

# METHOD STATEMENT



## Determinand:

48 Per and Polyfluorinated (PFAS) compounds

## Matrix:

Ground and Surface Waters

## Principle of Method:

The compounds of interest are extracted from an aqueous matrix by an offline SPE procedure utilising a weak anion exchange (WAX) sorbent. The compounds are then eluted with methanolic ammonia, and the extract concentrated to 250µl. Quantification is by high resolution, accurate mass (HRAM) liquid chromatography mass spectrometry (LC-MS) using internal standardisation.

## Sampling and Sample Preparation:

Samples are taken in a 125ml HDPE bottle (STL024). No preservative is used.

Due to the known instability of certain PFAS compounds - particularly the perfluorooctane sulfonamide ethanols and the perfluorooctane sulfonamide acetic acids - in surface water (See Refs 15.1 and 15.2), and confirmed in in-house stability trials, samples are stored in a freezer at  $\leq -20^{\circ}\text{C}$  pending extraction. Samples should be frozen within 3 days of sampling, where this is not possible the table below, which gives the stability of the PFAS compounds in surface water under refrigeration conditions ( $3 \pm 2^{\circ}\text{C}$ ), can be used to determine which analytes are within stability at the point that the sample is frozen.

Once frozen samples must be extracted within 90 days (Ref 15.1).

Compound	Stability (Days)	Source
PFBA	28	Ref 15.1
PFPeA	28	Ref 15.1
PFHxA	28	Ref 15.1
PFHpA	28	Ref 15.1
PFOA	28	Ref 15.1
PFNA	28	Ref 15.1
PFDA	28	Ref 15.1
PFUdA	28	Ref 15.1
PFDoA	28	Ref 15.1
PFTriA	28	Ref 15.1
PFTeA	28	Ref 15.1
PFHxDA	32	In house data
PFODA	32	In house data
PFBS	28	Ref 15.1
PFPeS	28	Ref 15.1
PFHxS	28	Ref 15.1
PFHpS	28	Ref 15.1
PFOS	28	Ref 15.1
PFNS	28	Ref 15.1
PFDS	28	Ref 15.1
PFUnDS	14	In house data
PFDoS	28	Ref 15.1
HFPO-DA (GenX)	28	Ref 15.1

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Compound	Stability (Days)	Source
HFPO-TA	32	In house data
ADONA	28	Ref 15.1
PFMOPrA	28	Ref 15.1
NFDHA	28	Ref 15.1
PFMOBA	28	Ref 15.1
PFecHS	32	In house data
3:3FTCA	28	Ref 15.1
5:3FTCA	28	Ref 15.1
7:3FTCA	28	Ref 15.1
PFEESA	28	Ref 15.1
6:2 CI-PFESA	28	Ref 15.1
8:2 CI-PFESA	28	Ref 15.1
4:2FTS	28	Ref 15.1
6:2FTS	28	Ref 15.1
8:2FTS	28	Ref 15.1
FBSA	32	In house data
FHxSA	32	In house data
FOSA	28	Ref 15.1
MeFOSA	5	In house data
EtFOSA	7	In house data
MeFOSE	3	In house data
EtFOSE	3	In house data
MeFOSAA	3	In house data
EtFOSAA	3	In house data
6:2FTAB	14	In house data

## Interferences:

The LC-MS system operates at a mass spectral resolution of 60,000 FWHM and therefore the technique is extremely selective, however in theory any substance with an equivalent LC retention time, and which generates ions within 5ppm of the analytes' monoisotopic mass, may interfere.

