PO-CON1827E

SHIMADZU
Excellence in Science

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

ASMS 2018

Gerard Byrne[1]; Evelyn Wang[1]; Katie Pryor[1]; Christopher Gilles[1]; Brahm Prakash[1]; Tairo Ogura[1]; William Lipps[2]
[1]Shimadzu Scientific Instruments, Columbia, MD
[2]Eurofins Eaton Analytical LLC, Monrovia, CA

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

Novel Aspects

The scope of EPA Method 537 has been expanded to include 7 additional perfluorinated alkyl acids.

Introduction

There has been an increasing awareness of the presence of perfluoroalkyl sulfonates (PFOS) and perfluoroalkyl carboxylic acids (PFCAs) in water. Although perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are the most studied polyfluoroalkyl substances (PFASs), perfluoroalkyl and polyfluoroalkyl substances with chain lengths varying from C2-C14 have also been detected in various sample matrices. The continued use of these compounds presents a long-term challenge to scientist, industry leaders, and public health officials worldwide. This presentation describes a highly sensitive Solid Phase Extraction (SPE) – Liquid Chromatography - Tandem Mass Spectrometry (LC-MS/MS) Method for the determination of twenty-four specific polyfluorinated chemical (PFCs), fourteen of which are listed in EPA M537 in drinking waters.

Methods

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) 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.

Calibration

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 calculated concentration as well as the %RSD. All calibration curves met the criteria listed in EPA 537. Compounds added to improve method performance are italicized.

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

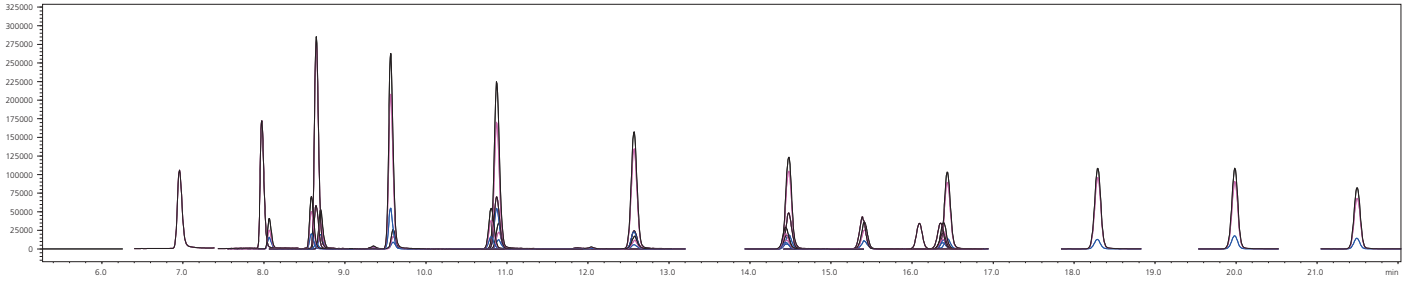

Figure 1: TIC from a low-level calibrator (20 ppb)

