Brazilian Journal of Analytical Chemistry
2024, Volume 11, Issue 43, pp 120-131

SPONSOR REPORT

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Quantitation of per- and polyfluoroalkyl substances (PFAS) in aqueous samples by LC-MS/MS following EPA Draft Method 1633

Kevin J. McHale
Thermo Fisher Scientific, Somerset, NJ

This report was extracted from the Thermo Scientific Application Note 002348

Keywords: EPA Method 1633, per- and polyfluoroalkyl substances (PFAS), environmental contaminants, solid phase extraction, Vanquish Flex Binary UHPLC, TSQ Quantis Plus triple quadrupole mass spectrometer

Goal: To demonstrate the measurement of 40 per- and polyfluoroalkyl substances (PFAS) in 500 mL water samples at or below the method detection limits (MDLs) reported in U.S. EPA Draft Method 1633 by LC-MS/MS on the Thermo Scientific™ TSQ Quantis™ Plus mass spectrometer.

INTRODUCTION

PFAS are per- and polyfluoroalkyl substances. They comprise a hydrophobic chain of C- F bonds and a hydrophilic end group. The chemical nature of the C-F bonds makes these compounds extremely stable. Hence, PFAS have been given the term “forever compounds”. They have been in use for decades in a wide variety of industrial uses and for many everyday consumer products. Because of their ubiquitous nature and chemical stability, PFAS have made their way into all aspects of the environment, including the water and soil and some even in the air. With contact with the environment, PFAS become integrated into plants, animals, and humans. Once in biological organisms, PFAS do not efficiently breakdown. This leads to bioaccumulation of PFAS, which has shown evidence of certain health effects in humans, including possible increased risk of cancer and infertility.[1]

The U.S. EPA has taken a more active approach to monitoring PFAS in the environment in recent years. In March 2023, the EPA proposed the National Primary Drinking Water Regulation (NPDWR) to establish legally enforceable levels of six PFAS in drinking water, including PFOA and PFOS at 4 ng/L.[2] Previously developed methods EPA 537.1 and EPA 533 were established to measure PFAS in drinking water, including the six PFAS designated under the NPDWR. More recently, EPA Method 1633 was developed, in conjunction with the Department of Defense, to measure PFAS in non-potable water, (bio)solids, and tissue samples for the intended use of regulating PFAS via the Clean Water Act (CWA). The third draft of EPA Method 1633 was released in December 2022 following a multi-laboratory validation study in spiked wastewaters.[3]

This application note will present data for measuring 40 PFAS in fortified water samples following the third draft of EPA Method 1633. An MDL study was conducted in reagent water to demonstrate that equivalent or better performance can be attained using the Thermo Scientific™ Vanquish™ Flex Binary UHPLC system and Thermo Scientific™ TSQ™ Quantis Plus mass spectrometer.

EXPERIMENTAL

Consumables

A list of materials used is included in Table A1 in the Appendix.

Sample preparation

High-density polyethylene (HDPE) bottles were thoroughly rinsed with Thermo Scientific™ UHPLC-MS grade methanol and air-dried prior to preparation of all water samples and sample processing solutions. Solid phase extraction (SPE) eluting solution was prepared on the day of sample extractions owing to the volatility of ammonium hydroxide.

PFAS standards were obtained from Wellington Laboratories (Guelph, ON), stored at 4 °C until needed, and used as received.

500 mL water samples (Optima™ LC-MS grade, Fisher Scientific™) were fortified with target PFAS analytes at concentrations consistent with a mid-level calibration point and at concentrations near the method's limit of quantitation for MDL determinations.

Shortly before adding water samples to the conditioned SPE cartridges, 25 µL extracted internal standards (EIS) solution was spiked into each water sample and mixed by inverting bottles numerous times for approximately 30 seconds.

Solid phase extraction (SPE) of water samples was accomplished according to the protocol detailed in Sections 11.2, 12.1, and 12.2 of EPA Draft Method 1633.

Calibration solutions were prepared according to Table 4 of EPA Draft Method 1633. Due to the sensitivity of the TSQ Quantis Plus mass spectrometer, two additional calibration solutions at concentrations equivalent to 25% and 50% of the lowest calibration solution (i.e., CS1) were also used for the LC-MS/MS calibration procedure. The Calibration Verification Standard (CV) used herein was the CS3 standard rather than the suggested CS4.

