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Application News

SSI-LCMS-098

Liquid Chromatography Mass Spectrometry

Analysis of Perfluorinated Alkyl Acids Specified in EPA M537 and Beyond Using the Triple Quad LCMS-8045

■ Summary

Analysis of the perfluorinated alkyl acids listed in EPA Method 537 along with fluorotelomeric alcohols and perfluorinated sulfonates were extracted using SPE and analyzed on the LCMS-8045. Minimum Detection Limits (MDL) ranged from 0.69 to 3.25 ppt. Extraction recoveries were greater than 80% for all compounds, with surrogate recoveries within 10% of the true value.

■ Background

There has been an increasing awareness of the presence of perfluoroalkyl sulfonates (PFASs) and perfluoroalkyl carboxylic acids (PFCAs) in water. EPA Method 537 is a LC/MS/MS method for analyzing perfluorinated alkyl acids (PFAAs) in drinking water. While many labs analyze only the compounds listed in the method, additional compounds may be added to the method in order to increase its scope. Fluorotelomer sulfonates can act as precursors to compounds listed in EPA Method 537, including PFOA and PFASs.

■ Method

MRM transitions were optimized using Flow Injection Analysis (FIA) for all compounds. Compounds were separated, including PFHxS and PFOS isomers (Figures 1 through 3), using a Restek Raptor ARC-18 150 x 2.1 mm (Part No. 9314A62) column using 20 mM ammonium acetate for mobile phase A and methanol for Mobile Phase B. Standards were purchased from Wellington Laboratories.

■ SPE Method

Extractions were performed using Biotage® ISOLUTE® 101 polystyrene-divinylbenze (SDVB) cartridges (Part No. 101-0050-C) as outlined in EPA 537. A vacuum manifold with a high-volume sampling kit outfitted with PEEK tubing was used to reduce potential contamination. Each cartridge was conditioned first with methanol, followed by LCMS grade water as outlined in EPA 537. Each water sample (250 mL) was fortified with surrogates and passed through the cartridge. Compounds were eluted from the solid phase with 8 mL of methanol and evaporated to dryness using nitrogen. Extracted samples were reconstituted to a final volume of 1 mL in 96:4 Methanol:H_2O with internal standards added.

