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Application News

SSI-LCMS-102

Liquid Chromatography Mass Spectrometry

Analysis of Per- and Polyfluoroalkyl Substances (PFAS) Specified in EPA M537.1 Using the Triple Quadrupole LCMS™-8045

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■ Abstract

The EPA recently updated Method 537 to 537.1 to incorporate the replacement PFAS introduced into the market after PFOA and PFOS were phased out in the US market. This application news demonstrates that analysis for all analytes listed in EPA 537.1[1] can be performed on the LCMS-8045, meeting the Quality Assurance and Quality Control criteria specified in the method. Recoveries were greater than 80% for all compounds, with surrogate recoveries within 10% of the true value. Method Detection Limits (MDL) were below 2 ppt for all the target analytes.

■ Background

Per- and Polyfluorinated Alkyl Substances (PFAS) are a group of anthropogenic chemicals widely used in consumer products (e.g. food packaging materials and non-stick coatings) and industrial applications (firefighting foams, polymers/plastics manufacturing). Their unique properties, such as being highly stable and resistant to degradation[2], together with their ubiquitous use, have resulted in the accumulation of PFAS in the environment.

EPA Method 537 was originally published in November of 2009 and focused on 20 PFAS (14 targets, 3 surrogates, 3 internal standards). Since then, a change in PFAS manufacturing practices led to PFOA and PFOS being phased out in the United States[3].

The EPA published EPA Method 537.1 in November of 2018, incorporating the replacement PFAS recently quantified in drinking water: GenX (or HFPO-DA), ADONA, 11Cl-PF3OUdS, and 9Cl-PF3ONS. This method allows laboratories to assess occurrence of these new chemicals together with the 14 original targets in drinking water[4].

This application news summarizes the performance of the Shimadzu LCMS-8045 for all analytes listed in EPA Method 537.1. Results demonstrate that the instrument's performance exceeds the requirements outlined in the method. Most importantly, results confirm that laboratories currently analyzing samples by method EPA 537 (published in Shimadzu Application News No. C184) can easily update their workflow to implement EPA method 537.1 in their instrument while maintaining the instrument's performance.

Keywords: Per- and Polyfluorinated Alkyl Substances, PFAS, Perfluorinated Compounds, PFCs, Drinking Water, PFOA, PFOS, Persistent Organic Pollutants, POPs, GenX, Triple Quad Reference original app note/news

EPA Method 537.1 analyzes 25 PFAS compounds including 4 surrogates and 3 internal standards. Target compounds and their respective acronyms, surrogate compounds, internal standards, and their chemical classes are listed in Table 1. For the remainder of this application news, refer to the acronyms in Table 1.

Table 1: Target compound list and acronyms

Acronym	Compound	Class
HFPO-DA	Hexafluoropropylene oxide dimer acid	PFECA
PFHxA	Perfluoro-n-hexanoic acid	PFCA
PFBS	Potassium perfluoro-1-butanesulfonate	PFAS
PFHpA	Perfluoro-n-heptanoic acid	PFCA
PFOA	Perfluoro-n-octanoic acid	PFCA
PFHxS	Sodium perfluoro-1-hexanesulfonate	PFAS
PFNA	Perfluoro-n-nonanoic acid	PFCA
PFHpS	Sodium perfluoro-1-hexanesulfonate	PFAS
N-MeFOSAA	N-methylperfluoro-1-octanesulfonamidoacetic acid	FOSAA
PFDA	Perfluoro-n-decanoic acid	PFCA
N-EtFOSAA	N-ethylperfluoro-1-octanesulfonamidoacetic acid	FOSAA
PFOS	Sodium perfluoro-1-octanesulfonate	PFAS
PFUdA	Perfluoro-n-undecanoic acid	PFCA
PFDoA	Perfluoro-n-dodecanoic acid	PFCA
PFDS	Sodium perfluoro-1-decanesulfonate	PFAS
PFTrDA	Perfluoro-n-tridecanoic acid	PFCA
11Cl-PF3OUdS	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	PFES
9Cl-PF3ONS	9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid	PFES
ADONA	P4,8-dioxa-3H-perfluorononanoic acid	PFPE
Internal Standards		
13C2-PFOA		IS1
13C4-PFOS		IS2
D3-NMeFOSAA		IS3
Surrogates		
13C2-PFHxA		Surr1
13C2-PFDA		Surr2
D5-NEtFOSAA		Surr3
13C3-HFPO-DA		Surr4

