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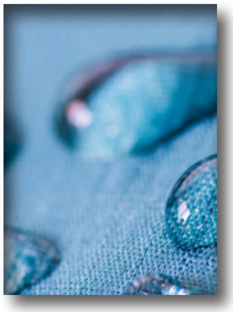
PFAS Analysis: Application Notebook


Solutions for

PFAS Analysis

Application Notebook

Per- and polyfluoroalkyl substances (PFAS) are currently of great public health and environmental concern. Because PFAS are ubiquitous and commonly used in materials routinely employed for chemical analysis, laboratories are in need of streamlined protocols to minimize background contamination from these chemicals and quickly generate accurate data. This notebook provides a number of examples showcasing the use of ultra fast LC-MS/MS for the analysis of PFAS according to multiple methods.

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WHITE PAPER

Ultra-fast LC-MS/MS Analysis of PFAS in Environmental Samples

There is increasing concern about the persistence and effects of Per- and Polyfluorinated Alkyl Substances (PFAS) in the environment. This white paper summarizes the state-of-the-art analytical methods for monitoring PFAS and demonstrates the use, speed and performance of Shimadzu Ultra-fast Mass Spectrometry (UFMS) for PFAS analysis in environmental waters. The described method consists of a simple methanol dilution, followed by a direct injection to LC-MS/MS. The Triple Quadrupole MS, LCMS-8060, was used in this study to effectively separate and quantify 49 PFAS, with all compounds eluting within 13 minutes. The stability of PFAS and the effect of solvents, vials and vortex on the recovery were studied. Method detection limit of 0.6 – 5.4 ng/L, recovery of 84 – 113% and calibration range of 5 – 200 ng/L were achieved for 94% of the PFAS compounds studied, including all the compounds listed in ASTM D7979. With high scan speed and short dwell time, the Shimadzu LCMS-8060 demonstrates to be fast, sensitive, and robust for PFAS analysis in environmental waters.

Keywords:
Per- and Polyfluorinated Alkyl Substances, PFAS, Perfluorinated compounds, PFCs, Environmental, Surface Water, Non-Potable Water, Groundwater, Wastewater, PFOA, PFOS, Persistent Organic Pollutants, POPs

Introduction

Increasing Need to Monitor PFAS

Per- and Polyfluorinated Alkyl Substances (PFAS) are a group of anthropogenic chemicals that are highly stable and resistant to degradation. These chemicals are manufactured and used in many consumer and industrial products (e.g. food packaging materials, fire-fighting foams and textiles) due to their heat-resistant and oil- and water-repellent properties. As these PFAS compounds are persistent, toxic and potentially harmful to humans [1], [2], [3], the leaching and presence of PFAS in our environment have raised serious concerns globally.

Exposure to PFAS through drinking water and various environmental sources has been studied and determined [4], [5], [6], [7]. In May 2016, the United States Environmental Protection Agency (US EPA) issued a health advisory of 70 parts per trillion (ppt) for combined PFOA and PFOS in drinking water [8]. Several states in the US (e.g. California, Minnesota, New Jersey, Colorado, Massachusetts, Vermont and Michigan) have followed the advisory and established similar or even stricter guideline levels for PFAS, which can go to 13-14 ppt [9], [10] [11]. Recent research has suggested that occurrence of PFAS compounds in tap water is markedly different by region [12] and around the world [13]. Growing evidence highlights the obvious need to continuously monitor the water sources as well as drinking water to keep PFAS exposure under control.

Water and Environmental Analysis

LCMS

https://www.shimadzu.com/an

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Validated Methods for Analyzing PFAS

Liquid chromatography coupled to triple-quadrupole mass spectrometry (LC-MS/MS) is widely used for the determination of PFAS in water matrices because of its high sensitivity and specificity. Given the social importance of PFAS monitoring, standardized analytical methods for LC-MS/MS need to be developed and validated to ensure that all results are consistent and reliable, particularly if the data were to be used for enforcing regulation.

In September 2009, US EPA published EPA Method 537 Version 1.1 [14] for the determination of fourteen PFAS compounds in drinking water. This method was later employed for the monitoring of the selected PFAS during the Unregulated Contaminant Monitoring Rule 3 (UCMR3). However, for environmental waters (e.g. non-potable water, surface water, wastewater and groundwater) and soil matrices, there are no standard EPA methods available. US EPA is currently developing EPA Method 8327 [15] for the analysis of PFAS in environmental waters using LC-MS/MS. In the interim, laboratories are using in-house developed methods (e.g. modified EPA Method 537) or methods that have been developed by non-governmental standardization bodies, such as ASTM International and ISO.

ASTM International has developed ASTM D7979-17 [16] and ASTM D7968-17a [17] for PFAS analysis in environmental waters and soil, respectively. The main difference between these ASTM methods lies in the sample preparation steps. After the extraction of samples, the procedures and LC-MS/MS methods are essentially the same. Shimadzu is one of the members of the ASTM D19.06 Task Group's independent, second laboratory validation of ASTM D7979. This white paper describes the work related to the validation. Table 1 summarizes the various LC-MS/MS methods for PFAS testing in various environmental water and soil matrices.

Table 1. Comparison between the various EPA and ASTM Methods for PFAS testing in water matrices.

Method	EPA 537 [14]	ASTM D7979 [16]	ASTM D7968 [17]	EPA 8327 [15]
PFAS Compounds	14 Targets 3 Surrogates 3 ISTDs	21 Targets 9 Surrogates	21 Targets 9 Surrogates	*24 PFAS compounds (details to be announced)*
Sample Matrices	Drinking Water	Sludge, Influent, Effluent and Wastewater (<0.2% solids)	Soil	*Groundwater, Surface water and Wastewater.* *Sample collection procedure to be prescribed.*
Sample Preparation	250 mL → SPE → 1 mL	Dilute 5 mL with 5 mL Methanol → Filter → Direct Injection	Extract 2 g with 10 mL 50% Methanol → Filter → Direct Injection	*Direct Injection Method*
Injection Volume	10 µL	30 µL	30 µL	*To be announced*
Quantitation	Internal Standard	External Calibration (Isotope Dilution or Internal Standard allowed)	External Calibration (Isotope Dilution or Internal Standard allowed)	*To be announced*

Growing List of PFAS Compounds

Due to the impact of PFAS on human health and the environment, EPA launched the 2010/2015 PFOA Stewardship Program [18] in early 2006 to reduce and ultimately eliminate PFOA, PFOS and long-chain PFAS from products and emissions. The eight participating companies with global operations have either stopped the production and import of these selected PFAS and then switched to alternatives or entirely move away from the PFAS industry.

GenX process and technology has emerged as a substitute to PFOA and PFOS; companies are able to make high-performance fluoropolymers (GenX chemicals), such as hexafluoropropylene oxide (HFPO) dimer acid and its ammonium salts. With the recent recommendation for a global ban on PFOA and its related chemicals by the UN global scientific committee [19], manufacturers and industries all over the world may turn to these GenX compounds as substitutes.

These alternatives have raised several health and environmental concerns as they possess similar properties as PFOA and PFOS [20]. To accelerate occurrence assessment, the EPA updated the drinking water method to EPA 537.1 Version 1.0 in November 2018 [21] to include GenX (HFPO-dimer acid) and three other compounds (i.e. 11Dl-PF3OUdS, 9Cl-PF3ONS and ADONA, [21]) in addition to the target list.

