16	0.46	0.40
HFPO-DA	0.08	0.13	0.32	0.24	0.06	0.20	0.16
ADONA	0.08	0.07	0.32	0.23	0.06	0.33	0.16
9Cl-PF3ONS	0.08	0.10	0.32	0.29	0.06	0.19	0.16
11Cl-PF3OUdS	0.08	0.13	0.32	0.16	0.06	0.30	0.16
3:3 FTCA	0.5	0.48	2.00	0.20	0.40	0.25	1.00
5:3 FTCA	0.5	0.41	2.00	1.32	0.40	0.38	1.00
7:3 FTCA	2.5	1.29	10.00	1.18	2.00	0.48	5.00
PFEESA	0.04	0.04	0.16	0.11	0.03	0.03	0.08
PFMPA	0.04	0.21	0.16	0.12	0.03	0.10	0.08
PFMBA	0.04	0.18	0.16	0.10	0.03	0.12	0.08
NFDHA	0.04	0.06	0.16	0.11	0.03	0.09	0.08