METHOD STATEMENT

Determinand:
Per- and Polyfluoroalkyl Substances (PFAS)

Matrix:
Sample types: treated and raw waters, i.e., waters that are abstracted for potable supply and potable waters.

Principle of Method:
The method is a solid phase extraction (SPE) high performance liquid chromatography tandem mass spectrometry (HPLC-TQ) procedure. The compounds of interest are extracted from a 125 ml water sample by an offline solid phase extraction (SPE) procedure utilising a weak anion exchange (WAX) sorbent. The compounds are eluted from the SPE cartridge with methanolic ammonia, and the elution solvent is concentrated to 0.5 ml. Sample extracts are analysed by liquid chromatography with a triple quadrupole mass spectrometer as detector. Compounds are separated by high performance liquid chromatography and then identified and quantified with mass spectrometric detection (MSD) in selected reaction monitoring (SRM) mode. Quantitation is based on an internal standardisation procedure.

Sampling and Sample Preparation:
Sampling – treated drinking water samples are taken in 125 ml high density polyethylene (PE/HD) bottles, with liner-less screw top caps containing sodium thiosulfate 1.8% w/v (STL036) as sample preservative. Raw water samples are taken in 125 ml PE/HD bottles (STL024) with no sample preservative added. Samples are stored at ≤-20°C on receipt at the laboratory.
Storage - samples should be analysed as soon as possible after collection. When this is not possible samples can be stored under refrigeration at 3±2°C until analysis can begin. Due to the known instability of certain PFAS compounds, particularly perfluorooctane sulphonamide ethanols (FOSEs) and perfluorooctane sulphonamide acetic acids (FOSAAs) in surface water (see References 1 and 2), samples are stored in a freezer at ≤-20°C pending extraction.
Samples should be frozen within 3 days of sampling. Where this is not possible, the maximum permissible storage time of samples prior to analysis when stored under refrigeration at 3±2°C is given in Table 1. This sample stability information can also be used to determine which compounds are within stability at the time the sample is frozen.

Table 1 - Storage time of samples prior to analysis when stored under refrigeration at 3±2°C

Determinand	Treated Drinking Waters		Raw Waters	
	Maximum period of analyte stability prior to any extraction step (days)	Data is quoted from US EPA Method 1633 ["USEPA"] or ALS in-house data ["ALS IHD"]	Maximum period of analyte stability prior to any extraction step (days)	Data is quoted from US EPA Method 1633 ["USEPA"] or ALS in-house data ["ALS IHD"]
PFBA	29	ALS IHD	28	USEPA
PFPeA	29	ALS IHD	28	USEPA
PFHxA	29	ALS IHD	28	USEPA
PFHpA	29	ALS IHD	28	USEPA
PFOA	29	ALS IHD	28	USEPA
PFNA	29	ALS IHD	28	USEPA
PFDA	29	ALS IHD	28	USEPA
PFUnA	29	ALS IHD	28	USEPA
PFDoA	29	ALS IHD	28	USEPA
PFTrDA	29	ALS IHD	28	USEPA
PFTeDA	29	ALS IHD	28	USEPA
PFHxDA	21	ALS IHD	32	ALS IHD
PFODA	21	ALS IHD	32	ALS IHD
PFBS	29	ALS IHD	28	USEPA
PFPeS	29	ALS IHD	28	USEPA
PFHxS	29	ALS IHD	28	USEPA
PFHpS	29	ALS IHD	28	USEPA

Determinand	Treated Drinking Waters		Raw Waters	
	Maximum period of analyte stability prior to any extraction step (days)	Data is quoted from US EPA Method 1633 ["USEPA"] or ALS in-house data ["ALS IHD"]	Maximum period of analyte stability prior to any extraction step (days)	Data is quoted from US EPA Method 1633 ["USEPA"] or ALS in-house data ["ALS IHD"]
PFOS	29	ALS IHD	28	USEPA
PFNS	29	ALS IHD	28	USEPA
PFDS	29	ALS IHD	28	USEPA
PFUnS	29	ALS IHD	7	ALS IHD
PFDoS	29	ALS IHD	28	USEPA
HFPO-DA	29	ALS IHD	28	USEPA
HFPO-TA	29	ALS IHD	32	ALS IHD
DONA	29	ALS IHD	28	USEPA
PFMOPrA	29	ALS IHD	28	USEPA
NFDHA	29	ALS IHD	28	USEPA
PFMOBA	29	ALS IHD	28	USEPA
PFecHS-K	29	ALS IHD	32	ALS IHD
3:3 FTCA	29	ALS IHD	28	USEPA
5:3 FTCA	29	ALS IHD	28	USEPA
7:3 FTCA	29	ALS IHD	28	USEPA
PFEESA	29	ALS IHD	28	USEPA
6:2 Cl-PFESA	29	ALS IHD	28	USEPA
8:2 Cl-PFESA	29	ALS IHD	28	USEPA
4:2 FTS	29	ALS IHD	28	USEPA
6:2 FTS	29	ALS IHD	28	USEPA
8:2 FTS	29	ALS IHD	28	USEPA
FBSA	29	ALS IHD	32	ALS IHD
FHxSA	29	ALS IHD	32	ALS IHD
PFOSA	29	ALS IHD	28	USEPA
MeFOSA	29	ALS IHD	5	ALS IHD
EtFOSA	29	ALS IHD	7	ALS IHD
MeFOSE	29	ALS IHD	3	ALS IHD
EtFOSE	29	ALS IHD	3	ALS IHD
MeFOSAA	29	ALS IHD	3	ALS IHD
EtFOSAA	29	ALS IHD	3	ALS IHD
6:2 FTAB	28	ALS IHD	14	ALS IHD