Liquid chromatography

To prevent interferences from PFAS attributable to the liquid chromatography (LC) system, the Vanquish Flex Binary UHPLC system was modified with the PFAS Upgrade Kit. This kit includes PEEK tubing and a PFAS delay column to shift any residual PFAS in the LC system away from the target PFAS compound injected onto the analytical column. Fresh mobile phase was prepared after every five days of use. The LC method details are shown in Table 1.

Table 1. LC method parameters

Parameter	Value	
Analytical column	Thermo Scientific™ Acclaim™ 120 C18, 2.1 × 50 mm, 2.2 um	
Delay column	Thermo Scientific™ Hypersil GOLD™, 3.0 × 50 mm, 1.9 µm	
Column temperature	40 °C	
Injection volume	5 µL	
Autosampler temperature	20 °C	
Mobile phase	(A) H_2O + 2% ACN + 2 mM ammonium acetate + 0.1% acetic acid (B) ACN + 2% H_2O + 2 mM ammonium acetate + 0.1% acetic acid	
Flow rate	0.4 mL/min	
Gradient	Time (min)	% B
	0.0	10
	1.0	30

Table 1. LC method parameters (continued)

Parameter	Value	
Gradient	Time (min)	% B
	5.0	46
	10.0	76
	10.5	86
	10.9	86
	11.0	10
	13.0	10

Mass spectrometry

All PFAS target analytes, extracted internal standards (EIS), and non-extracted internal standards (NIS) for EPA Method 1633 were detected using timed SRM (t-SRM) on the TSQ Quantis Plus mass spectrometer. Table 2 provides the ion source and TSQ Quantis Plus mass spectrometer detection settings used for data acquisition. The SRM transitions table of measured PFAS is included in Table A2 in the Appendix.

Table 2. TSQ Quantis Plus mass spectrometer parameters

Parameter	Value
Ion source	H-ESI
Polarity	Negative
Spray voltage	-1,000 V
Sheath gas	50 a.u.
Aux gas	12 a.u.
Sweep gas	0.5 a.u.
Ion	225 °C
Vaporizer temperature	300 °C
Q1, Q3 resolution	0.7 FWHM
CID gas	2.5 mTorr argon
SRM cycle time	0.4 s

Data analysis

All LC-MS/MS data were acquired and processed using the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS), version 7.2.

RESULTS AND DISCUSSION

Separation of PFOS and bile acids

The third draft of EPA Method 1633 includes a requirement that certain bile acids, such as taurodeoxycholic

acid (TDCA), taurochenodeoxycholic acid (TCDCA), and tauroursodeoxycholic acid (TUDCA), must be analyzed to ensure that they do not elute within a 1-minute window of PFOS linear and branched isomers, even in aqueous samples. This is because PFOS and TDCA (and its isomers TCDCA and TUDCA) have precursor ions that differ by 0.64 u, which cannot be differentiated with a quadrupole mass filter at unit resolution, and the same product *m/z* 79.96. Hence, if these compounds are not sufficiently separated chromatographically, these bile acids would cause a positive bias in the measurement of PFOS.

The initial LC method employed for EPA Draft Method 1633 used methanol as the organic solvent in the mobile phases, as it is also used in EPA Methods 537.1 and 533. However, during the bile acid check experiments, it was observed that PFOS could not be sufficiently separated from TDCA, TCDCA, and TUDCA (data not shown). When methanol was changed to acetonitrile in the mobile phases, these bile acids shifted to much earlier retention times relative to PFOS. Figure 1 shows TDCA is separated from the branched isomers PFOS by more than 2 minutes using the LC method in Table 1. Furthermore, TCDCA and TUDCA have retention times of 3.2 and 4.1 minutes, respectively, using the same method (data not shown).