PFECA - Perfluoroalkyl Ether Carboxylic Acids
PFCA - Perfluorinated Carboxylic Acid
PFAS - Per- and Polyfluoroalkyl Substances
FOSAA – Perfluoroalkane Sulfonamido Substances
PFES - Perfluoroelastomers
PFPE - Perfluoropolyethers

■ Method

This application news describes and demonstrates the use and performance of Shimadzu UFMS™ for the analysis of 25 PFAS (18 targets, 4 surrogates, and 3 internal standards) in drinking water. Standards were purchased from Wellington Laboratories.

The Shimadzu LCMS-8045, a triple quadrupole mass spectrometer, was used in this study. MRM transitions were optimized using Flow Injection Analysis (FiA) for all compounds. Source parameters were optimized to reduce in-source fragmentation for GenX. No compounds suffered a loss in signal intensity because of the re-optimized conditions for GenX.

PFAS may be present in sampling containers and other consumables employed during the sample preparation and analysis steps. To minimize the contribution of PFAS background contamination, a Shim-pack™ XR-ODS 50 x 3.0 mm column was used as a delay column (Part No. 228-41606-92). This column is situated before the autosampler and causes a delay in the elution of PFAS present in the background, allowing for their separation from the target analytes in the samples. Mobile Phase A consisted of 20 mM ammonium acetate and Mobile Phase B consisted of LC-MS grade methanol with no additives. Compounds, including PFHxS and PFOS isomers, were separated using a Shim-pack Velox™, 2.1 mm ID × 150 mm, 2.7 µm particle size (Shimadzu Part No. 227-32009-04).

Figures 1 and 2 compare the chromatograms for all PFAS in the original EPA Method 537 as well as the updated EPA Method 537.1.

A detailed description of the LC/MS/MS parameters is included in Tables 2 and 3.

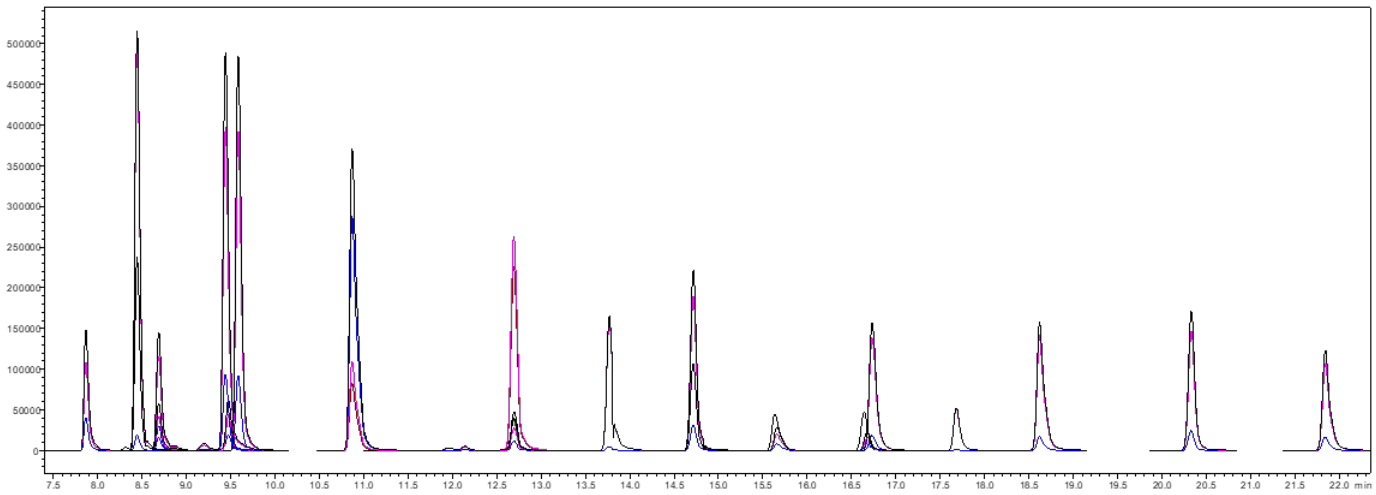

Figure 1: MRM (Pink and Blue) and TIC (black) chromatograms of all PFAS in EPA 537.1 at 80 ppt sample concentration