Once frozen the maximum permissible storage time of samples prior to analysis when stored in a freezer at ≤-20°C is given in Table 2.

Table 2 - Storage time of samples prior to analysis when stored in a freezer at ≤-20°C

Determinand	Treated Drinking Waters		Raw Waters	
	Maximum period of analyte stability prior to any extraction step (days)	Data is quoted from US EPA Method 1633 ["USEPA"] or ALS in-house data ["ALS IHD"]	Maximum period of analyte stability prior to any extraction step (days)	Data is quoted from US EPA Method 1633 ["USEPA"] or ALS in-house data ["ALS IHD"]
PFBA	28	ALS IHD	90	USEPA
PFPeA	28	ALS IHD	90	USEPA
PFHxA	28	ALS IHD	90	USEPA
PFHpA	28	ALS IHD	90	USEPA
PFOA	28	ALS IHD	90	USEPA
PFNA	28	ALS IHD	90	USEPA
PFDA	28	ALS IHD	90	USEPA

Determinand	Treated Drinking Waters		Raw Waters	
	Maximum period of analyte stability prior to any extraction step (days)	Data is quoted from US EPA Method 1633 ["USEPA"] or ALS in-house data ["ALS IHD"]	Maximum period of analyte stability prior to any extraction step (days)	Data is quoted from US EPA Method 1633 ["USEPA"] or ALS in-house data ["ALS IHD"]
PFUnA	28	ALS IHD	90	USEPA
PFDoA	28	ALS IHD	90	USEPA
PFTrDA	28	ALS IHD	90	USEPA
PFTeDA	28	ALS IHD	90	USEPA
PFHxDA	22	ALS IHD	29	ALS IHD
PFODA	22	ALS IHD	29	ALS IHD
PFBS	28	ALS IHD	90	USEPA
PFPeS	28	ALS IHD	90	USEPA
PFHxS	28	ALS IHD	90	USEPA
PFHpS	28	ALS IHD	90	USEPA
PFOS	28	ALS IHD	90	USEPA
PFNS	28	ALS IHD	90	USEPA
PFDS	28	ALS IHD	90	USEPA
PFUnS	28	ALS IHD	90	ALS IHD
PFDoS	28	ALS IHD	90	USEPA
HFPO-DA	28	ALS IHD	90	USEPA
HFPO-TA	28	ALS IHD	29	ALS IHD
DONA	28	ALS IHD	90	USEPA
PFMOPrA	28	ALS IHD	90	USEPA
NFDHA	28	ALS IHD	90	USEPA
PFMOBA	28	ALS IHD	90	USEPA
PFecHS-K	28	ALS IHD	90	ALS IHD
3:3 FTCA	28	ALS IHD	90	USEPA
5:3 FTCA	28	ALS IHD	90	USEPA
7:3 FTCA	28	ALS IHD	90	USEPA
PFEESA	28	ALS IHD	90	USEPA
6:2 Cl-PFESA	28	ALS IHD	90	USEPA
8:2 Cl-PFESA	28	ALS IHD	90	USEPA
4:2 FTS	28	ALS IHD	90	USEPA
6:2 FTS	28	ALS IHD	90	USEPA
8:2 FTS	28	ALS IHD	90	USEPA
FBSA	28	ALS IHD	90	ALS IHD
FHxSA	28	ALS IHD	90	ALS IHD
PFOSA	28	ALS IHD	90	USEPA
MeFOSA	28	ALS IHD	90	USEPA
EtFOSA	28	ALS IHD	90	USEPA
MeFOSE	28	ALS IHD	90	USEPA
EtFOSE	28	ALS IHD	90	USEPA
MeFOSAA	28	ALS IHD	90	USEPA
EtFOSAA	28	ALS IHD	90	USEPA
6:2 FTAB	28	ALS IHD	90	ALS IHD

Interferences

HPLC-MS/MS is an extremely selective technique and interferences should only be encountered very rarely. Any interfering compounds would have to display the identical SRM transition at the same retention time, this is extremely unlikely in potable water samples. However, any compound, which passes through the extraction procedure, and has a similar liquid chromatographic retention time and mass spectrometric properties to the compound of interest, will cause interference. Samples containing high humic or fulvic loading have been demonstrated to not cause significant ion suppression for the compounds.