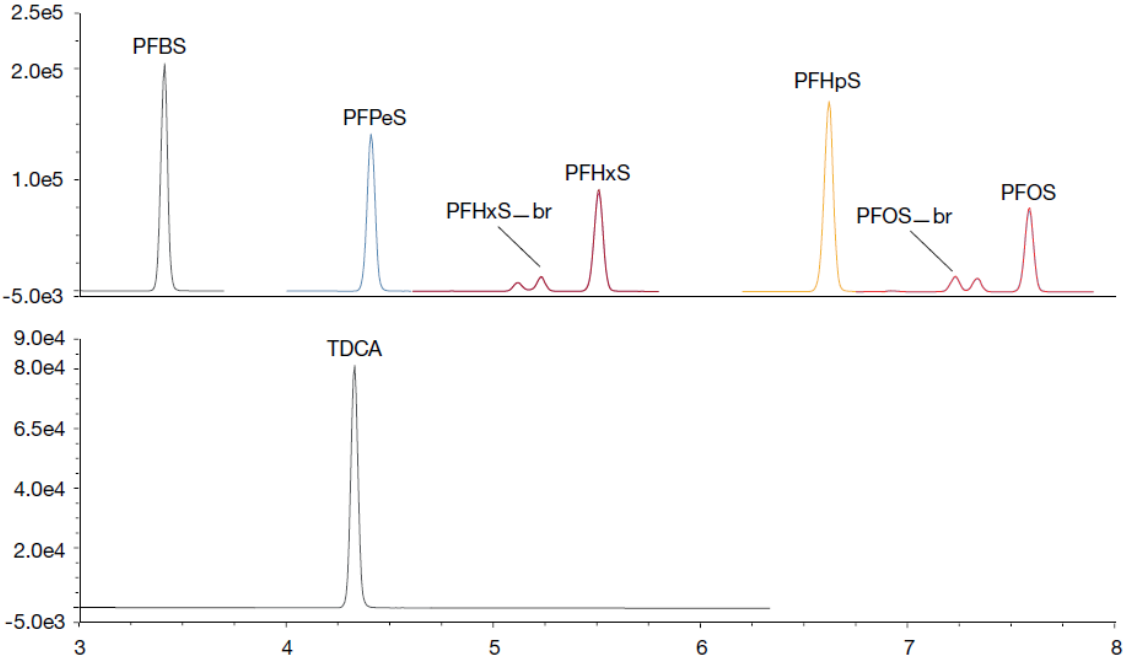

Figure 1. Chromatograms for PFAS separation, including PFOS shown in top chromatogram, compared to the analysis of bile acid TDCA in bottom chromatogram. The LC method uses acetonitrile as the organic mobile phase instead of methanol according to EPA Draft Method 1633 to ensure separation of PFOS and TDCA.

Calibration data

Following the procedure described in Section 10.3 of EPA Draft Method 1633, a total of nine calibration solutions were used for the purpose of LC-MS/MS system calibration on the TSQ Quantis Plus mass spectrometer. Calibration curves for all target PFAS were fit using 1/x (concentration) weighting and not forced through zero. Target PFAS had linear regression fits with the exceptions of 5:3FTCA, 7:3FTCA, and the three x:2FTS compounds, which used quadratic regression curves. $R^2 > 0.997$ was achieved for all compounds. Relative standard errors (RSE) were calculated for all method analytes, accounting for the calibration curve type in the calculations. The vast majority of RSE values were <10%, while six native PFAS compounds had RSEs between 10% and 16%.

Precision and recovery data

Reagent water samples were fortified with native PFAS at concentrations consistent with a mid-level ongoing precision and recovery (OPR) standard. Table A3 in the Appendix shows the native PFAS spiked concentrations, mean percent recovery, and precision results for N=5 fortified water samples. With the exception of 6:2FTS, very good precision and recovery data are obtained.

Extracted internal standards (EIS) had mean percent recoveries of 77–110% and RSDs of 2.3–11.9%, with median values of 106% and 4.2%, respectively. Not surprisingly, the lowest recovery and poorest precision came from the most hydrophobic compounds, D5-N-EtFOSA and D9-N-EtFOSE.

6:2FTS was observed in the extraction method blanks at varying amounts, leading to its biased high percent recovery and poor precision values. Because of these results, an investigation into the potential sources of the contamination was conducted. After a thorough examination of all reagents and materials used during the SPE process, it was discovered that 6:2FTS contamination was from the polypropylene stopcocks used to control the sample flow through the SPE cartridges.

Method detection limits data

To determine the overall quantitative performance, an MDL study was conducted. Table A4 in the Appendix presents MDL values for the native PFAS measured on the TSQ Quantis Plus mass spectrometer and results from EPA Draft Method 1633 in aqueous samples. MDLs on the TSQ Quantis Plus mass spectrometer are equivalent or better for all but two analytes – the aforementioned 6:2FTS and PFBA.