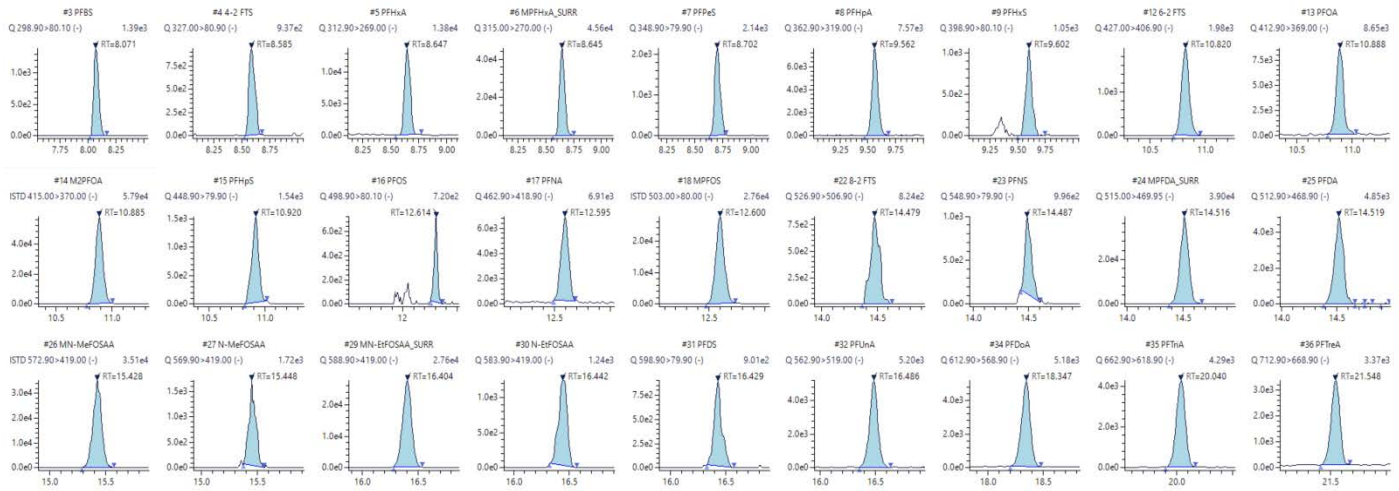

Figure 1: Chromatograms for all compounds at the LLOQ (1.25 ppb).
Isomers of PFOS and PFHxS were detected and chromatographically separated

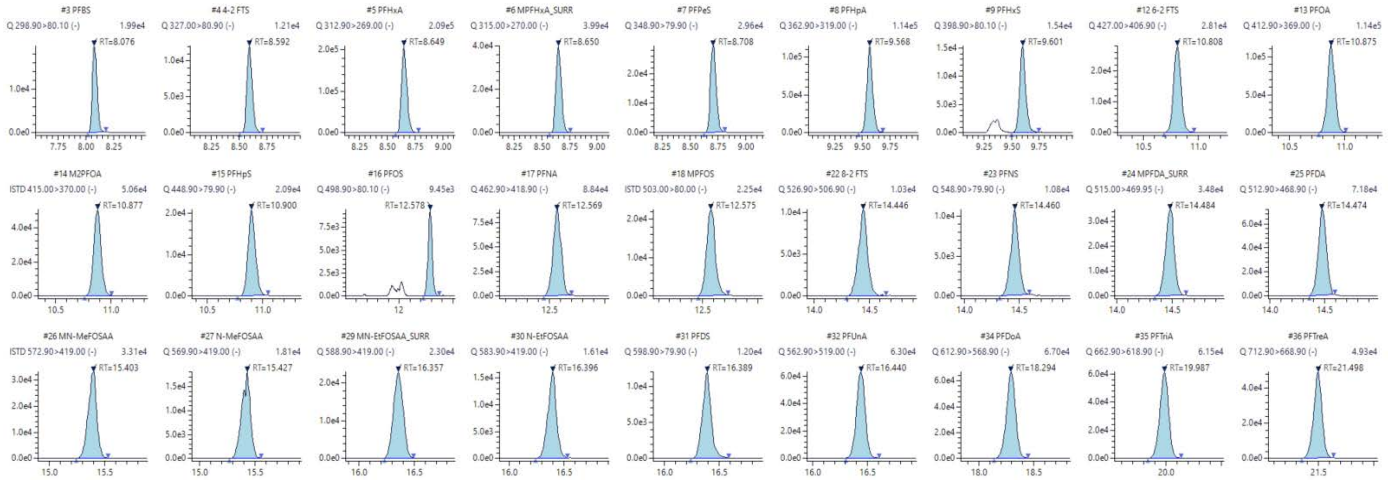

Figure 2: Chromatograms for all compounds at the Mid-Level Calibrator (20 ppb). Isomers of PFOS and PFHxS were detected and chromatographically separated