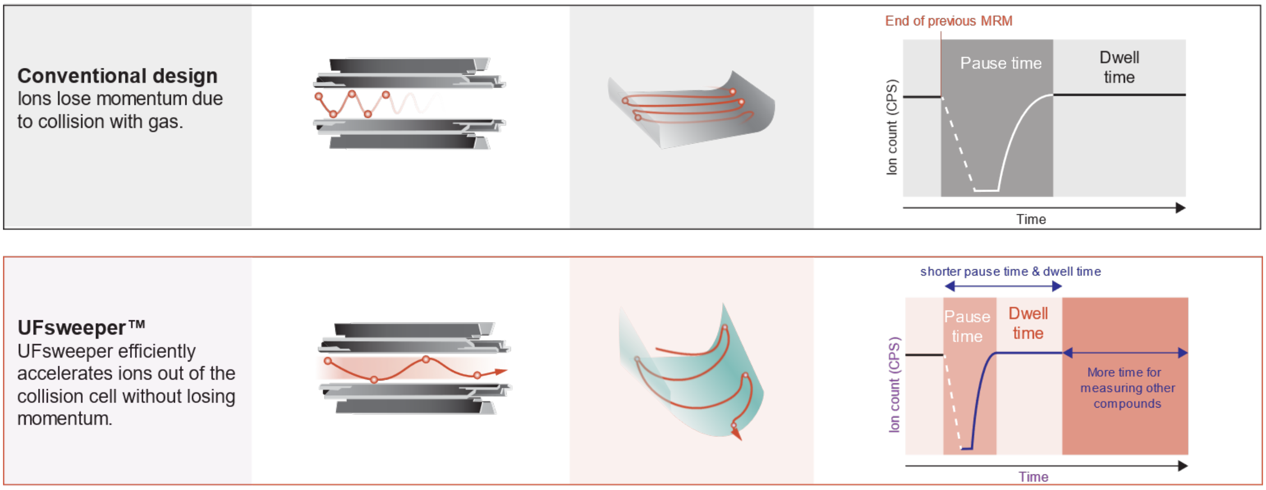
With the release of EPA's Health Advisory for PFAS in 2017, the availability of validated methods and increase of public awareness, PFAS monitoring and testing is becoming routine. Together with this trend of using similar compounds as alternatives, the list of PFAS that are of concern may continue to grow.

Flexibility of Analytical Instruments

To incorporate the growing list of PFAS compounds and to enhance the specificity and sensitivity of the LC-MS/MS analysis, Multiple Reaction Monitoring (MRM) is commonly utilized. Shimadzu's Ultra-fast Mass Spectrometry (UFMS) systems, featuring an ultra-fast acquisition rate of 555 MRM/sec and which can operate without any compromise in sensitivity, prove to be ideal for the fast and sensitive analysis of many PFAS compounds in a single run.

Shimadzu's collision cell, UFsweeper™, is one of the key features that contributes to the high acquisition rate. The redesign of the collision cell allows for an ultra-fast ion sweeping where ions are efficiently accelerated out of the collision cell without losing momentum. With these features in Shimadzu UFMS, short dwell time[1] and pause time[2] are achieved and data can be acquired at a high speed with no loss in sensitivity. With more time for data collection, the UFMS technology addresses the need of large-compound-panel testing in PFAS analysis and ensures potential extendibility of the LC-MS/MS method for PFAS.

In this white paper, the state-of-the-art analytical methods for monitoring PFAS are described, with emphasis on the work related to the validation of ASTM D7979. A robust method consisting of simple sample preparation with direct injection to LC-MS/MS (Shimadzu LCMS-8060) is demonstrated, showcasing the setup, performance and compatibility of LCMS-8060 for the separation and analysis of 49 PFAS in environmental samples.



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[1] Dwell time is the time allocated for acquiring the data of an ion of a particular m/z in a mass spectrometer.

[2] LC-MS/MS measurement conditions must be switched to perform simultaneous measurements of multiple compounds. The time needed for this is termed as pause time. As data cannot be acquired during the pause time, it should be as short as possible.

Experimental

List of PFAS Compounds and Preparation of Calibration Standards

Table 2 lists all 49 PFAS compounds (30 targets and 19 isotopically-labeled surrogates) used in this study. The list covers the PFAS compounds named in ASTM D7979 method and includes additional compounds listed for consideration in the appendix of the method. All PFAS standards were purchased from Wellington Laboratories (Guelph, Ontario).

Stock standard solution at a concentration of 200 ng/L for all 49 compounds was prepared from the commercially available stock solutions. The stock standard solution was further diluted using a 50:50 (vol:vol) methanol/water with 0.1% acetic acid to obtain the other eight calibration solutions; their final concentrations were at 150, 100, 80, 60, 40, 20, 10 and 5 ng/L. These standards were not filtered. Calibration was performed using a 9-point curve, ranging from 5 – 200 ng/L. Due to the high method detection limit (MDL) obtained for FHEA, FOEA and FDEA, the calibration range for these compounds was adjusted to 100 – 4000 ng/L and calibration standards were prepared as described above.

The stock solutions were prepared and stored in PFAS-free polypropylene (PP) containers. Prior to the analysis, the solutions were shaken thoroughly then transferred to a 2 mL amber glass LC vial, and analyzed within 24 hours to achieve optimum results. In the event that samples or standards are allowed to sit in the LC vials, some PFAS compounds may settle, precipitate or adsorb on the surface. To ensure a homogenous solution and optimum results, it is necessary to vortex the solution prior to injection.

Preparation of Samples

A surrogate spiking solution containing each isotopically-labelled PFAS was added to all samples, including method blanks, duplicates, laboratory control samples, matrix spikes and reporting limit checks. The stock surrogate spiking solution was prepared at 20 µg/L in 95:5% (vol/vol) acetonitrile (ACN):water. Water samples (5 mL) were collected in 15 mL PP/HDPE centrifuge vials. Also, the blank (containing 5 mL of reagent water) and laboratory control sample (containing the lowest calibration concentration for each PFAS) were prepared for the study.

The samples (5 mL) were diluted 1:1 with methanol and spiked with 40 µL of the surrogate spiking solution and vortexed for 2 minutes, resulting in a surrogate concentration of 80 ng/L in the diluted solution. The samples were filtered and acetic acid (10 µL) was added to the filtrate to adjust the pH. The aliquots were transferred to the LC vials for injection and analysis by LC-MS/MS.

LCMS Analytical and Instrument Conditions

The analytical and instrument conditions are listed in Table 3. Each PFAS standard was injected and analyzed separately to ensure positive identification and maximum resolution. Upon collating the individual retention time and optimized MRM parameters, the PFAS standard mixture (containing all PFAS compounds) was prepared and used for subsequent analysis. All compound parameters, including precursor ion, product ion and collision energies, were optimized bypassing the analytical column using LabSolutions software. At least two MRM transitions were used.

Shimadzu UFMS, possessing an ultra-fast acquisition rate of 555 MRM/sec and a high polarity switching speed of 5 msec, is capable of MRM transitions with a fast-enough cycle time to obtain high sensitivity with at least ten data points over a peak. The target compounds were identified by comparing the MRM transitions of the sample to that of the standards. The target analytes were quantitated using the quantifier MRM transitions (Table 4) of the target compounds. Concentrations were calculated using LabSolutions software to generate a linear regression. The point of origin was excluded, and a fit weighting of 1/x was used to give more emphasis to the lower concentrations.

Table 2. List of 49 PFAS (target compounds and isotopically-labeled surrogates) included in this paper.