## Performance of Method:

LOD, Precision and Bias

Determinand	LOD	MRL	0.01µg/l Std		0.04µg/l Std	
	µg/l	µg/l	Bias	RSD	Bias	RSD
PFBA	0.00053	0.001	2.10%	4.40%	1.08%	3.11%
PFPeA	0.00049	0.001	3.02%	3.43%	1.94%	3.40%
PFHxA	0.00048	0.001	3.75%	4.19%	1.05%	3.15%
PFHpA	0.00056	0.001	5.50%	5.63%	1.13%	3.54%
PFOA	0.00051	0.00065	1.55%	4.86%	2.04%	4.04%
PFNA	0.00055	0.001	4.88%	5.31%	1.13%	5.36%
PFDA	0.00037	0.001	0.35%	5.49%	-0.80%	4.16%

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Determinand	LOD	MRL	0.01µg/l Std		0.04µg/l Std	
	µg/l	µg/l	Bias	RSD	Bias	RSD
PFUdA	0.00049	0.001	2.17%	7.36%	0.81%	8.51%
PFDoA	0.00064	0.001	3.09%	5.02%	-1.94%	4.26%
PFTriA	0.00042	0.001	4.74%	4.00%	3.97%	6.70%
PFTeA	0.00058	0.001	2.40%	3.38%	0.83%	6.17%
PFHxDA	0.00045	0.001	2.82%	3.54%	0.14%	2.86%
PFODA	0.00049	0.001	0.98%	8.76%	2.87%	8.85%
PFBS	0.00026	0.001	4.70%	3.98%	2.03%	3.83%
PFPeS	0.00043	0.001	1.77%	4.31%	-1.17%	3.88%
PFHxS	0.00033	0.001	5.41%	8.67%	5.37%	4.56%
PFHpS	0.00049	0.001	-0.02%	5.59%	-0.09%	6.33%
PFOS	0.00046	0.00065	4.30%	5.13%	0.17%	3.81%
PFNS	0.00038	0.001	5.17%	5.98%	0.51%	6.47%
PFDS	0.00043	0.001	7.12%	8.55%	0.59%	10.33%
PFUnDS	0.00032	0.001	8.45%	9.02%	1.71%	11.38%
PFDoS	0.00045	0.001	7.60%	10.39%	2.05%	11.98%
HFPO-DA (GenX)	0.00049	0.001	0.58%	5.25%	-0.51%	3.03%
HFPO-TA	0.00083	0.005	-2.29%	9.59%	1.33%	8.80%
ADONA	0.00049	0.001	2.68%	4.38%	2.32%	3.27%
PFMOPrA	0.00050	0.001	-1.62%	7.01%	-2.34%	6.82%
NFDHA	0.00070	0.001	1.00%	5.51%	0.83%	6.44%
PFMObA	0.00047	0.001	2.20%	5.61%	3.97%	4.45%
PFecHS	0.00037	0.001	-0.77%	4.73%	-0.68%	7.07%
3:3FTCA	0.00056	0.010	4.16%	15.48%	0.05%	13.50%
5:3FTCA	0.00057	0.001	-5.15%	14.71%	-6.79%	15.54%
7:3FTCA	0.00043	0.001	-0.26%	14.15%	-0.72%	15.00%
PFEESA	0.00044	0.001	1.74%	3.79%	-0.04%	2.97%
6:2 CI-PFESA	0.00046	0.001	5.90%	8.71%	0.77%	5.73%
8:2 CI-PFESA	0.00044	0.001	9.16%	10.63%	0.90%	10.33%
4:2FTS	0.00046	0.001	1.45%	2.94%	0.81%	2.71%
6:2FTS	0.00074	0.001	0.60%	5.91%	0.22%	3.39%
8:2FTS	0.00045	0.001	2.34%	2.65%	1.04%	2.75%
FBSA	0.00053	0.001	-1.44%	15.01%	-0.86%	15.43%
FHxSA	0.00041	0.001	-7.27%	13.12%	-4.28%	12.53%
FOSA	0.00056	0.001	3.44%	3.29%	2.03%	3.92%
MeFOSA	0.00048	0.001	2.05%	6.15%	5.29%	8.53%
EtFOSA	0.00052	0.001	1.90%	6.24%	5.97%	6.72%
MeFOSE	0.00054	0.001	2.45%	6.94%	3.94%	5.61%
EtFOSE	0.00070	0.001	4.71%	7.49%	4.76%	5.77%
MeFOSAA	0.00043	0.001	2.98%	7.93%	4.92%	9.15%
EtFOSAA	0.00075	0.001	3.05%	4.89%	1.46%	5.74%
6:2FTAB	0.00060	0.001	-8.85%	10.13%	-5.63%	18.63%