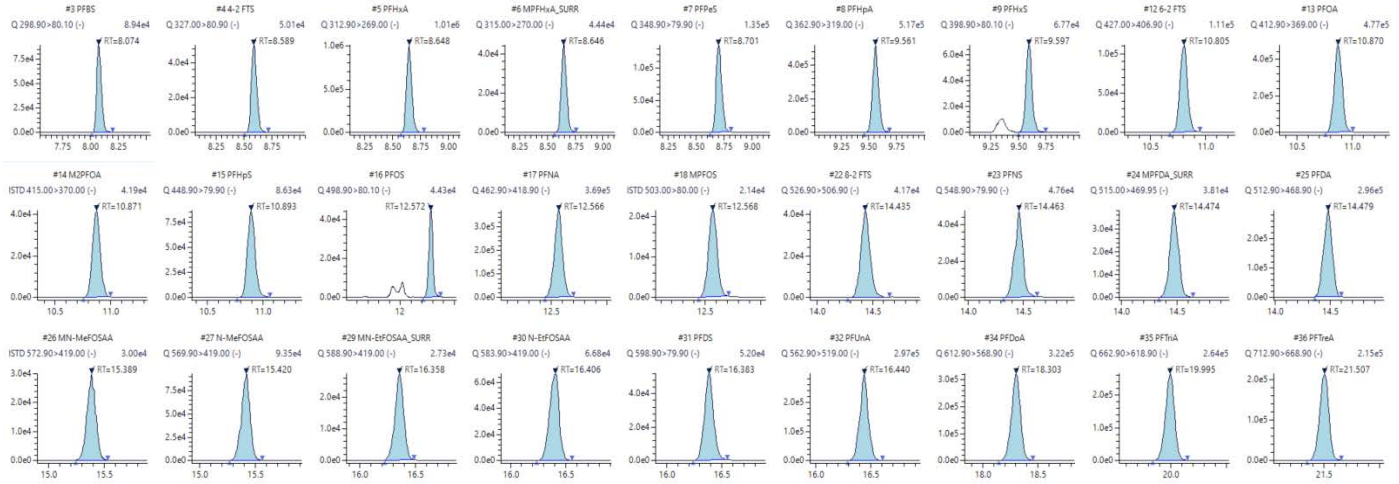

Figure 3: Chromatograms for all compounds at the ULOQ (100 ppb).
Isomers of PFOS and PFHxS were detected and chromatographically separated

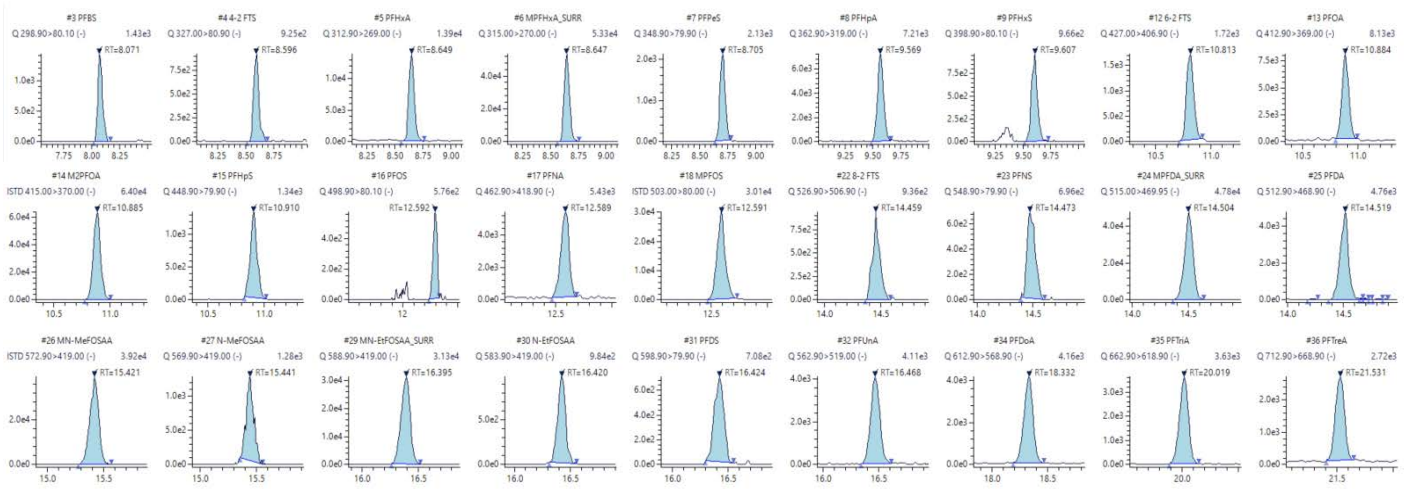

Figure 4: Chromatograms for all compounds for the MDL Study (5 ppt).
Isomers of PFOS and PFHxS were detected and chromatographically separated