PFBA was fortified in water samples at 4 ng/L in this MDL study. However, PFBA was observed in the extracted method blanks between 0.9 and 1.8 ng/L. The relatively high concentration of PFBA in the method blanks contributed to the higher MDL concentration.

CONCLUSIONS

Following the protocols in 1633, the TSQ Quantis Plus mass spectrometer has demonstrated MDLs at, or in most cases, below those listed in EPA Draft Method 1633 for aqueous samples. For extractions of mid-level fortified samples, results well within the recovery range of 70–130% and RSDs <20% were obtained, with the exception of 6:2FTS.

PFBA, which had slightly higher MDL value than in EPA Draft Method 1633, is notoriously challenging to quantify at or below 1 ng/L owing to cross-contamination issues. While many sources of PFBA contamination have been identified, further investigations are needed.

The unsatisfactory results for sample extractions of 6:2FTS, which was later found to be caused by contamination of the SPE stopcocks, reinforces the need to evaluate all reagents and materials, as well as thoroughly clean all equipment touched by the samples, to achieve the validation criteria in EPA Draft Method 1633. A selection of suggested Thermo Scientific branded materials for use in EPA Method 1633 are listed in Table A1 of the Appendix.

Despite the challenges presented from cross-contamination of PFBA and 6:2FTS, the combination of the Vanquish Flex UHPLC system and the TSQ Quantis Plus mass spectrometer is more than capable to fulfill the requirements of EPA Draft Method 1633 for aqueous samples delivering excellent value and productivity.

REFERENCES

1. Potential health effects of PFAS chemicals | ATSDR (cdc.gov)
2. Proposed Rule, Per- and Polyfluoroalkyl Substances National Primary Drinking Water Regulation, March 2023. https://www.regulations.gov/document/EPA-HQ-OW-2022-0114-0027
3. U.S. EPA 3rd Draft Method 1633, Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS, December 2022. https://www.epa.gov

APPENDIX

Table A1. Suggested materials for EPA Draft Method 1633. All products are from Thermo Fisher Scientific unless specifically noted.

Item	Product	Part number
PFAS delay column	Hypersil GOLD, 3.0 × 50 mm, 1.9 µm	25002-053030
Analytical column	Acclaim 120 C18, 2.1 × 50 mm, 2.2 µm	068981
Guard column	Acclaim 120 C18, 2.1 × 10 mm, 5 µm	069689
Guard column kit	Acclaim guard kit (holder and coupler) V-2	069707
Mobile phase chemicals	Water, UHPLC-MS grade, 1 L	W8-1
	Acetonitrile, UHPLC-MS grade, 1 L	A9561
	Ammonium acetate, LC-MS grade, 50 g	A114-50
	Acetic acid, LC-MS grade, 1 mL ampoules	A113-10X1AMP
Other reagents	Methanol, UHPLC-MS grade, 1 L	A458-1
	Ammonium hydroxide, ACS Plus grade, 500 mL, glass bottle	A669-500
	Formic acid, LC-MS grade, 1 mL ampoules	A117-10X1AMP
	Optima™ LC-MS grade water, 4 L, Fisher Chemical™	W64
Centrifuge tubes	15 mL conical polypropylene centrifuge tubes	05-539-12
Syringes	Luer-slip syringes, PE barrels, PP plungers, 5 mL	S7510-5
Filters	Disposable syringe filters, 25 mm, 0.2 µm, nylon membrane	CH4513-NN
SPE cartridges	Biotage™ EVOLUTE™ PFAS, WAX, 150 mg/6 mL, 30/pk	614-0015-CP
Autosampler vials	Polypropylene, 1.5 mL, screw-top, Level 1	6ESV9-1PP
Autosampler caps	Polypropylene caps, 9 mm, screw-thread	C5000-50

Table A2. Timed SRM on the TSQ Quantis Plus mass spectrometer

Compound	Start time (min)	End time (min)	Precursor (*m/z*)	Product (*m/z*)	Collision energy (V)	RF lens (V)
PFBA	1.1	2.3	213	169	9	72
M3PFBA	1.1	2.3	216	172	9	72
MPFBA	1.1	2.3	217	172	9	72
TDCA	1.1	8	498.29	80	67	250
TDCA	1.1	8	498.29	124	53	250
PFMPA	2	2.7	229	85	10.5	72
PFMPA	2	2.7	229	185	7	72
PFPeA	2.3	3	263	219	8.5	77
M5PFPeA	2.3	3	268	223	8.5	77