No.	PFAS Compound	Abbreviation	Molecular Formula	Surrogate and its Abbreviation
PERFLUOROALKYLCARBOXYLIC ACIDS				
1	Perfluorobutanoic acid	**PFBA**	$C_4F_7O_2H$	**MPFBA** ($^{13}C_4F_7O_2H$)
2	Perfluoropentanoic acid	**PFPeA**	$C_5F_9O_2H$	**MPFPeA** ($^{13}C_5F_9O_2H$)
3	Perfluorohexanoic acid	**PFHxA**	$C_6F_{11}O_2H$	**MPFHxA** ($^{13}C_2{}^{12}C_4F_{11}O_2H$)
4	Perfluoroheptanoic acid	**PFHpA**	$C_7F_{13}O_2H$	**MPFHpA** ($^{13}C_4{}^{12}C_3F_{13}O_2H$)
5	Perfluorooctanoic acid	**PFOA**	$C_8F_{15}O_2H$	**MPFOA** ($^{13}C_8F_{15}O_2H$)
6	Perfluorononanoic acid	**PFNA**	$C_9F_{17}O_2H$	**MPFNA** ($^{13}C_9F_{17}O_2H$)
7	Perfluorodecanoic acid	**PFDA**	$C_{10}F_{19}O_2H$	**MPFDA** ($^{13}C_6{}^{12}C_4F_{19}O_2H$)
8	Perfluoroundecanoic acid	**PFUnA**	$C_{11}F_{21}O_2H$	**MPFUnA** ($^{13}C_7{}^{12}C_4F_{21}O_2H$)
9	Perfluorododecanoic acid	**PFDoA**	$C_{12}F_{23}O_2H$	**MPFDoA** ($^{13}C_2{}^{12}C_{10}F_{23}O_2H$)
10	Perfluorotridecanoic acid	**PFTriA**	$C_{13}F_{25}O_2H$	-
11	Perfluorotetradecanoic acid	**PFTreA**	$C_{14}F_{27}O_2H$	**MPFTreA** ($^{13}C_2{}^{12}C_{12}F_{27}O_2H$)
PERFLUOROALKYLSULFONATES				
12	Perfluorobutyl sulfonate	**PFBS**	$C_4F_9SO_3H$	**MPFBS** ($^{13}C_3{}^{12}C_1F_9SO_3Na$)
13	Perfluoropentane sulfonate	**PFPeS**	$C_5F_{11}SO_3H$	-
14	Perfluorohexyl sulfonate	**PFHxS**	$C_6F_{13}SO_3H$	**MPFHxS** ($^{13}C_3{}^{12}C_3F_{13}SO_3Na$)
15	Perfluoroheptane sulfonate	**PFHpS**	$C_7F_{15}SO_3H$	-
16	Perfluorooctyl sulfonate	**PFOS**	$C_8F_{17}SO_3H$	**MPFOS** ($^{13}C_8F_{17}SO_3Na$)
17	Perfluorononane sulfonate	**PFNS**	$C_9F_{19}SO_3H$	-
18	Perfluorodecane sulfonate	**PFDS**	$C_{10}F_{21}SO_3H$	-
UNSATURATED FLUOROTELOMER ACIDS				
19	2H-Perfluoro-2-octenoic acid (6:2)	**FHUEA**	$C_8H_2O_2F_{12}$	**-**
20	2H-Perfluoro-2-decenoic acid (8:2)	**FOUEA**	$C_{10}H_2O_2F_{16}$	**-**
FLUOROTELOMER ACIDS				
21	2-Perfluorohexyl ethanoic acid (6:2)	**FHEA**	$C_8H_3O_2F_{13}$	**-**
22	3-Perfluoroheptyl propanoic acid (7:3)	**FHpPA**	$C_{10}H_5O_2F_{15}$	**-**
23	2-Perfluorooctyl ethanoic acid (8:2)	**FOEA**	$C_{10}H_3O_2F_{17}$	**-**
24	2-Perfluorodecyl ethanoic acid (10:2)	**FDEA**	$C_{12}H_3O_2F_{21}$	**-**
FLUORINATED TELOMER SULFONATES				
25	Sodium 1H,1H,2H,2H-perfluorohexane sulfonate	**4-2 FTS**	$C_6H_4F_9SO_3Na$	**M4-2 FTS** ($^{13}C_2{}^{12}C_4H_4F_9SO_3Na$)
26	Sodium 1H,1H,2H,2H-perfluorooctane sulfonate	**6-2 FTS**	$C_8H_4F_{13}SO_3Na$	**M6-2 FTS** ($^{13}C_2{}^{12}C_6H_4F_{13}SO_3Na$)
27	Sodium 1H,1H,2H,2H-perfluorodecane sulfonate	**8-2 FTS**	$C_{10}H_4F_{17}SO_3Na$	**M8-2 FTS** ($^{13}C_2{}^{12}C_8H_4F_{17}SO_3Na$)
PERFLUOROOCTANESULFONAMIDE AND PERFLUOROOCTANESULFONAMIDOACETIC ACIDS				
28	2-(N-methylperfluorooctanesulfonamido) acetic acid	**N-MeFOSAA**	$C_{11}H_6F_{17}NSO_4$	**MN-MeFOSAA** ($C_{11}{}^2H_3H_3F_{17}NSO_4$)
29	2-(N-ethylperfluorooctanesulfonamido) acetic acid	**N-EtFOSAA**	$C_{12}H_8F_{17}NSO_4$	**MN-EtFOSAA** ($C_{12}{}^2H_5H_3F_{17}NSO_4$)
30	Perfluorooctanesulfonamide	**FOSA**	$C_8H_2F_{17}NSO_2$	**MFOSA** ($^{13}C_8H_2F_{17}NSO_2$)

Table 3. LCMS system and instrument conditions.

<table>
<tr><td>LCMS Instrument</td><td>Shimadzu LCMS-8060</td></tr>
<tr><td>Analytical Column</td><td>Shim-pack GIST Phenyl-Hexyl, 2.1 mm ID × 100 mm, 3 µm particle size</td></tr>
<tr><td>Solvent Delay Column</td><td>Shim-pack XR-ODS, 3 mm ID × 50 mm, 2.2 µm particle size</td></tr>
<tr><td>Column Temperature</td><td>40 °C</td></tr>
<tr><td>Injection Volume</td><td>10 µL</td></tr>
<tr><td>LC Flow Rate</td><td>0.4 mL/min</td></tr>
<tr><td>Mobile Phase A</td><td>20 mM Ammonium Acetate in LCMS-grade Water</td></tr>
<tr><td>Mobile Phase B</td><td>Acetonitrile</td></tr>
<tr><td>Gradient Conditions</td><td>
<table>
<tr><th>Time (min)</th><th>% Solvent Line A</th><th>% Solvent Line B</th></tr>
<tr><td>0</td><td>90</td><td>10</td></tr>
<tr><td>1</td><td>90</td><td>10</td></tr>
<tr><td>3</td><td>70</td><td>30</td></tr>
<tr><td>14</td><td>35</td><td>65</td></tr>
<tr><td>14.1</td><td>2</td><td>98</td></tr>
<tr><td>17.1</td><td>90</td><td>10</td></tr>
<tr><td>20</td><td>90</td><td>10</td></tr>
</table>
</td></tr>
<tr><td>Run / Acquisition Cycle Time</td><td>20 minutes (all 49 PFAS compounds are eluted in 13 minutes)</td></tr>
<tr><td>Interface</td><td>Electrospray Ionization (ESI)</td></tr>
<tr><td>Interface Temperature</td><td>300 °C</td></tr>
<tr><td>Desolvation Line Temperature</td><td>100 °C</td></tr>
<tr><td>Heat Block Temperature</td><td>200 °C</td></tr>
<tr><td>Heating Gas Flow</td><td>15 L/min</td></tr>
<tr><td>Drying Gas Flow</td><td>5 L/min</td></tr>
<tr><td>Nebulizing Gas Flow</td><td>3 L/min</td></tr>
<tr><td>Total MRMs</td><td>74</td></tr>
</table>

The described LC-MS/MS method was run exactly as indicated in ASTM Method D7979. One such modification concerns the ASTM liquid chromatography (LC) conditions. Only two LC mobile phases were employed in this study. Reagent C (400 mM ammonium acetate in 95:5% acetonitrile-water) specified in ASTM method was not used. The LC mobile phases used in this study (Table 3) are easy to prepare. In addition, the shape and sensitivity of chromatographic peaks obtained are similar or even better than when using the mobile phases specified in the ASTM method.

■ Avoiding Contamination

PFAS may be found in sampling and storage containers and may even contaminate the samples. It is important to account for these sources of PFAS during and, at best, minimize them with the use of PFAS-free materials, high-grade solvents and flushing the instrument by injecting multiple method blanks.

In this study, a solvent delay column was used to account for the PFAS contamination present in the glass containers, laboratory consumables (e.g. pipette tips) and LC system (e.g. pumps and tubing). This solvent delay column is situated before the autosampler and helps delay the elution of the PFAS present in the background. As shown in Figure 1, the use of the delay column and this impurity delay method allows the distinction of PFOA originating solely from the sample. Furthermore, with Shimadzu's team of service engineers, we can set up the exact HPLC configuration (involving solvent lines, tubing, bypassing of solvent lines and more) that is proven to give contamination-free data.