Method Performance:

Range of Application:

The operational range for each per- and polyfluoroalkyl compound is from the limit of quantification to 25 ng L^{-1}. Samples producing results above this range should be diluted.

Limit of Quantification, Recoveries of Compounds and Uncertainty of measurement:

Determinand	LOQ, ng L^{-1}	UoM	Direct Standards				Elvington Treated	
			Low Standard, 20%		High Standard, 80%		Spike, 10 ng L^{-1}	
			Recovery	RSD	Recovery	RSD	Recovery	RSD
PFBA	1.71	9.922%	95.79%± 3.26%	7.13%	98.94%± 1.14%	2.54%	99.00%± 3.01%	9.26%
PFPeA	1.57	11.648%	99.56%± 2.12%	3.98%	99.63%± 0.96%	1.85%	101.21%± 2.81%	5.49%
PFHxA	0.37	10.906%	97.98%± 2.19%	4.33%	99.43%± 1.25%	2.32%	98.07%± 1.63%	3.59%
PFHpA	0.55	10.401%	98.79%± 1.90%	3.76%	98.99%± 1.05%	2.27%	98.25%± 1.49%	3.16%
PFOA	0.53	12.31%	97.89%± 1.88%	3.57%	98.59%± 1.72%	3.08%	97.57%± 2.34%	4.63%
PFNA	0.50	11.058%	96.32%± 2.30%	4.17%	99.11%± 1.14%	2.45%	98.83%± 1.49%	3.22%
PFDA	0.27	11.3%	96.71%± 2.23%	4.63%	98.85%± 1.21%	2.73%	97.53%± 1.47%	2.81%
PFUnA	0.64	11.553%	96.89%± 1.99%	4.87%	98.81%± 1.85%	3.93%	97.26%± 2.19%	4.02%
PFDoA	1.27	12.019%	96.79%± 3.79%	8.54%	97.86%± 1.65%	3.61%	97.55%± 2.70%	4.46%
PFTrDA	1.26	20.731%	94.75%± 4.73%	7.83%	99.02%± 2.36%	4.59%	97.67%± 3.30%	8.33%
PFTeDA	0.45	11.108%	95.88%± 1.67%	3.43%	98.63%± 1.00%	2.03%	97.86%± 1.43%	2.73%
PFHxDA	0.51	15.474%	95.73%± 1.59%	3.20%	98.92%± 1.05%	2.42%	94.89%± 1.52%	3.21%
PFODA	0.57	26.462%	99.99%± 3.06%	6.79%	100.12%± 2.90%	5.48%	98.19%± 6.43%	16.71%
PFBS	0.36	12.331%	97.08%± 1.30%	4.30%	100.48%± 1.99%	5.22%	98.10%± 1.70%	3.26%
PFPeS	0.47	15.389%	96.03%± 2.14%	5.28%	99.52%± 1.76%	4.07%	96.11%± 2.25%	4.87%
PFHxS	0.48	13.471%	97.33%± 2.10%	4.65%	99.75%± 1.61%	4.12%	97.29%± 1.87%	3.97%
PFHpS	0.50	17.558%	97.85%± 1.41%	4.87%	98.86%± 1.88%	4.01%	94.47%± 2.85%	6.09%
PFOS	0.51	13.213%	96.79%± 1.99%	4.25%	99.38%± 1.81%	3.65%	96.74%± 1.96%	4.30%
PFNS	0.63	17.289%	98.41%± 2.65%	6.10%	101.64%± 2.36%	5.16%	102.80%± 1.99%	4.12%
PFDS	1.06	16.032%	95.41%± 3.77%	9.05%	96.94%± 2.41%	5.62%	101.67%± 4.22%	8.34%
PFUnS	1.40	23.485%	95.66%± 5.53%	10.15%	97.30%± 3.50%	7.06%	109.04%± 6.43%	11.61%
PFDoS	0.85	24.165%	102.31%± 5.13%	11.04%	97.66%± 3.59%	8.05%	107.64%± 7.61%	13.39%