Table A2. Timed SRM on the TSQ Quantis Plus mass spectrometer (continued)

Compound	Start time (min)	End time (min)	Precursor (*m/z*)	Product (*m/z*)	Collision energy (V)	RF lens (V)
PFMBA	2.5	3.15	279	85	10.5	80
PFMBA	2.5	3.15	279	235	7.5	80
4:2FTS	2.7	3.35	327	81	28	160
4:2FTS	2.7	3.35	327	307	20	160
M2-4:2FTS	2.7	3.35	329	81	28	160
M2-4:2FTS	2.7	3.35	329	309	20	160
NFDHA	2.9	3.5	295	85	22	63
NFDHA	2.9	3.5	295	201	8	63
PFHxA	2.9	3.6	313	119	19	92
PFHxA	2.9	3.6	313	269	9	92
MPFHxA	2.9	3.6	315	119	19	92
MPFHxA	2.9	3.6	315	270	9	92
M5PFHxA	2.9	3.6	318	120	19	92
M5PFHxA	2.9	3.6	318	273	9	92
PFBS	3	3.7	298.94	80	32	190
PFBS	3	3.7	298.94	99	29	190
M3PFBS	3	3.7	302	80	32	190
M3PFBS	3	3.7	302	99	29	190
HFPO-DA	3.2	3.9	285	169	7	80
HFPO-DA	3.2	3.9	285	185	17	80
13C3-HFPO-DA	3.2	3.9	287	169	7	80
13C3-HFPO-DA	3.2	3.9	287	185	17	80
PFEESA	3.4	4.1	314.95	83	19	135
PFEESA	3.4	4.1	314.95	135	22	135
PFHpA	3.7	4.4	363	169	17	102
PFHpA	3.7	4.4	363	319	9.5	102
M4PFHpA	3.7	4.4	367	322	9.5	102
3:3FTCA	3.9	4.8	241	117	32	82
3:3FTCA	3.9	4.8	241	177	7	82
PFPeS	4	4.7	348.94	80	35	200

Table A2. Timed SRM on the TSQ Quantis Plus mass spectrometer (continued)

Compound	Start time (min)	End time (min)	Precursor (*m/z*)	Product (*m/z*)	Collision energy (V)	RF lens (V)
PFPeS	4	4.7	348.94	99	32	200
ADONA	4	4.8	377	85	22	94
ADONA	4	4.8	377	251	10	94
6:2FTS	4.2	5	427	81	30	195
6:2FTS	4.2	5	427	407	22.5	195
M2-6:2FTS	4.2	5	429	81	30	195
M2-6:2FTS	4.2	5	429	409	22.5	195
PFOA	4.5	5.4	413	169	17	114
PFOA	4.5	5.4	413	369	10	114
PFHxS	4.7	5.8	398.94	80	38	220
PFHxS	4.7	5.8	398.94	99	34	220
M4PFOA	4.7	5.4	417	172	17	114
M8PFOA	4.7	5.4	421	376	10	114
M3PFHxS	5.1	5.8	402	80	38	220
M3PFHxS	5.1	5.8	402	99	34	220
MPFHxS	5.1	5.8	403	84	38	220
PFNA	5.55	6.35	463	219	17	122
PFNA	5.55	6.35	463	419	10.5	122
MPFNA	5.55	6.35	468	423	10.5	122
M9PFNA	5.55	6.35	472	427	10.5	122
PFHpS	5.9	6.8	448.93	80	40	240
PFHpS	5.9	6.8	448.93	99	37	240
8:2FTS	6.1	6.9	527	81	33	280
8:2FTS	6.1	6.9	527	507	26	280
M2-8:2FTS	6.2	6.9	529	81	33	220
M2-8:2FTS	6.2	6.9	529	509	26	220
PFOS	6.3	7.8	498.93	80	46	270
PFOS	6.3	7.8	498.93	99	40	270
5:3FTCA	6.6	7.5	341	217	25	102
5:3FTCA	6.6	7.5	341	237	13	102

Table A2. Timed SRM on the TSQ Quantis Plus mass spectrometer (continued)