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## Matrix Spike Recoveries

Determinand	Groundwater				Surface Water			
	0.01µg/l Spike		0.04µg/l Spike		0.01µg/l Spike		0.04µg/l Spike	
	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD
PFBA	97.44%	4.48%	96.94%	2.82%	102.50%	15.44%	98.19%	3.58%
PFPeA	100.87%	3.31%	101.02%	1.96%	93.65%	6.86%	94.17%	5.94%
PFHxA	99.32%	3.03%	100.35%	2.61%	99.63%	4.77%	99.06%	3.16%
PFHpA	100.95%	4.58%	101.44%	3.31%	104.79%	8.64%	102.66%	4.35%
PFOA	97.61%	5.16%	99.54%	4.08%	99.62%	4.31%	102.12%	4.47%
PFNA	104.63%	5.30%	99.07%	4.73%	104.19%	7.43%	99.21%	4.91%
PFDA	99.34%	4.95%	98.83%	4.24%	88.59%	7.56%	92.28%	5.86%
PFUDa	98.15%	11.43%	95.80%	8.09%	99.01%	11.04%	99.14%	8.91%
PFDaA	103.06%	5.69%	100.31%	4.13%	93.65%	7.34%	92.32%	5.30%
PFTriA	104.63%	6.04%	104.45%	5.88%	102.36%	8.36%	99.93%	9.72%
PFTeA	102.94%	6.14%	102.09%	5.63%	102.02%	3.76%	102.78%	3.48%
PFHxDA	100.21%	2.68%	100.14%	2.42%	99.65%	5.51%	100.85%	4.01%
PFODA	102.30%	12.07%	102.83%	8.66%	96.32%	10.28%	102.56%	9.28%
PFBS	102.77%	4.34%	101.71%	2.98%	104.88%	3.63%	104.07%	3.16%
PFPeS	99.58%	4.42%	99.63%	3.09%	98.29%	4.94%	99.10%	4.40%
PFHxS	102.22%	7.58%	101.66%	6.12%	114.47%	8.83%	115.45%	7.75%
PFHpS	100.67%	5.35%	102.86%	9.08%	93.96%	6.03%	96.89%	4.96%
PFOS	99.14%	3.90%	98.74%	3.10%	101.45%	4.15%	99.31%	4.16%
PFNS	99.13%	7.01%	94.34%	6.04%	112.04%	5.68%	104.42%	6.12%
PFDS	100.01%	10.35%	93.64%	9.33%	117.86%	10.05%	104.80%	8.82%
PFUnDS	100.88%	10.65%	96.65%	10.21%	118.08%	12.58%	104.28%	11.00%
PFDoS	101.81%	9.51%	98.67%	11.09%	112.36%	10.05%	98.39%	8.68%
HFPO-DA (GenX)	100.16%	3.49%	100.48%	2.40%	96.82%	3.44%	98.92%	2.44%
HFPO-TA	95.40%	11.08%	100.40%	8.29%	83.08%	9.56%	89.25%	9.66%
ADONA	99.93%	5.41%	100.45%	3.20%	103.47%	8.00%	104.47%	4.70%
PFMOPrA	102.80%	7.28%	100.37%	5.16%	99.66%	10.23%	97.27%	7.33%
NFDHA	101.76%	5.13%	104.01%	4.10%	91.13%	16.37%	98.29%	13.98%
PFMOBA	102.75%	3.27%	102.32%	4.22%	99.19%	7.16%	99.54%	6.70%
PFecHS	97.87%	7.56%	99.06%	9.26%	85.79%	7.73%	88.90%	7.21%
3:3FTCA	107.32%	17.58%	103.80%	15.61%	95.91%	17.07%	82.32%	14.93%
5:3FTCA	102.05%	18.16%	101.30%	16.84%	84.82%	22.66%	83.00%	17.48%
7:3FTCA	104.24%	15.89%	107.53%	13.15%	99.27%	16.78%	101.49%	15.63%
PFEESA	102.19%	2.74%	102.64%	3.59%	99.40%	2.93%	99.68%	2.51%
6:2 Cl-PFESA	100.91%	4.47%	97.51%	4.48%	107.54%	4.24%	100.76%	4.20%
8:2 Cl-PFESA	98.85%	11.48%	93.55%	9.93%	122.14%	12.31%	107.85%	9.53%