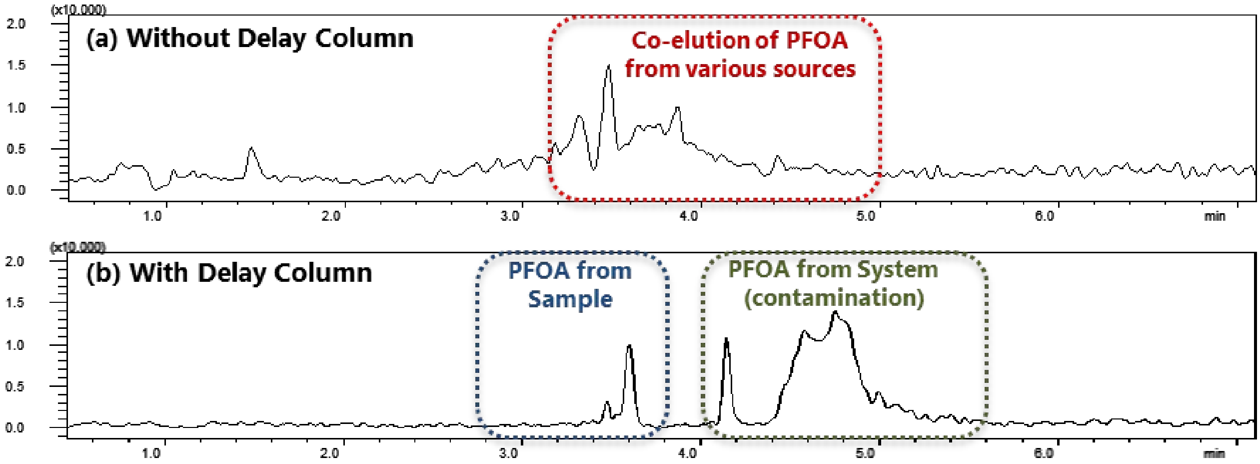


Figure 1. Chromatogram of PFOA: (a) without delay column and (b) with delay column.

Results and Discussion

Chromatographic Separation

Figure 2 shows the overlaid MRM and total ion current (TIC) chromatograms of all 49 PFAS compounds in a mixed standard solution at 100 ng/L. All PFAS compounds eluted within 13 minutes. The retention time and MRM transition (quantifying ions) for each of the PFAS compounds are listed in Table 4.

Chromatography separation was optimized and adjusted to obtain maximum resolution between peaks in the shortest time possible. Good peak shapes were obtained for these PFAS, even for early-eluting PFBS.

Most importantly, the isomers (e.g. PFOS and PFHxS) were chromatographically separated. These were achieved by selecting a column with a phenyl-hexyl functional group. The total LC-MS/MS run time of 20 minutes included a final wash-out with acetonitrile to remove contamination.

Fluorotelomer acids, observed as $[M-H]^-$ and $[M-HF-H]^-$, can result in an ion with the same formula as the unsaturated fluorotelomer acid. Even under the optimized chromatography conditions, these compounds have near identical retention times. To successfully reduce HF loss and minimize false identification of the fluorotelomer acids, a lower desolvation line temperature was employed.

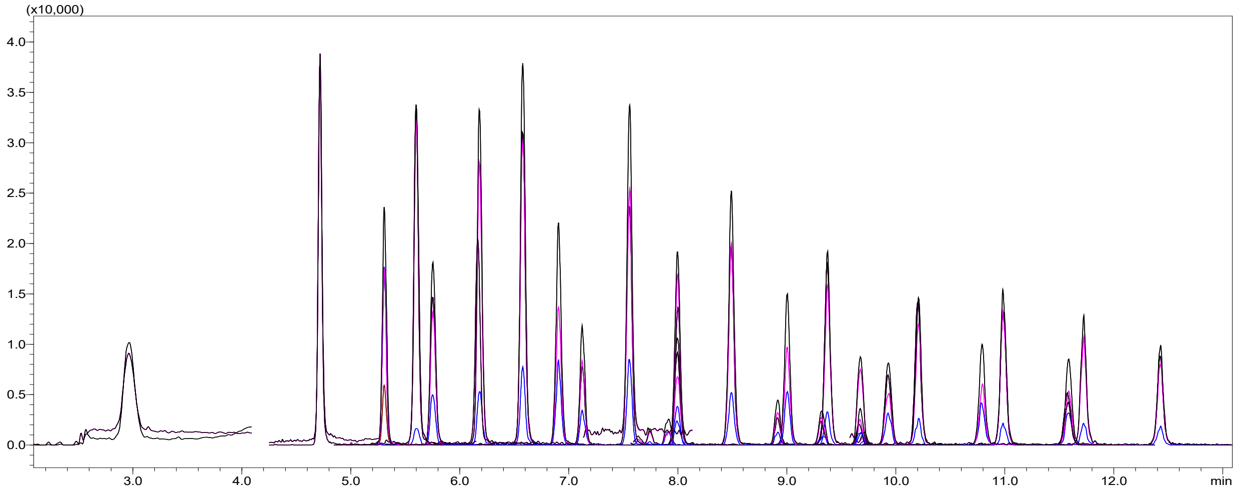


Figure 2. MRM (pink & blue) and TIC (black) chromatograms of all 49 PFAS in a mixed standard solution, with each PFAS at 100 ng/L.

Table 4. MRM Transition (quantifying ions), retention time, method detection limit (MDL), calibration range, accuracy and precision results for PFAS.

No.	Compound	MRM Transition (Quantifier Ion)	RT (min)	Method Detection Limit (ng/L)	Calibration Range (ng/L)	% Recovery at 20 ng/L	% RSD at 20 ng/L
1	PFBA	212.90 > 169.00	3.092	4.1	5 – 200	112	6.6
2	MPFBA	217.00 > 172.10	3.095	5.0	5 – 200	86	10.2
3	PFPeA	263.00 > 219.00	4.753	0.9	5 – 200	101	2.9
4	MPFPeA	268.00 > 223.00	4.754	0.6	5 – 200	100	1.4
5	4-2 FTS	327.00 > 307.00	5.347	1.7	5 – 200	102	3.2
6	M4-2 FTS	329.00 > 309.00	5.347	1.2	5 – 200	92	3.0
7	PFHxA	312.90 > 269.00	5.652	1.3	5 – 200	101	3.9
8	MPFHxA	317.90 > 273.00	5.653	1.1	5 – 200	101	2.3
9	PFBS	298.90 > 80.10	5.824	1.5	5 – 200	101	10.4
10	MPFBS	301.90 > 80.10	5.825	1.1	5 – 200	98	4.1
11	FHUEA	357.00 > 293.00	6.210	2.6	5 – 200	108	5.6
12	FHEA	376.90 > 293.00	6.225	32.5	100 – 4000	99*	5.3*
13	PFHpA	362.90 > 319.00	6.642	1.4	5 – 200	103	4.2
14	MPFHpA	366.90 > 322.00	6.643	0.7	5 – 200	99	2.2
15	PFPeS	348.90 > 79.90	6.992	1.1	5 – 200	100	4.7
16	6-2 FTS	427.00 > 406.90	7.194	2.5	5 – 200	113	7.3
17	M6-2 FTS	429.00 > 408.90	7.195	1.8	5 – 200	101	3.8
18	PFOA	412.90 > 369.00	7.635	5.1	5 – 200	96	5.7
19	MPFOA	420.90 > 376.00	7.636	0.7	5 – 200	99	2.0
20	FHpPA	440.90 > 337.00	7.965	9.4	5 – 200	84	28
21	FOEA	476.90 > 393.00	8.066	48.3	100 – 4000	103*	5.5*
22	FOUEA	456.90 > 392.90	8.076	1.6	5 – 200	104	3.6
23	PFHxS	398.90 > 80.10	8.094	1.5	5 – 200	96	9.8
24	MPFHxS	401.90 > 80.10	8.102	1.7	5 – 200	100	3.4
25	PFNA	462.90 > 418.90	8.588	1.7	5 – 200	104	6.3
26	M9PFNA	471.90 > 426.90	8.589	1.6	5 – 200	103	4.2
27	8-2 FTS	526.90 > 506.90	9.011	3.2	5 – 200	90	25.2
28	M8-2 FTS	528.90 > 508.90	9.012	1.8	5 – 200	89	12.3
29	PFHpS	448.90 > 79.90	9.131	1.6	5 – 200	99	8.2
30	N-MeFOSAA	569.90 > 419.00	9.410	3.6	5 – 200	101	15.0
31	MN-MeFOSAA	572.90 > 419.00	9.420	5.4	5 – 200	102	9.6
32	PFDA	512.90 > 468.90	9.486	2.3	5 – 200	108	5.7
33	MPFDA	518.90 > 473.90	9.487	1.1	5 – 200	98	4.7
34	FDEA	576.90 > 493.00	9.762	35.5	100 – 4000	89*	7.0*
35	N-EtFOSAA	583.90 > 419.00	9.767	5.3	5 – 200	118	16.3
36	MN-EtFOSAA	588.90 > 419.00	9.768	4.2	5 – 200	130	13.0
37	PFOS	498.90 > 80.10	10.076	3.0	5 – 200	105	7.8
38	MPFOS	506.90 > 80.10	10.077	1.5	5 – 200	107	5.0
39	PFUnA	562.90 > 519.00	10.330	2.9	5 – 200	100	11.6
40	MPFUnA	569.90 > 525.00	10.331	1.5	5 – 200	103	4.6
41	PFNS	548.90 > 79.90	10.946	1.3	5 – 200	112	7.3
42	PFDoA	612.90 > 568.90	11.122	2.2	5 – 200	98	6.5
43	MPFDoA	614.90 > 569.90	11.123	0.8	5 – 200	100	4.1
44	FOSA	497.90 > 77.90	11.586	0.6	5 – 200	88	6.8
45	MFOSA	505.90 > 77.90	11.588	1.6	5 – 200	94	5.4
46	PFDS	598.90 > 79.90	11.760	2.1	5 – 200	108	5.4
47	PFTriA	662.90 > 618.90	11.877	1.1	5 – 200	99	4.6
48	PFTreA	712.90 > 668.90	12.586	1.1	5 – 200	92	3.5
49	MPFTreA	714.90 > 669.90	12.587	0.7	5 – 200	92	4.3