Compound	Start time (min)	End time (min)	Precursor (*m/z*)	Product (*m/z*)	Collision energy (V)	RF lens (V)
PFDA	6.6	7.4	512.96	269	17	138
PFDA	6.6	7.4	512.96	469	11	138
MPFDA	6.6	7.4	515	470	11	138
M6PFDA	6.6	7.4	519	474	11	138
MPFOS	7	7.8	503	80	46	270
MPFOS	7	7.8	503	99	40	270
M8PFOS	7	7.8	507	80	46	270
M8PFOS	7	7.8	507	99	40	270
PFUdA	7.4	8.2	562.96	269	18	151
PFUdA	7.4	8.2	562.96	518.97	11	151
M7PFUdA	7.4	8.2	570	525	11	151
9Cl-PF3ONS	7.6	8.5	530.9	350.95	25	175
9Cl-PF3ONS_37Cl	7.6	8.5	532.9	352.95	25	175
PFNS	7.7	8.7	548.93	80	49	275
PFNS	7.7	8.7	548.93	99	43	275
N-MeFOSAA	7.8	9.2	570	419	18	220
N-MeFOSAA	7.8	9.2	570	483	16	220
N-MeFOSAA	7.8	9.2	570	512	19	220
PFDoA	8.2	9	612.95	169	25	163
PFDoA	8.2	9	612.95	569	11.5	163
MPFDoA	8.2	9	615	570	10.5	163
d3-N-MeFOSAA	8.3	9.2	573	419	18	220
N-EtFOSAA	8.4	10.1	584	419	20	200
N-EtFOSAA	8.4	10.1	584	483	18	200
N-EtFOSAA	8.4	10.1	584	526	20	200
PFDS	8.5	9.4	598.92	80	50	280
PFDS	8.5	9.4	598.92	99	46	280
7:3FTCA	8.6	9.5	441	317	20	129
7:3FTCA	8.6	9.5	441	337	11	129
d5-N-EtFOSAA	8.9	10.1	589	419	20	235

Table A2. Timed SRM on the TSQ Quantis Plus mass spectrometer (continued)

Compound	Start time (min)	End time (min)	Precursor (*m/z*)	Product (*m/z*)	Collision energy (V)	RF lens (V)
PFTrDA	8.9	9.7	662.95	169	26	174
PFTrDA	8.9	9.7	662.95	618.96	12	174
FOSA	9.1	9.9	497.95	78	30	240
FOSA	9.1	9.9	497.95	169	27	240
FOSA	9.1	9.9	497.95	478	23	240
M8FOSA	9.2	9.9	506	78	30	240
11Cl-PF2OUdS	9.2	10	630.9	450.94	27	163
11Cl-PF2OUdS_37Cl	9.2	10	632.9	452.94	27	163
PFTeDA	9.6	10.5	712.95	169	28	188
PFTeDA	9.6	10.5	712.95	668.96	12.5	188
M2PFTeDA	9.6	10.5	715	670	12.5	188
PFDoS	9.8	10.8	698.9	80	53	280
PFDoS	9.8	10.8	698.9	99	48	280
NMeFOSE	9.9	10.9	616	59	16	133
D7-NMeFOSE	9.9	10.9	623	59	16	133
NMeFOSA	10.2	11.1	512	169	26	222
NMeFOSA	10.2	11.1	512	219	24	222
D3-NMeFOSA	10.3	11.1	515	219	24	222
NEtFOSE	10.5	11.4	630	59	16	137
D9-NEtFOSE	10.5	11.4	639	59	16	137
NEtFOSA	10.8	11.8	526	169	26	227
NEtFOSA	10.8	11.8	526	219	23	227
D5-NEtFOSA	10.8	11.8	531	219	23	227

Table A3. Precision and recovery of native PFAS from fortified water samples

Analyte	Spiked conc. (ng/L)	Mean %Recovery (N=5)	%RSD (N=5)	Analyte	Spiked conc. (ng/L)	Mean %Recovery (N=5)	%RSD (N=5)
PFBA	50.0	91.2%	3.4	6:2 FTS	50.0	232.9%*	52.4
PFPeA	25.0	92.4%	2.8	8:2 FTS	50.0	89.5%	1.4
PFHxA	12.5	91.3%	3.7	PFOSA	12.5	85.9%	3.9
PFHpA	12.5	88.5%	3.1	N-MeFOSA	12.5	85.6%	4.2
PFOA	12.5	89.8%	3.3	N-EtFOSA	12.5	83.2%	3.8

Table A3. Precision and recovery of native PFAS from fortified water samples (continued)