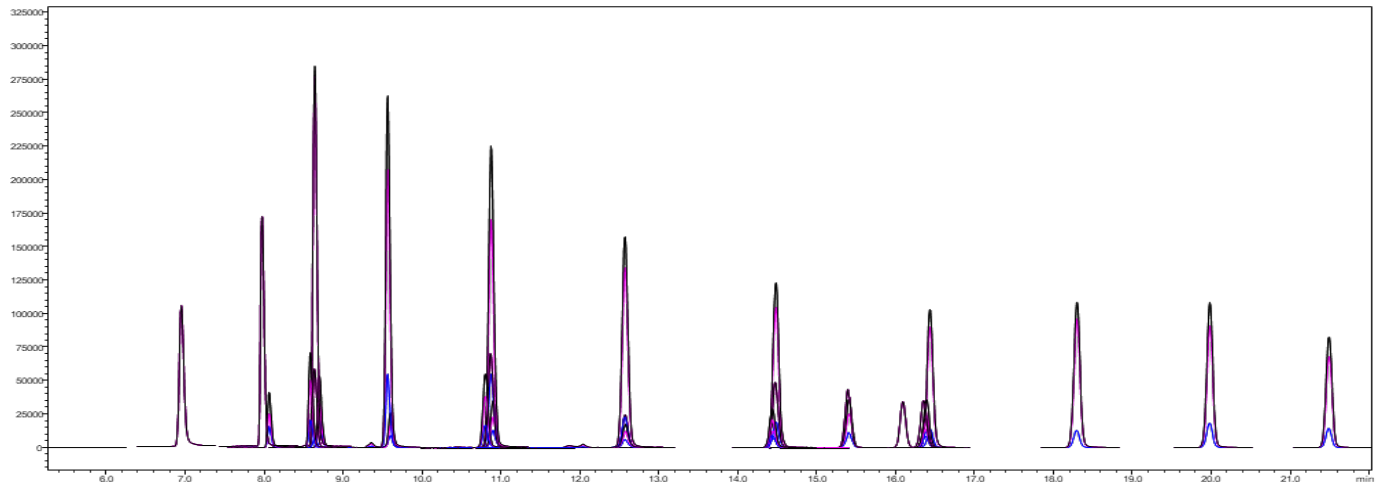

Figure 2: MRM (Pink and Blue) and TIC (black) chromatograms of all PFAS in EPA 537 at 80 ppt sample concentration

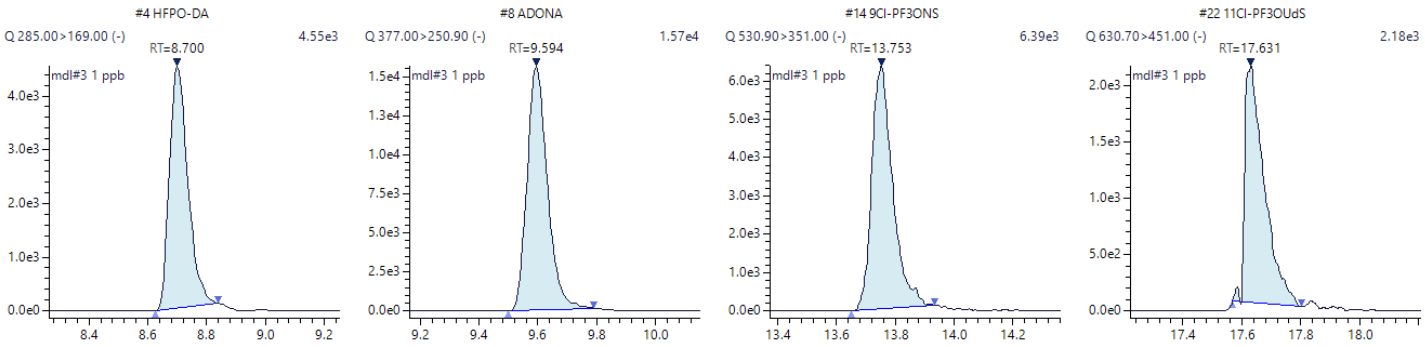

Figure 3: Chromatograms for all new compounds in EPA 537.1 at a representative MDL study