*FHEA, FOEA and FDEA (spiked concentration for MDL study at 100 ng/L, Precision and Accuracy study, concentration at 400 ng/L)

PFAS Stability Study – Effects of Solvents, LC Vial Materials and Vortex

The shelf life of the prepared PFAS standards was evaluated using the following solvents: 10%, 30%, 50%, 70% and 90% methanol, in both glass and polypropylene vials. The plots of relative intensity of PFAS against shelf life (time/hours) shown in Figure 3 demonstrate that the 50% methanol in water used in the ASTM methods sufficiently dissolves the PFAS compounds and keeps them in solution. The lower concentrations of methanol (10% and 30% methanol) show significant loss of PFAS due to the insolubility of PFAS in the solvent used. The recovery results for 90% methanol are similar to that of 70% methanol.

Furthermore, the materials of the LC vial, amber glass and polypropylene, were investigated to determine the potential adsorption of PFAS on the vial surface Similar recovery and quantitation were observed regardless of the material of the LC vials. Rather than the material of the LC vial, the effect of vortex on the recovery of PFAS is considerable (Figure 4). To demonstrate the importance of utilizing the vortex mixer, a PFAS standard solution was allowed to sit for 24 hours. An end mid-level calibration check (50 ng/L) was prepared and the recovery of the PFAS compounds from the vial, before and after mixing, was determined. Figure 4 shows the chromatogram of the PFAS compounds before and after vortex. The recovery of the long-chain PFAS is noticeably lower before vortex. The use of vortex ensures that the solution is homogenous and consistent results are obtained.

The PFAS concentration in the vial may change after the vial cap is pierced as the organic solvent (i.e. methanol:water solution) and/or PFAS compound can be lost through the puncture. If calibration standards are to be used multiple times, it is recommended to use amber glass vial with sealed replaceable caps. This sealing of vials immediately after injection may alleviate the loss of PFAS.

Calibration Range and Method Detection Limit (MDL)

Calibration was performed for all PFAS compounds using a nine-point calibration curve, ranging from 5 ng/L – 200 ng/L with some exceptions. FHEA, FOEA and FDEA, the fluorotelomer acids, were calibrated in the range of 100 – 4000 ng/L. The linearity of the curves was evaluated using 1/x weighting, ignoring the origin. The calibration range are shown in Table 4 and all calibration curves had a regression coefficient (R^2) higher than 0.99. The calibration curves and regression coefficient (R^2) of some selected PFAS compounds are illustrated in Figure 5.

A MDL study was conducted by spiking the water samples (5 mL). FHEA, FOEA and FDEA were spiked at a concentration of 100 ng/L; the rest of the PFAS compounds were spiked at 20 ng/L. The MDL, %recovery and % RSD were determined and are shown in Table 4. The MDLs using the LCMS-8060 are in the range of 0.6 – 5.4 ng/L for the 44 PFAS compounds (excluding fluorinated telomer acids). Similarly, the % recovery and % RSD for these 44 PFAS were within the acceptable limits (70-130%).

Summary and Conclusion

This white paper summarized and illustrated the use, performance and compatibility of Shimadzu UFMS for the analysis of PFAS in environmental samples. With reference to ASTM D7979, 49 PFAS compounds were separated and quantified with a simple direct injection method and rapid LC-MS/MS analysis (LCMS-8060). Direct injection without SPE allows for maximum throughput and minimal background, loss and contamination cause by sample preparation. The high-speed and high-sensitivity characteristics of the LCMS-8060 achieve a method detection limit of 0.6 – 5.4 ng/L and recovery of 84 – 113% for all PFAS compounds, excluding FTAs. These results fall within the quality control requirements and limits. Together with a high scanning speed and a short dwell time, the Shimadzu LCMS-8060 achieves rapid, reliable and highly sensitive quantitation of PFAS in environmental waters.

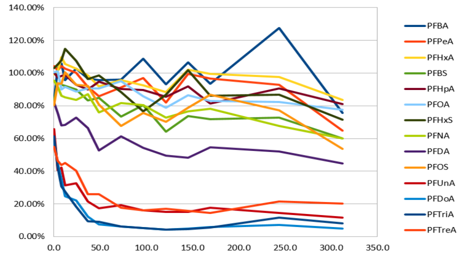
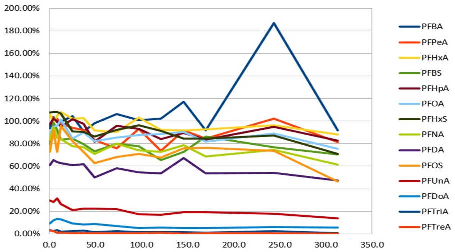
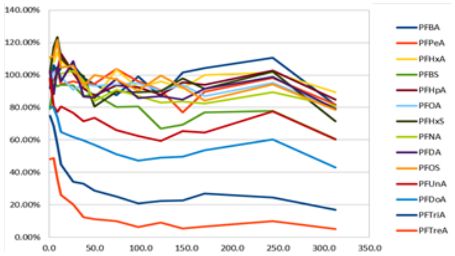
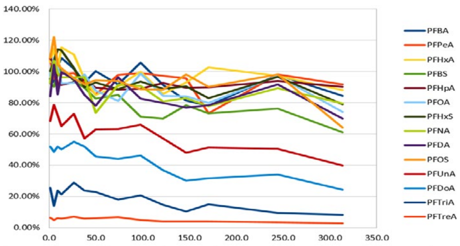
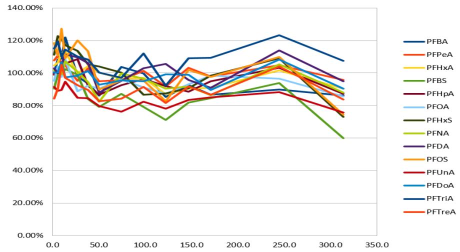
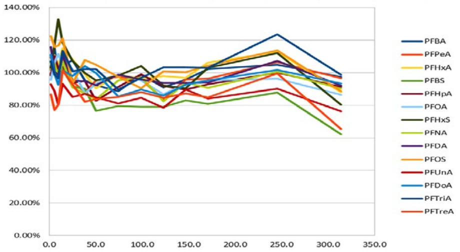
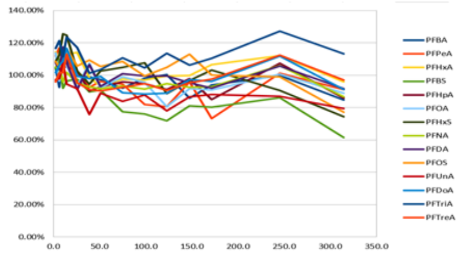
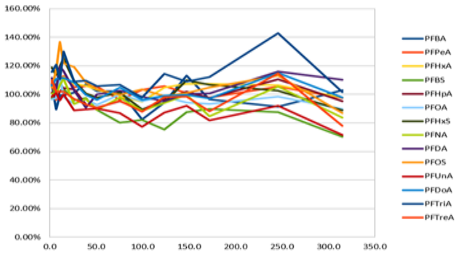
Solvent	**Materials of Vials**	
	Glass	**Polypropylene**
10% Methanol		
30% Methanol		
50% Methanol		
70% Methanol		