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Determinand	Groundwater				Surface Water			
	0.01µg/l Spike		0.04µg/l Spike		0.01µg/l Spike		0.04µg/l Spike	
	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD
4:2FTS	101.18%	2.14%	100.32%	1.60%	97.15%	2.81%	100.50%	1.72%
6:2FTS	99.18%	5.43%	100.27%	3.49%	99.91%	5.45%	103.38%	4.06%
8:2FTS	99.48%	2.51%	99.77%	2.31%	99.29%	2.80%	101.30%	2.13%
FBSA	107.74%	17.14%	109.18%	15.35%	106.07%	17.45%	102.21%	8.94%
FHxSA	101.93%	16.35%	106.99%	14.40%	79.09%	16.76%	80.92%	12.88%
FOSA	102.15%	3.62%	102.39%	3.21%	101.24%	3.25%	99.88%	3.40%
MeFOSA	100.08%	7.36%	101.73%	6.02%	113.63%	10.03%	113.32%	8.27%
EtFOSA	100.26%	9.29%	103.01%	6.67%	110.12%	5.31%	112.11%	8.47%
MeFOSE	99.99%	6.96%	100.91%	4.63%	110.60%	5.85%	111.67%	9.54%
EtFOSE	101.62%	9.29%	101.70%	5.46%	112.32%	7.76%	112.10%	7.70%
MeFOSAA	99.75%	9.82%	106.55%	7.13%	113.06%	8.85%	119.82%	9.22%
EtFOSAA	102.84%	8.74%	102.75%	6.02%	100.97%	5.57%	97.56%	4.57%
6:2FTAB	81.94%	13.73%	91.53%	21.55%	80.69%	16.35%	84.02%	15.97%

## Uncertainty of Measurement:

Determinand	Uncertainty of Measurement %
PFBA	10.97
PFPeA	14.89
PFHxA	12.97
PFHpA	16.56
PFOA	13.46
PFNA	15.90
PFDA	20.19
PFUdA	19.96
PFDaA	18.34
PFTriA	19.61
PFTeA	15.20
PFHxDA	11.02
PFODA	24.98
PFBS	18.67
PFPeS	15.67
PFHxS	27.97
PFHpS	17.01
PFOS	12.53
PFNS	21.88
PFDS	29.58
PFUnDS	29.96
PFDoS	28.22
HFPO-DA (GenX)	10.23

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Determinand	Uncertainty of Measurement %
HFPO-TA	32.77
ADONA	16.33
PFMOPrA	17.51
NFDHA	21.12
PFMOBA	14.47
PFecHS	24.38
3:3FTCA	37.45
5:3FTCA	42.37
7:3FTCA	37.56
PFEESA	13.40
6:2 CI-PFESA	18.79
8:2 CI-PFESA	35.39
4:2FTS	8.62
6:2FTS	9.19
8:2FTS	9.22
FBSA	39.73
FHxSA	43.52
FOSA	13.25
MeFOSA	29.53
EtFOSA	26.20
MeFOSE	22.40
EtFOSE	22.67
MeFOSAA	33.41
EtFOSAA	19.98
6:2FTAB	43.39

## References:

- 15.1 Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS  
US EPA Draft Method 1633
- 15.2 Effect of Sample Storage on the Quantitative Determination of 29 PFAS: Observation of Analyte Interconversions during Storage Woudneh, Chandramouli et al  
Environ. Sci. Technol. 2019, 53, 21, 12576-12585