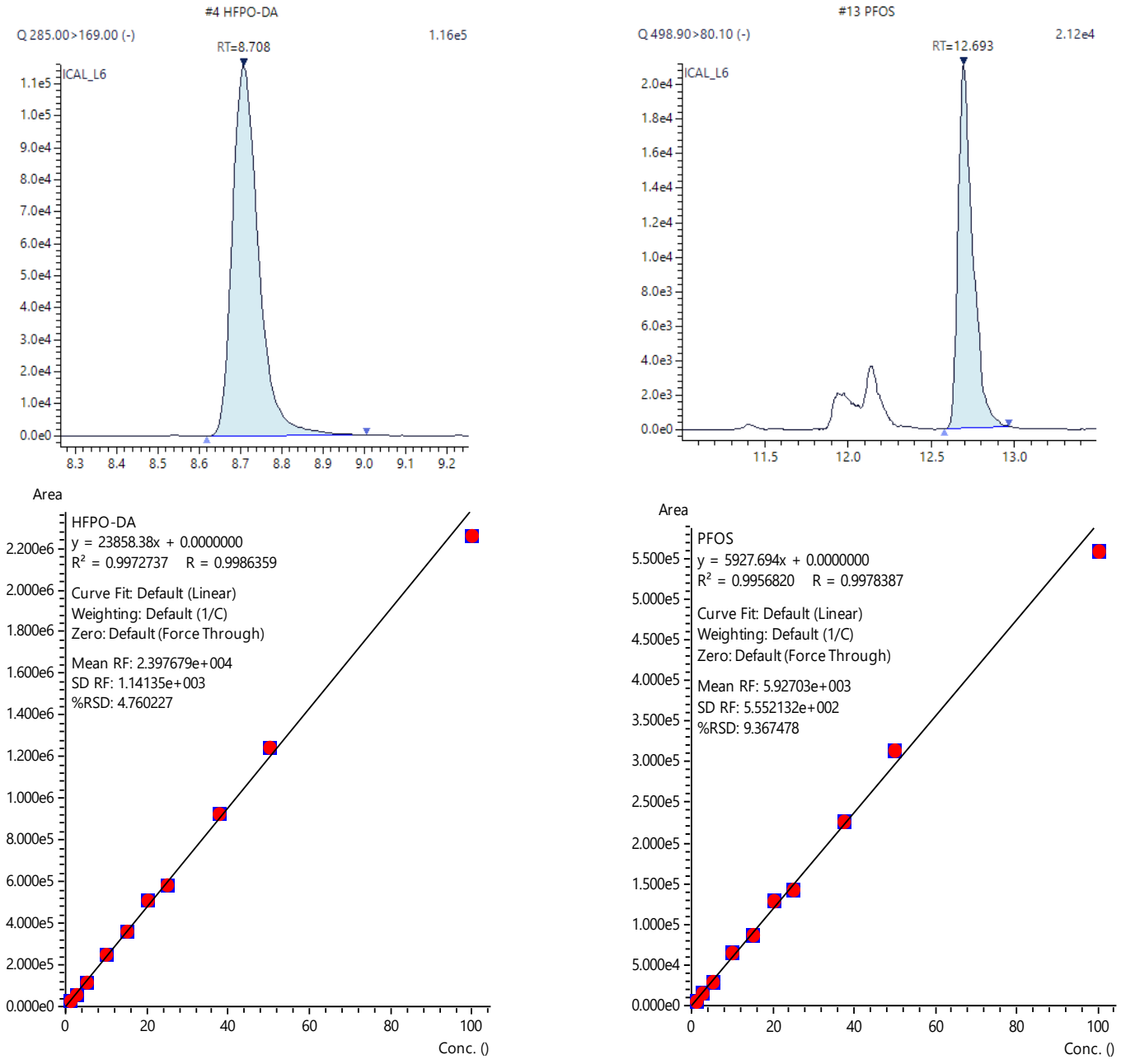

Figure 4: MRM chromatogram (for 80 ppt sample concentration) and calibration curve for HFPO-DA and PFOS using LCMS-8045

■ Results and Discussion

Calibration Data

A series of 10 calibration levels ranging from 1.25 ppb to 100 ppb with an injection volume of 5 uL was used in this study. These concentrations were used to reflect the 250-fold sample concentration required in EPA Method 537.1 (250 ml of sample are extracted and concentrated down to 1 mL for injection in the LC/MS/MS).