Figure 3. Plots of PFAS recovery against shelf life (time/hour) for the various solvents in glass and polypropylene LC vials.

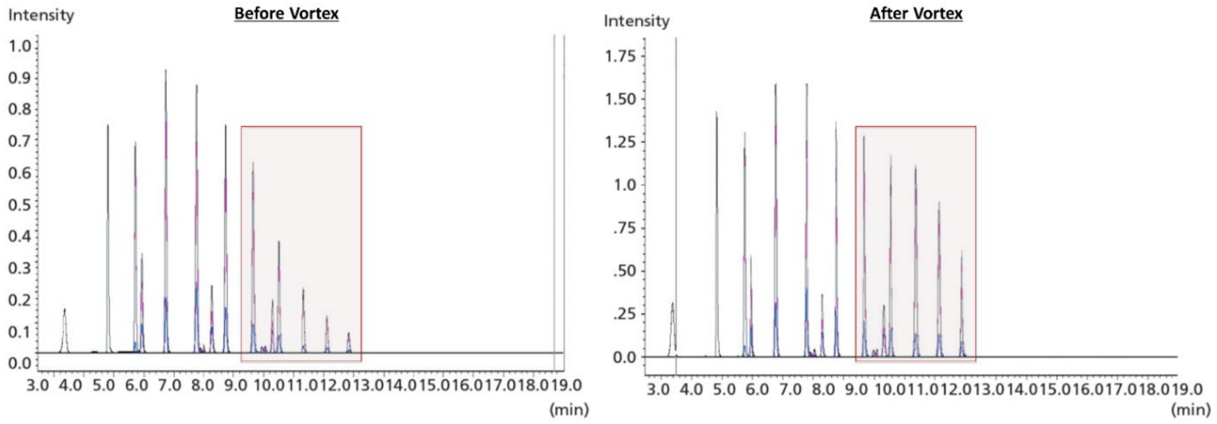


Figure 4. Recovery of PFAS before (left) and after (right) mixing the standard PFAS solution vial.

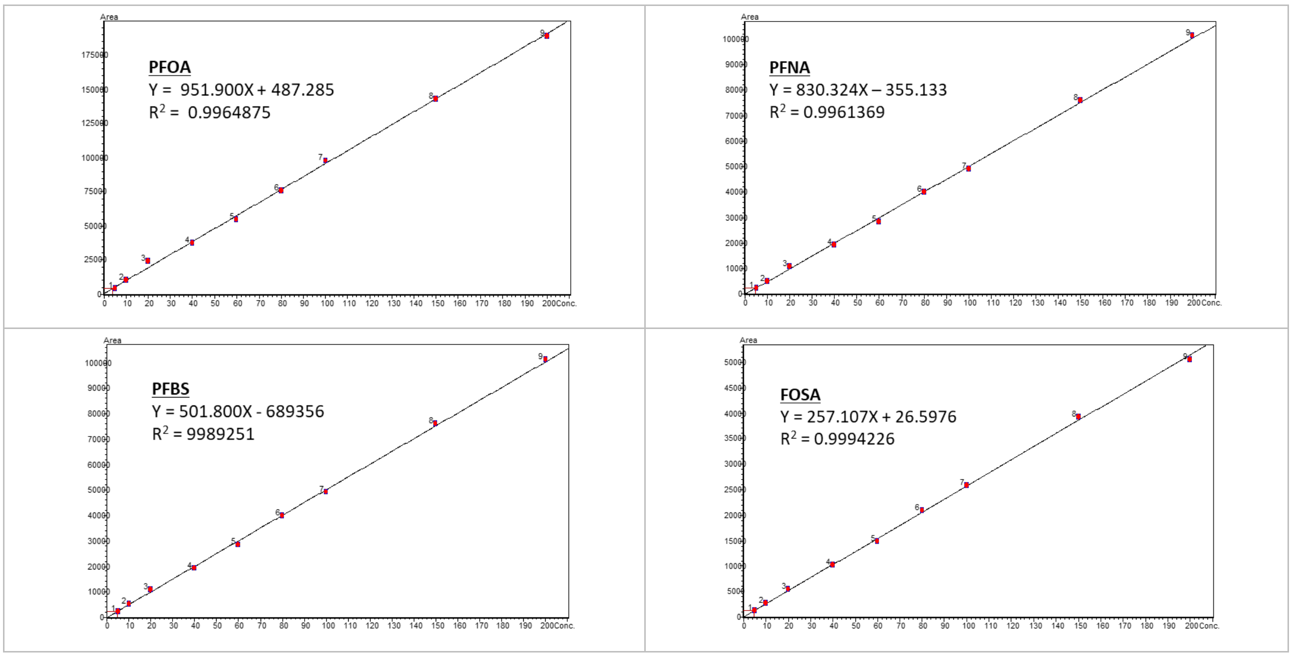


Figure 5. Representative calibration curves (PFOA, PFBS, PFNA and FOSA) at 10 µL injection using LCMS-8060.

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Application News

No. C184

Water Analysis / LCMS

Analysis of PFAS Specified in EPA Method 537 and Beyond using Shimadzu UFMS™

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❑ Abstract

This application news demonstrates the use, performance and compatibility of Shimadzu Ultra-fast Mass Spectrometry (UFMS™) for EPA Method 537 with an expanded compound panel of seven additional PFAS. A total of 27 PFAS compounds were extracted, separated and detected with triple quadrupole mass spectrometers, LCMS-8045 and LCMS-8050. Recoveries of 86–106% (LCMS-8050) and 77–104% (LCMS-8045) were well within the limits outlined in EPA 537. Method detection limits of 0.7–1.7 ng/L (ppt) (LCMS-8050) and 0.7–3.3 ng/L (LCMS-8045) were obtained and both systems fulfilled all of the EPA's requirements for PFAS analysis in drinking water.

Keywords: Per- and Polyfluorinated Alkyl Substances, PFAS, Perfluorinated Compounds, PFCs, Drinking Water, PFOA, PFOS, Persistent Organic Pollutants, POPs

❑ Introduction

Per- and Polyfluorinated Alkyl Substances (PFAS) are a group of anthropogenic chemicals widely used as fire retardants, food packaging materials, and non-stick coatings because of their heat-resistant, and oil- and water-repellent properties. These properties result in resistance to degradation, hence, PFAS accumulate in the environment. Moreover, PFAS are capable of long-range transport and can potentially affect human health (e.g. developmental and reproductive effects).