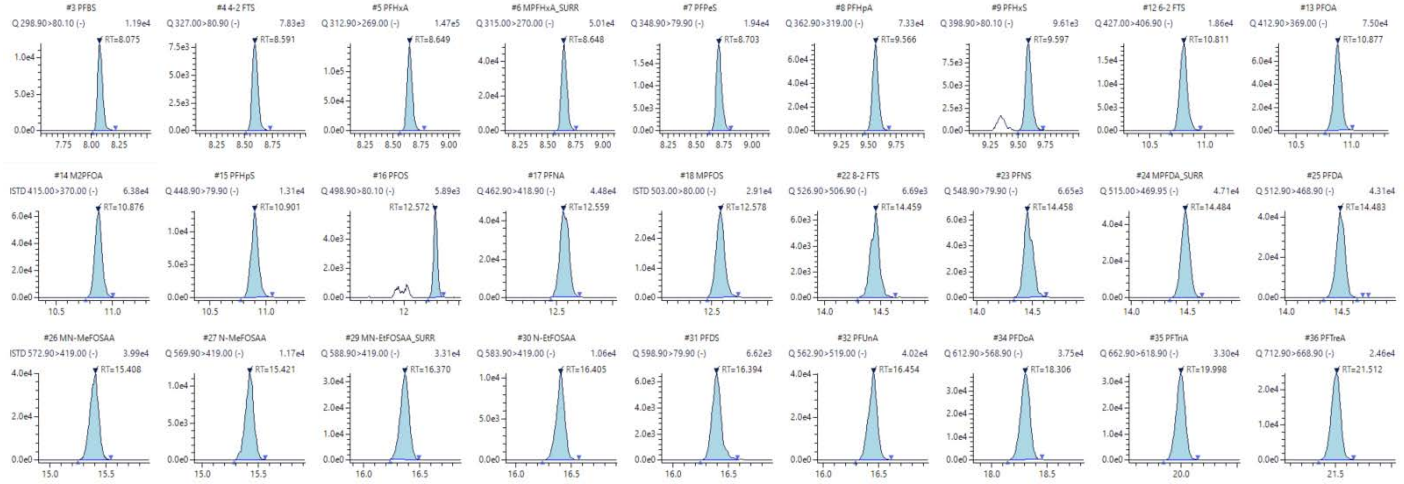

Figure 5: Chromatograms for all compounds for the Precision and Accuracy Study (60 ppt).
Isomers of PFOS and PFHxS were detected and chromatographically separated