The initial calibration curve was used to quantitate the subsequent injections. Table 4 lists representative concentrations and percent recovery for all targets in EPA Method 537.1.

Table 2: LC System and Parameters

LC System	Nexera™-X2 UHPLC System
Analytical Column	Shim-pack Velox, 2.1mm ID × 150mm, 2.7 µm, Part No. 227-32009-04
Solvent Delay Column	Shim-pack XR-ODS 50mm x 2mm x 2.2µm, Part No. 228-41605-93
Column Temp.	40 °C
Injection Volume	5 µL
Mobile Phase	A: 20 mM Ammonium Acetate B: Methanol
Flow Rate	0.25 mL/min
Run Time	35 minutes

Table 3: LC-MS Acquisition Parameters

MS Instrument	LCMS-8045
Interface	Electrospray Ionization (ESI)
Interface Temp.	100 °C
Desolvation Line Temp.	100 °C
Heat Block Temp.	200 °C
Heating Gas Flow	15 L/min
Drying Gas Flow	5 L/min
Nebulizing Gas Flow	3 L/min
Total MRMs	48

Table 4: Calculated concentrations for the low, mid, and high level standards for all targets in EPA Method 537.1

Compound	Retention Time	R^2	Low (80 ppt)		Mid (200 ppt)		High (400 ppt)	
			Concentration	%Recovery	Concentration	%Recovery	Concentration	%Recovery
PFBS	7.883	0.99328	86.8	108	217	108	384	96
PFHxA	8.462	0.99632	84.0	105	210	105	379	94.7
HFPO-DA	8.704	0.99727	85.2	107	210	105	380	94.9
PFHpA	9.451	0.99459	88.8	111	212	106	368	92.1
PFHxS	9.487	0.99419	84.8	106	212	106	369	92.2
ADONA	9.593	0.99770	84.4	106	211	106	383	95.8
PFOA	10.885	0.99611	84.4	106	213	106	374	93.6
PFNA	12.678	0.99633	86.0	108	210	105	375	93.7
PFOS	12.681	0.99568	87.2	109	212	106	378	94.4
9Cl-PF3ONS	13.743	0.99833	83.6	105	210	105	386	96.5
PFDA	14.678	0.99718	85.2	107	212	106	381	95.3
N-MeFOSAA	15.610	0.99724	82.8	104	214	107	382	95.4
N-EtFOSAA	16.618	0.99557	85.6	107	212	106	376	93.9
PFUnA	16.677	0.99736	81.6	102	212	106	382	95.4
11Cl-PF3OUdS	17.635	0.99810	82.0	102	212	106	388	96.9
PFDoA	18.590	0.99653	83.6	105	214	107	376	94.1
PFTriA	20.309	0.99644	85.2	107	211	106	376	94.0
PFTreA	21.835	0.99753	85.2	107	210	105	382	95.4

Method Detection Limit

A Method Detection Limit (MDL) study was conducted by spiking standards at 4 ppt. The Method Detection Limit was calculated as described in 40 CFR Part 136 Appendix B. The MDL for all targets listed in EPA Method 537.1 ranged from 0.48 ppt to 1.64 ppt. All compounds showed %RSD of less than 20% with 8 injections.

Table 5 lists the average calculated sample concentration as well as the Accuracy, %RSD, and the Method Detection Limit.