Over the past several years, the issue of PFAS contamination in drinking water has become a global concern. To safeguard public health and minimize human exposure to these chemicals, the US, EU and Australia have issued health advisory guidelines for perfluorooctanoic acid (PFOA) and perfluorooctane-sulfonic acid (PFOS) in drinking water (e.g. US: 70 ppt for combined PFOS and PFOA). Furthermore, some states in the US (e.g. California, Minnesota, Colorado, Michigan and New Jersey) have established similar or even stricter limits for PFAS and these can go as low as 13 ppt and 14 ppt for PFOS and PFOA respectively.

US Environmental Protection Agency (US EPA) has established Method 537 for PFAS in drinking water. It utilizes a solid phase extraction (SPE) followed by liquid chromatography tandem mass spectrometry (LC-MS/MS) for the determination of 14 perfluorinated alkyl acids in drinking water. Besides the analysis of these

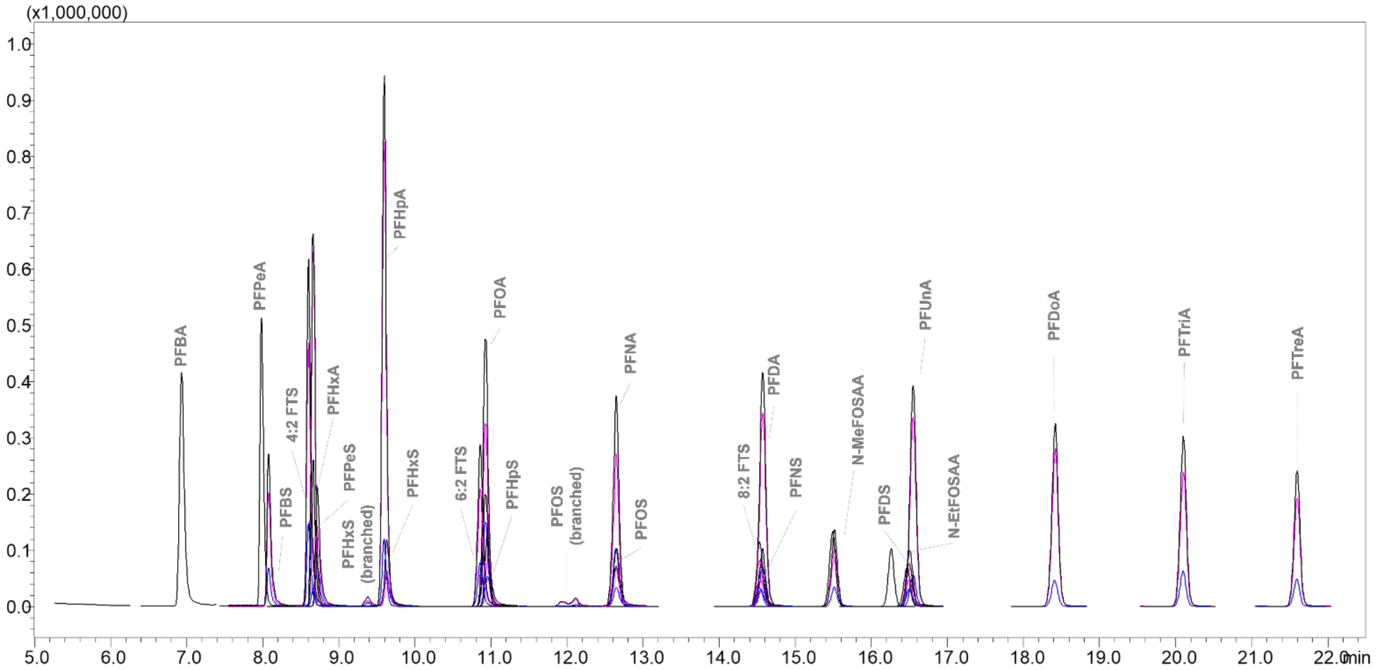

Figure 1. MRM (pink and blue) and TIC (black) chromatograms of all PFAS in a mixed standard solution with each PFAS at 20 ng/mL (LCMS-8050)

PFAS (e.g. PFOA and PFOS), there are other classes gaining attention due to their increasing use, occurrence and persistence in the environment. In this study, apart from the compounds listed in EPA Method 537, the scope of PFAS has been expanded to include seven additional compounds such as fluorotelomeric alcohols (precursor of PFOA).

This application news describes and demonstrates the use and performance of Shimadzu UFMS™ for the analysis of 21 PFAS (including all 14 stated in EPA Method 537) in drinking water. Shimadzu triple quadrupole mass spectrometers, LCMS-8045 and LCMS-8050, were used in this study. Possessing an ultra-fast acquisition rate of 555 MRM/sec and a high polarity switching speed (5 msec), these UFMS™ instruments achieve rapid, reliable and highly-sensitive quantitation of PFAS in drinking water.

❑ Experimental

PFAS and Preparation of Calibration Standards

Table 1 lists the 27 PFAS compounds (21 target compounds, 3 internal standards (IS) and 3 surrogates) used in this study. All PFAS standards were purchased from Wellington Laboratories (Guelph, Ontario). A series of 10 calibration standards at concentrations of 1.25, 2.50, 5.00, 10.0, 15.0, 20.0, 25.0, 37.5, 50.0 and 100 ng/mL were prepared by dilution with 96:4% (vol/vol) methanol:water. These concentrations were 250 times higher than the target concentration range in consideration of analyte enrichment over the course of sample preparation, such that a 1.25 ng/mL calibration standard was equivalent to 5 ng/L of field sample.

Table 1. List of PFAS (target compounds, internal standards and surrogates)

PFAS Compounds	Abbreviation	CAS	Molecular Weight	Molecular Formula	IS, Surrogates and its Abbreviation	PFAS Listed in EPA Method 537
PERFLUOROALKYLCARBOXYLIC ACIDS						
Perfluorohexanoic acid	**PFHxA**	307-24-4	314.06	$C_6F_{11}O_2H$	M2PFHxA (Surr.) ($^{13}C_2{}^{12}C_4F_{11}O_2H$)	✓
Perfluoroheptanoic acid	**PFHpA**	375-85-9	364.06	$C_7F_{13}O_2H$	-	✓
Perfluorooctanoic acid	**PFOA**	335-67-1	414.07	$C_8F_{15}O_2H$	M2PFOA (IS) ($^{13}C_2{}^{12}C_6F_{15}O_2H$)	✓
Perfluorononanoic acid	**PFNA**	375-95-1	464.08	$C_9F_{17}O_2H$	-	✓
Perfluorodecanoic acid	**PFDA**	335-76-2	514.09	$C_{10}F_{19}O_2H$	M2PFDA (Surr.) ($^{13}C_2{}^{12}C_8F_{19}O_2H$)	✓
Perfluoroundecanoic acid	**PFUnA**	2058-94-8	564.09	$C_{11}F_{21}O_2H$	-	✓
Perfluorododecanoic acid	**PFDoA**	307-55-1	614.10	$C_{12}F_{23}O_2H$	-	✓
Perfluorotridecanoic acid	**PFTriA**	72629-94-8	664.11	$C_{13}F_{25}O_2H$	-	✓
Perfluorotetradecanoic acid	**PFTreA**	376-06-7	714.12	$C_{14}F_{27}O_2H$	-	✓
PERFLUOROALKYLSULFONATES						
Perfluorobutyl sulfonate	**PFBS**	375-73-5	300.10	$C_4F_9SO_3H$	-	✓
Perfluoropentane sulfonate	**PFPeS**	2706-91-4	350.11	$C_5F_{11}SO_3H$	-	Additional
Perfluorohexyl sulfonate	**PFHxS**	355-46-4	400.11	$C_6F_{13}SO_3H$	-	✓
Perfluorohexyl sulfonate	**PFHpS**	375-92-8	450.12	$C_7F_{15}SO_3H$	-	Additional
Perfluoroheptane sulfonate	**PFOS**	1763-23-1	500.13	$C_8F_{17}SO_3H$	M4PFOS (IS) ($^{13}C_4{}^{12}C_4F_{17}SO_3Na$)	✓
Perfluorooctyl sulfonate	**PFNS**	68259-12-1	550.14	$C_9F_{19}SO_3H$	-	Additional
Perfluorononane sulfonate	**PFDS**	335-77-3	600.14	$C_{10}F_{21}SO_3H$	-	Additional
FLUORINATED TELOMER SULFONATES						
1H, 1H, 2H, 2H-perfluorohexane sulfonic acid	**4:2 FTS**	757124-72-4	328.15	$C_6H_5F_9SO_3$	-	Additional
1H, 1H, 2H, 2H-perfluorooctane sulfonic acid	**6:2 FTS**	27619-97-2	428.17	$C_8H_5F_{13}SO_3$	-	Additional
1H, 1H, 2H, 2H-perfluorodecane sulfonic acid	**8:2 FTS**	39108-34-4	528.18	$C_{10}H_5F_{17}SO_3$	-	Additional
PERFLUOROOCTANESULFONAMIDE AND PERFLUOROOCTANESULFONAMIDOACETIC ACIDS						
2-(N-Methylperfluorooctanesulfonamido) acetic acid	**N-MeFOSAA**	2355-31-9	571.21	$C_{11}H_6F_{17}NSO_4$	d3-NMeFOSAA (IS) ($C_{11}{}^2H_3H_3F_{17}NSO_4$)	✓
2-(N-Ethylperfluorooctanesulfonamido) acetic acid	**N-EtFOSAA**	2991-50-6	585.24	$C_{12}H_8F_{17}NSO_4$	d5-NEtFOSAA (Surr.) ($C_{12}{}^2H_5H_3F_{17}NSO_4$)	✓