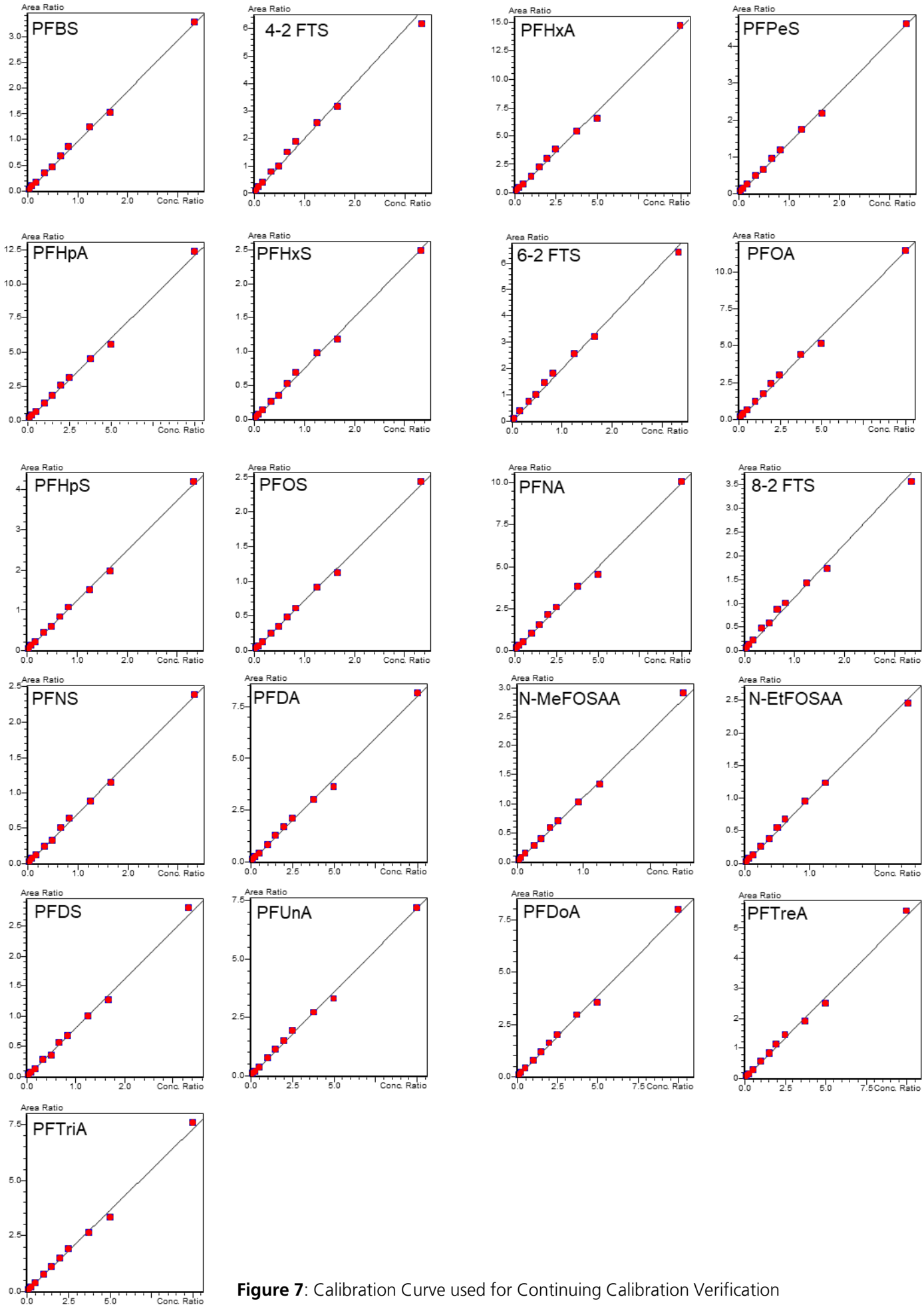

Figure 7: Calibration Curve used for Continuing Calibration Verification

■ Results and Discussion

Continuing Calibration Verification

A series of 10 calibration levels ranging from 1.25 ppb to 100 ppb were injected four times over the course of two weeks. The initial calibration curve was used to quantitate the subsequent injections. Table 1 lists the averaged concentration as well as the %RSD. All calibration curves met the criteria listed in EPA 537. Additional compounds not listed in EPA 537 are italicized. Example chromatograms from this study are shown in Figures 1 through 3.