Determinand	LOQ, ng L^{-1}	UoM	Direct Standards				Elvington Treated	
			Low Standard, 20%		High Standard, 80%		Spike, 10 ng L^{-1}	
			Recovery	RSD	Recovery	RSD	Recovery	RSD
HFPO-DA	0.39	14.256%	98.55%± 1.79%	4.65%	99.31%± 1.79%	4.09%	97.81%± 2.52%	5.15%
HFPO-TA	0.57	19.301%	99.02%± 2.36%	5.03%	98.78%± 2.14%	4.70%	98.06%± 2.56%	5.71%
DONA	0.36	12.464%	98.10%± 1.87%	3.85%	98.20%± 1.36%	2.91%	97.64%± 1.72%	3.61%
PFMOPrA	0.32	29.924%	98.11%± 1.56%	3.09%	99.99%± 1.23%	2.44%	84.93%± 1.78%	4.16%
NFDHA	0.47	14.886%	96.89%± 3.14%	6.36%	99.68%± 1.96%	4.09%	98.09%± 2.52%	4.98%
PFMOBA	0.38	15.361%	96.62%± 1.74%	3.94%	98.81%± 1.07%	2.24%	102.71%± 1.96%	3.70%
PFecHS-K	0.42	13.817%	96.94%± 1.90%	4.59%	101.16%± 2.07%	4.87%	95.54%± 2.57%	5.23%
3:3 FTCA	0.66	26.379%	98.66%± 3.03%	6.91%	97.74%± 2.88%	6.61%	96.64%± 4.20%	8.97%
5:3 FTCA	0.65	23.593%	100.43%± 2.54%	5.91%	99.52%± 2.94%	7.25%	91.16%± 2.75%	7.36%
7:3 FTCA	0.64	20.28%	97.70%± 3.43%	7.08%	98.09%± 2.17%	4.63%	93.10%± 2.01%	4.81%
PFEESA	0.27	12.368%	100.25%± 1.76%	3.75%	101.87%± 1.90%	4.80%	99.16%± 1.63%	3.37%
6:2 Cl-PFESA	0.38	13.549%	96.90%± 2.52%	5.61%	100.95%± 2.19%	4.62%	100.30%± 1.14%	2.48%
8:2 Cl-PFESA	1.13	18.063%	94.27%± 4.59%	10.12%	97.18%± 2.90%	6.74%	105.63%± 5.40%	9.00%
4:2 FTS	0.45	13.576%	103.17%± 2.75%	5.39%	100.79%± 1.12%	2.79%	104.04%± 1.98%	3.98%
6:2 FTS	0.49	12.842%	103.62%± 2.28%	4.66%	99.23%± 1.36%	3.25%	101.95%± 1.78%	3.82%
8:2 FTS	1.51	17.427%	107.10%± 2.54%	9.07%	100.53%± 2.88%	6.14%	102.43%± 1.98%	4.65%
FBSA	0.42	23.123%	98.50%± 3.64%	7.10%	97.51%± 2.16%	4.77%	94.00%± 3.24%	6.85%
FHxSA	0.44	21.833%	96.09%± 4.02%	8.47%	95.84%± 3.79%	8.74%	103.16%± 4.35%	8.57%
PFOSA	2.60	12.974%	96.84%± 2.86%	7.00%	97.65%± 1.98%	4.22%	95.58%± 1.50%	2.94%
MeFOSA	1.18	15.705%	96.26%± 1.78%	4.73%	99.47%± 1.59%	3.52%	98.24%± 2.85%	5.26%
EtFOSA	0.91	14.189%	97.62%± 2.81%	6.33%	98.99%± 2.28%	5.01%	98.75%± 1.94%	4.17%
MeFOSE	1.80	14.692%	95.90%± 3.48%	7.82%	99.35%± 1.49%	3.84%	98.56%± 2.59%	4.64%
EtFOSE	1.73	17.958%	99.70%± 4.39%	9.64%	98.02%± 3.14%	6.68%	99.42%± 4.88%	10.99%
MeFOSAA	0.86	12.611%	97.99%± 2.74%	5.74%	99.40%± 1.92%	3.93%	98.12%± 2.07%	3.83%
EtFOSAA	0.85	13.494%	93.91%± 3.17%	9.10%	98.35%± 1.70%	4.36%	96.08%± 1.96%	3.52%
6:2 FTAB	1.93	29.785%	102.53%±	5.52%	104.29%±	7.17%	111.87%±	7.43%

Determinand	LOQ, ng L^{-1}	UoM	Direct Standards				Elvington Treated	
			Low Standard, 20%		High Standard, 80%		Spike, 10 ng L^{-1}	
			Recovery	RSD	Recovery	RSD	Recovery	RSD
			2.36%		3.39%		4.11%	

References:

1. Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS. 4th Draft Method 1633*, July 2023, US EPA, (*Finalized for the Aqueous Matrices: Wastewater, Surface Water, and Groundwater).
https://www.epa.gov/system/files/documents/2022-12/3rdDraftMethod1633December202212-20-22_508
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
3. In-house method, WPC78.