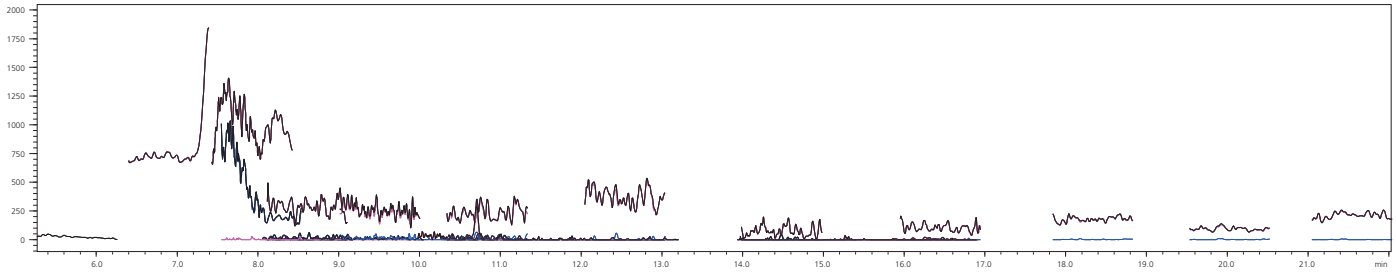

Figure 2: TIC from a method blank

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

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

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

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

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

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

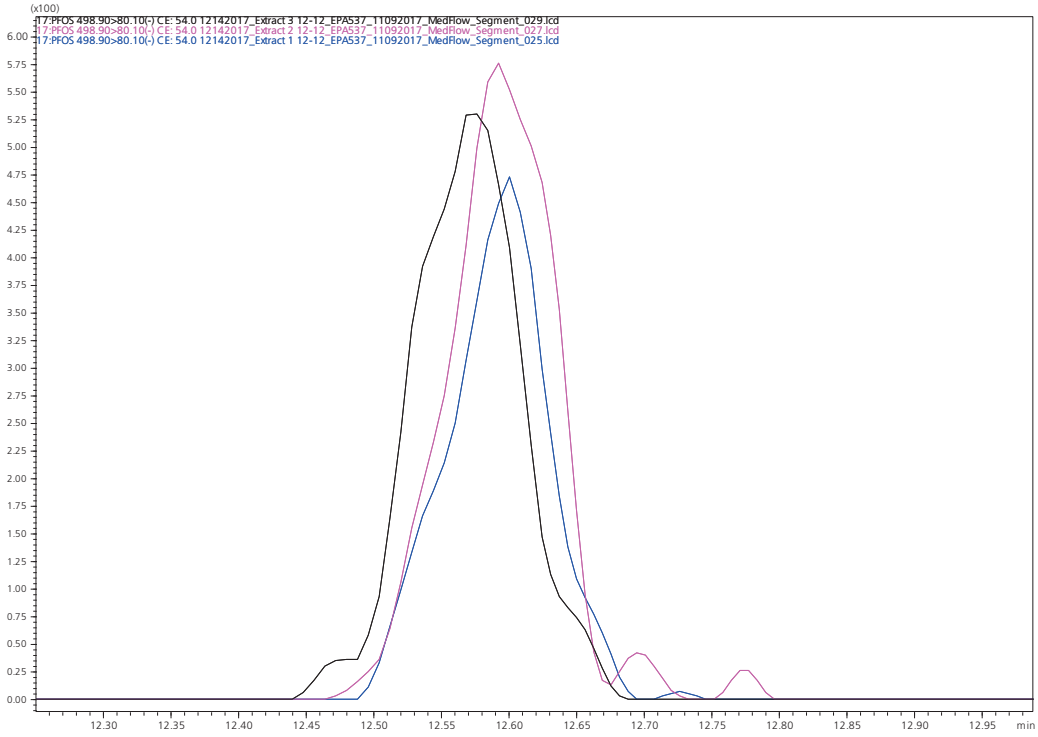

Figure 3: Overlaid Chromatograms for PFOS from the Method Detection Limit Study

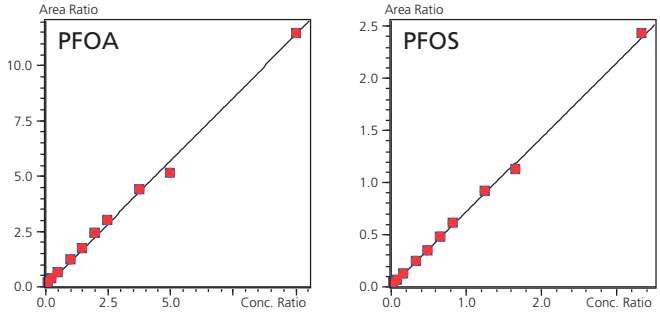

Figure 4: Calibration Curves for PFOA and PFOS ranging from 1.25 ppb to 100 ppb

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

Results and Discussion

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, as described in 40 CFR Part 136 Appendix B. The results from this study are outlined in Table 2. Compounds added to improve method performance are italicized.
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. Compounds that were added to improve method performance are italicized.
All extracted saples 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 there requirements of section 9.3.5 of EPA 537.

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.

Acknowledgements

Shimadzu Scientific Instruments would like to thank Biotage for providing the cartridges used to generate this data

References

(1) EPA Method 537 rev1.1, *Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)* (U.S. Environmental Protection Agency, Washington, D.C., Sept. 2009).
(2) ASTM D7979-16, *Standard Test Method for Determination of Perfluorinated Compounds*

For research purposes only. Not for use in diagnostic procedures.

First Edition: June, 2018

SHIMADZU

Shimadzu Corporation
www.shimadzu.com/an/