Table 1: Results from Initial Calibration and repeat injections

Compound	Retention Time	R^2	Low (20 ppb)		Mid (50 ppb)		High (100 ppb)	
			Conc	%RSD	Conc	%RSD	Conc	%RSD
PFBS	8.046	0.9977	20.68	1.97	45.85	2.53	102.91	1.87
4-2FTS	8.558	0.9928	22.21	2.48	45.16	6.96	94.19	1.09
PFHxA	8.614	0.9968	21.02	3.54	48.19	6.48	102.05	3.45
PFPeS	8.666	0.9985	20.89	2.00	46.17	1.87	99.64	1.11
PFHpA	9.512	0.9974	20.96	4.92	46.44	4.67	101.33	2.33
PFHxS	9.558	0.9968	20.64	2.68	46.04	4.84	104.38	2.70
6-2 FTS	10.77	0.9968	20.96	4.15	43.81	4.34	94.52	2.28
PFOA	10.84	0.9967	21.04	4.63	47.23	7.39	103.01	2.63
PFHpS	10.859	0.9982	20.61	4.29	44.98	7.56	103.75	5.86
PFOS	12.55	0.9986	19.99	6.13	43.74	7.42	102.64	12.29
PFNA	12.545	0.9975	21.11	10.35	46.75	1.60	100.12	3.36
8-2 FTS	14.436	0.994	22.67	13.73	45.39	12.80	94.29	12.62
PFNS	14.469	0.9978	21.07	2.38	45.84	5.58	100.05	4.74
PFDA	14.486	0.9969	20.83	2.62	47.20	3.04	98.24	1.67
N-MeFOSAA	15.423	0.9979	21.04	3.28	46.68	1.09	100.38	2.68
N-EtFOSAA	16.411	0.998	21.66	3.98	47.79	2.17	101.97	4.93
PFDS	16.397	0.997	20.89	3.57	45.39	11.22	102.82	5.33
PFUnA	16.449	0.9973	20.87	4.15	47.57	4.22	100.21	5.99
PFDoA	18.339	0.9975	20.60	3.45	47.91	3.40	103.32	5.65
PFTriA	20.035	0.9967	20.37	5.03	45.30	5.08	100.55	4.82
PFTreA	21.549	0.9966	21.05	5.39	47.36	4.05	102.69	2.92

Method Detection Limit

A Method Detection Limit (MDL) study was conducted by spiking 250 mL samples at 5 ng/L (5 ppt). These samples were then extracted and concentrated to a final volume of 1 mL in 96:4 MeOH:H_2O. Nine samples were extracted over the course of three days. Table 2 lists the averaged concentration as well as the Accuracy, %RSD, and the Method Detection Limit. The Method Detection Limit was calculated as described in 40 CFR Part 136 Appendix B. Additional compounds not listed in EPA 537 are italicized. Example chromatograms are shown in Figure 4

Table 2: Method Detection Limit (MDL) results.

Compound	Spiked Conc (ppt)	Calculated Conc (ppt)	Accuracy	%RSD	MDL
PFBS	5	4.17	83.31	12.19	1.47
4-2FTS	5	5.22	104.45	14.09	2.13
PFHxA	5	4.07	81.44	9.95	1.17
PFPeS	5	4.06	81.16	12.84	1.51
PFHpA	5	4.18	83.64	8.72	1.06
PFHxS	5	4.25	84.95	5.61	0.69
6-2 FTS	5	4.59	91.88	17.06	2.27
PFOA	5	4.59	91.83	11.94	1.59
PFHpS	5	3.99	79.74	8.92	1.03
PFOS	5	4.03	80.65	14.94	1.74
PFNA	5	3.99	79.73	7.13	0.82
8-2 FTS	5	5.02	100.41	22.38	3.25
PFNS	5	4.04	80.78	9.05	2.06
PFDA	5	4.13	82.61	8.11	0.97
N-MeFOSAA	5	3.87	77.50	15.14	1.70
N-EtFOSAA	5	3.82	76.49	10.75	1.19
PFDS	5	4.12	82.34	18.04	2.15
PFUnA	5	4.10	81.98	12.22	1.45
PFDoA	5	3.97	79.41	13.98	1.61
PFTriA	5	3.92	78.41	12.55	1.43
PFTreA	5	3.97	79.38	15.30	1.76

Precision and Accuracy

The precision and accuracy study was carried out by spiking LCMS grade water at 60 ppt and extracted seven times each. Table 3 lists the results of this study. All recoveries were within 20 percent of the true value, exceeding the criteria listed in EPA 537.