Analyte	Spiked conc. (ng/L)	Mean %Recovery (N=5)	%RSD (N=5)	Analyte	Spiked conc. (ng/L)	Mean %Recovery (N=5)	%RSD (N=5)
PFNA	12.5	87.8%	4.7	N-MeFOSAA_branched	3.0	94.4%	10.5
PFDA	12.5	89.0%	1.9	N-MeFOSAA	9.5	90.5%	3.2
PFUdA	12.5	87.0%	3.5	N-EtFOSAA_branched	2.8	87.7%	5.2
PFDoA	12.5	93.3%	3.3	N-EtFOSAA	9.7	87.0%	2.4
PFTrDA	12.5	88.0%	3.2	N-MeFOSE	125.0	90.5%	3.7
PFTeDA	12.5	93.6%	2.5	N-EtFOSE	125.0	92.6%	3.1
PFBS	12.5	86.8%	5.5	HFPO-DA	50.0	94.1%	2.0
PFPeS	12.5	92.7%	3.4	ADONA	50.0	102.5%	4.5
PFHxS_branched	2.4	86.6%	5.4	PFEESA	25.0	93.4%	3.3
PFHxS	10.1	86.9%	5.7	PFMPA	25.0	84.3%	3.4
PFHpS	12.5	82.7%	1.6	PFMBA	25.0	89.9%	3.1
PFOS_branched	2.6	85.8%	4.6	NFDHA	25.0	97.3%	1.7
PFOS	9.9	87.8%	2.3	9Cl-PF3ONS	50.0	97.1%	1.5
PFNS	12.5	90.0%	5.8	11Cl-PF3OUdS	50.0	110.5%	6.1
PFDS	12.5	92.4%	1.9	3:3FTCA	62.5	86.2%	5.3
PFDoS	12.5	116.8%	6.6	5:3FTCA	312.5	71.8%	2.8
4:2 FTS	50.0	97.6%	4.1	7:3FTCA	312.5	101.7%	2.4

*Biased high recovery from cross-contamination. See text for details.

Table A4. MDLs of native PFAS in fortified water samples

Analyte	TSQ Quantis Plus mass spectrometer MDL (ng/L, N=7)	EPA 1633 Draft 3 aqueous MDL (ng/L, pooled)	Analyte	TSQ Quantis Plus mass spectrometer MDL (ng/L, N=7)	EPA 1633 Draft 3 aqueous MDL (ng/L, pooled)
PFBA	1.92	0.80	6:2 FTS	135.26**	2.52
PFPeA	0.20	0.53	8:2 FTS	2.27	2.58
PFHxA	0.21	0.48	PFOSA	0.11	0.32
PFHpA	0.05	0.39	N-MeFOSA	0.36	0.41
PFOA	0.15	0.55	N-EtFOSA	0.36	0.43
PFNA	0.12	0.46	N-MeFOSAA	0.27	1.04
PFDA	0.15	0.53	N-EtFOSAA	0.23	0.80
PFUdA	0.15	0.44	N-MeFOSE	1.66	3.93
PFDoA	0.16	0.37	N-EtFOSE	1.53	5.13
PFTrDA	0.08	0.46	HFPO-DA	0.28	1.54
PFTeDA	0.14	0.51	ADONA	0.14	1.47
PFBS	0.13	0.37	PFEESA	0.21	0.79
PFPeS	0.07	0.53	PFMPA	0.23	0.54
PFHxS	0.13	0.56	PFMBA	0.19	0.53
PFHpS	0.21	0.87	NFDHA	0.21	1.92

Table A4. MDLs of native PFAS in fortified water samples (continued)

Analyte	TSQ Quantis Plus mass spectrometer MDL (ng/L, N=7)	EPA 1633 Draft 3 aqueous MDL (ng/L, pooled)	Analyte	TSQ Quantis Plus mass spectrometer MDL (ng/L, N=7)	EPA 1633 Draft 3 aqueous MDL (ng/L, pooled)
PFOS	0.19	0.64	9Cl-PF3ONS	0.17	1.42
PFNS	0.37	0.49	11Cl-PF3OUdS	0.43	1.78
PFDS	0.36	0.90	3:3FTCA	1.30	2.54
PFDoS	0.55	0.64	5:3FTCA	3.07	9.92
4:2 FTS	0.45	1.74	7:3FTCA	3.83	9.14

**Biased high MDL from cross-contamination. See text for details.

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