Table 5: Method Detection Limit (MDL) results

Compound	Spiked Concentration (ppt)	Calculated Concentration (ppt)	Accuracy	%RSD (n=8)	MDL (ppt)
PFBS	4	3.84	96.0	4.4	0.484
PFHxA	4	3.70	92.5	7.3	0.787
HFPO-DA	4	3.55	88.8	8.6	0.881
PFHpA	4	3.87	96.8	6.2	0.693
PFHxS	4	3.74	93.5	5.7	0.615
ADONA	4	3.72	93.0	5.4	0.585
PFOA	4	3.71	92.8	5.5	0.595
PFNA	4	3.79	94.8	5.2	0.566
PFOS	4	3.76	94.0	11.1	1.213
9Cl-PF3ONS	4	3.63	90.8	7.9	0.825
PFDA	4	3.67	91.8	5.7	0.602
N-MeFOSAA	4	3.55	88.8	15.9	1.637
N-EtFOSAA	4	3.81	95.3	7.3	0.808
PFUnA	4	3.56	89.0	10.2	1.052
11Cl-PF3OUdS	4	3.41	85.2	12.7	1.255
PFDoA	4	3.73	93.3	5.4	0.584
PFTriA	4	3.74	93.5	5.7	0.618
PFTreA	4	3.67	91.8	5.7	0.601

Precision and Accuracy Study

A precision and accuracy study was performed to assess the long-term performance of the instrument. Eight replicates of a 40 ppt and 80 ppt sample concentration were injected. The percent recovery for all compounds was within ±15% for both concentrations. All QC requirements for EPA Method 537.1 were met. These requirements include %RSD of less than 20% and peak asymmetry factors for PFBS and PFHxA (first two compounds eluting in the method) between 0.8 and 1.5 (calculated for a mid-level calibration standard).

Table 6 shows the results for the precision and accuracy study.

Table 6: Precision and Accuracy Study Results at 40 ppt sample concentration

Compound	Fortified Concentration	Average Concentration	Percent Recovery	%RSD	Fortified Concentration	Average Concentration	Percent Recovery	%RSD
PFBS	40	43.7	109	3.9	80	87.7	110	5.1
PFHxA	40	43.5	109	4.2	80	85.9	107	5.0
HFPO-DA	40	39.6	99	4.8	80	86.5	108	5.0
PFHpA	40	44.7	112	4.7	80	88.6	111	6.2
PFHxS	40	43.9	110	18.5	80	87.0	109	4.9
ADONA	40	40.6	101	4.2	80	88.6	111	7.4
PFOA	40	42.4	106	4.7	80	84.6	106	5.7
PFNA	40	44.2	110	5.5	80	88.3	110	5.4
PFOS	40	44.6	111	5.5	80	90.0	113	8.3
9Cl-PF3ONS	40	41.1	103	5.0	80	82.7	103	7.4
PFDA	40	42.5	106	3.9	80	84.2	105	5.6
N-MeFOSAA	40	44.1	110	5.7	80	87.0	109	7.7
N-EtFOSAA	40	42.7	107	6.4	80	84.2	105	7.5
PFUnA	40	43.0	108	5.2	80	85.7	107	5.8
11Cl-PF3OUdS	40	41.7	104	4.9	80	82.8	103	10.2
PFDoA	40	43.6	109	4.9	80	85.5	107	5.4
PFTriA	40	42.3	106	5.9	80	85.0	106	5.1
PFTreA	40	42.7	107	3.8	80	84.8	106	5.9

■ Summary and Conclusions

The Shimadzu LCMS-8045 exceeds the performance criteria specified by EPA Method 537.1 for all specified compounds. Method detection limits ranging from 0.48 to 1.64 ppt were obtained with recoveries of at least 80% for all compounds. The Shimadzu LCMS-8045 achieves rapid, reliable and highly sensitive quantitation of PFAS in drinking water by method 537.1. The LCMS-8045 can easily be upgraded to a LCMS-8050 or a LCMS-8060 for improved method detection limits. A 5 uL injection volume was used in contrast to the 10 uL injection described in EPA Method 537.1, making the method more robust and reducing long-term cost of ownership.

■ References

1. US EPA. Method 537.1, Detections of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS). Version 1.0, November 2018 https://www.epa.gov/water-research/epa-drinking-water-research-methods
2. Environmental Science and Technology. "Polyfluorinated Compounds: Past, Present, and Future" http://www.greensciencepolicy.org/wp-content/uploads/2014/10/Lindstrom-Strynar-and-Libelo-2011.pdf
3. US EPA. Basic Information about Per- and Polyfluoroalkyl Substances (PFAS). https://www.epa.gov/pfas/basic-information-about-and-polyfluoroalkyl-substances-pfass
4. US EPA. Drinking Water Health Advisories for PFOA and PFOS. https://www.epa.gov/ground-water-and-drinking-water/drinking-water-health-advisories-pfoa-and-pfos

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