Additional compounds not listed in EPA 537 are italicized. Example chromatograms are shown in Figure 5

Table 3: Precision and Accuracy Study Results

Compound	Extract 1	Extract 2	Extract 3	Extract 4	Extract 5	Extract 6	Extract 7	Average	Percent Recovery	%RSD
PFBS	56.51	53.06	54.00	62.97	47.78	42.11	50.85	52.47	87.4	12.6
4-2FTS	57.18	64.03	53.27	58.52	46.92	43.49	55.36	54.11	90.2	12.9
PFHxA	56.22	52.76	52.34	61.03	46.62	42.27	52.80	52.01	86.7	11.8
PFPeS	64.33	53.80	56.44	63.02	47.02	43.18	52.42	54.31	90.5	14.3
PFHpA	62.71	57.86	51.39	59.75	42.22	41.87	52.44	52.61	87.7	15.6
PFHxS	64.20	54.20	52.08	60.50	47.16	43.88	52.84	53.55	89.3	13.2
6-2 FTS	69.30	58.81	57.66	56.75	44.84	47.45	49.37	54.88	91.5	15.3
PFOA	61.39	49.06	49.13	62.86	46.19	43.49	50.81	51.85	86.4	14.3
PFHpS	63.59	56.78	52.94	59.57	49.45	42.77	51.64	53.82	89.7	12.8
PFOS	63.93	55.54	56.96	59.89	42.73	40.21	52.39	53.09	88.5	16.5
PFNA	62.92	52.69	48.53	58.59	44.04	39.20	53.49	51.35	85.6	15.9
8-2 FTS	61.41	58.87	57.68	56.63	36.93	43.16	44.83	51.36	85.6	18.5
PFNS	67.17	54.84	53.66	58.26	46.52	42.96	51.95	53.62	89.4	14.7
PFDA	59.59	51.56	50.29	60.47	45.73	42.59	53.15	51.91	86.5	12.7
N-MeFOSAA	60.48	56.23	59.16	56.22	52.97	38.88	44.63	52.65	87.8	15.2
N-EtFOSAA	63.56	59.29	57.93	59.58	50.20	40.35	47.10	54.00	90.0	15.4
PFDS	58.38	59.38	50.25	54.26	42.70	37.82	58.55	51.62	86.0	16.5
PFUnA	55.83	50.89	51.21	56.52	50.66	40.11	52.99	51.17	85.3	10.6
PFDoA	57.20	53.99	54.28	57.77	47.48	36.54	52.75	51.43	85.7	14.4
PFTriA	55.42	50.69	48.72	56.65	45.61	36.63	49.87	49.08	81.8	13.6
PFTreA	54.28	51.17	49.84	54.57	49.46	34.95	50.11	49.20	82.0	13.5

Surrogate Recovery

All extracted samples were spiked with 10 ng of MPFxA, 10 ng of MPFDA, and 40 ng of MNEt-FOSAA giving a sample concentration of 40 ppt for MPFxA and MPFDA and 160 ppt for MNEt-FOSAA.

The calculated recoveries are shown in Table 4 using a Mean Response Factor. All recoveries were within +/- 10 percent, well exceeding the requirements of section 9.3.5 of EPA 537.

Table 4: Surrogate Recovery Results

Compound	Extract 1	Extract 2	Extract 3	Extract 4	Extract 5	Extract 6	Extract 7	Average	Percent Recovery	%RSD
MPFxA	44.16	42.51	40.33	52.78	38.95	33.90	45.57	42.60	106.5	13.9
MPFDA	47.88	44.26	44.68	51.56	41.80	35.31	40.65	43.73	109.3	11.9
MNEt-FOSAA	191.14	188.34	182.79	206.44	157.42	138.83	157.02	174.57	109.1	13.7

■ Summary and Conclusion

The Shimadzu LCMS-8045 and Biotage® ISOLUTE 101 cartridges exceed the performance criteria specified by EPA 537. Method Detection limits ranging from 0.69 to 3.25 ppt were obtained with recoveries of at least 80% for all compounds.

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Shimadzu Corporation
www.shimadzu.com/an/

SHIMADZU SCIENTIFIC INSTRUMENTS, INC.
Applications Laboratory
7102 Riverwood Drive, Columbia, MD 21045
Phone: 800-477-1227 Fax: 410-381-1222
URL http://www.ssi.shimadzu.com

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