Preparation of Samples

Sample preparation and SPE were carried out according to EPA Method 537. A vacuum manifold with a high-volume sampling kit fitted with PEEK tubing was used to reduce potential PFAS contamination. Extractions were performed using Biotage-ISOLUTE® 101 polystyrenedivinylbenzne (SDVB) cartridges (500 mg / 6 mL, Part No. 101-0050-C). Each cartridge was first conditioned with methanol, followed by LCMS-grade water. The water sample was first fortified with surrogates and passed through the SPE 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:water after adding IS. It is recommended to vortex the LC vials prior to injection and analysis by LC-MS/MS to ensure that all solutions are homogenized and consistent results are obtained.

LCMS Analytical and Instrument Conditions

PFAS analyses were carried out by injecting 1 µL of the extracted aliquot into the Shimadzu LCMS-8045 and LCMS-8050 with the conditions shown in Table 2 and Table 3. PFAS compounds, including branched and linear isomers of PFHxS and PFOS, were separated using a Shim-pack™ Velox SP-C18 column.

Table 2. LC System and Parameters

LC System	:	Nexera™-X2 UHPLC System
Analytical Column	:	Shim-pack™ Velox SP-C18, 150mm x 2.1mm x 2.7µm, Part No. 227-32003-04
Solvent Delay Column	:	Shim-pack™ XR-ODS II, 75mm x 2mm x 2.2µm, Part No. 228-41605-93
Column Temp.	:	40 ^{o}C
Injection Volume	:	1 µL[#]
Mobile Phase	:	A: 20 mM Ammonium Acetate B: Methanol
Flow Rate	:	0.25 mL/min
Run Time	:	35 minutes

[#] A much lower injection volume was used as compared to the injection volume of 10 µL in EPA Method 537.

Table 3. LCMS Acquisition Parameters

MS Instrument	:	**LCMS-8045** and **LCMS-8050**
Interface	:	Electrospray Ionization (ESI)
Interface Temp.	:	300 ^{o}C
Desolvation Line Temp.	:	100 ^{o}C
Heat Block Temp.	:	200 ^{o}C
Heating Gas Flow	:	15 L/min
Drying Gas Flow	:	5 L/min
Nebulizing Gas Flow	:	3 L/min
Total MRMs	:	48

Table 4. Retention times (RT) and MRM transitions

PFAS Compound	RT (mins)	Precursor Ion	Product Ion
PFBS	8.046	298.90	80.10* 99.10
4:2 FTS	8.558	327.00	80.90* 307.00
PFHxA	8.614	312.90	269.00* 119.10
M2PFHxA (Surr.)	8.650	315.00	270.00*
PFPeS	8.666	348.90	79.90* 98.90
PFHpA	9.512	362.90	319.00* 169.00
PFHxS	9.558	398.90	80.10* 99.10
6:2 FTS	10.770	427.00	406.90* 80.00
PFOA	10.840	412.90	369.00* 169.00
PFHpS	10.859	448.90	79.90* 98.90
M2PFOA (IS)	10.877	415.00	370.00*
PFNA	12.545	462.90	418.90* 219.00
PFOS	12.550	498.90	80.10* 99.10
M4PFOS (IS)	12.575	503.00	80.00*
8:2 FTS	14.436	526.90	506.90* 80.90
PFNS	14.469	548.90	79.90* 98.90
M2PFDA (Surr.)	14.484	515.00	469.95*
PFDA	14.486	512.90	468.90* 219.00
M-N-MeFOSAA (IS)	15.403	572.90	419.00*
N-MeFOSAA	15.423	569.90	419.00* 482.90
M-N-EtFOSAA (Surr.)	16.357	588.90	419.00*
PFDS	16.397	598.90	79.90* 98.90
N-EtFOSAA	16.411	583.90	419.00* 482.90
PFUnA	16.449	562.90	519.00* 269.00
PFDoA	18.339	612.90	568.90* 169.00
PFTriA	20.035	662.00	618.90* 169.00
PFTreA	21.549	712.90	668.90* 169.00

* Quantifying ions

Since PFAS is ubiquitously present on laboratory equipment such as tubing and HPLC systems, it is impossible to completely eliminate PFAS from LC mobile phases even if LCMS-grade reagent solvents have been used. This necessitates the use of a solvent delay column for high-sensitivity analysis. A small C18 column that have higher retention of PFAS than the analytical column is placed directly upstream of autosampler to trap all PFAS contained in the mobile phase. During chromatographic elution, the analytical column gives sample-derived PFAS peaks first, separated from secondary peaks derived from mobile phase contamination trapped on the delay column.

❑ Results and Discussion

Chromatographic Separation

Two MRM transitions (one for quantifying and the other for confirmation) were selected for each target PFAS (Table 4). Figure 1 shows the overlaid MRM and total ion current (TIC) chromatograms of all PFAS in a mixed standard solution (20 ng/mL), obtained using LCMS-8050 to demonstrate the representative separation profile.

The branched and linear isomers of PFHxS (Figure 2) and PFOS (Figure 3 and Figure 4) were chromatographically separated using the Shim-pack™ Velox SP-C18 column.

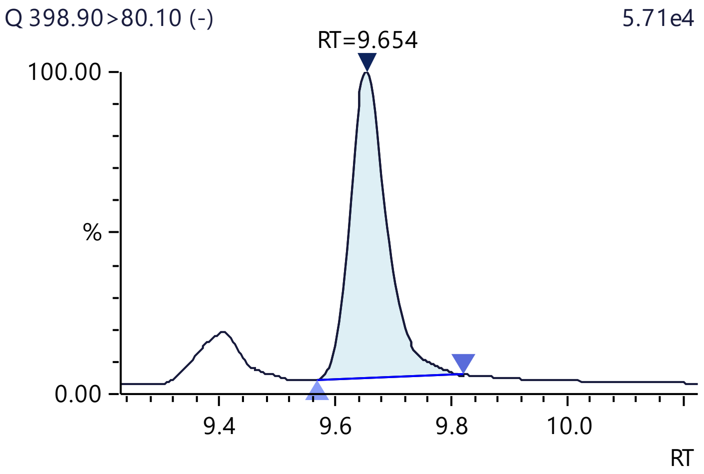

Figure 2. Separation of PFHxS isomers (20 ng/mL)

Calibration Curve Linearity and Continuing Calibration Check

The calibration solutions for target PFAS were prepared and analyzed at one injection each to generate ten-point calibration curves. All calibration curves (Table 5) had the regression coefficient (R^2) higher than 0.99 and quantitation of PFAS was performed using these calibration curves. Continuing Calibration Checks (CCC) was conducted at low (20 ng/mL), mid (50 ng/mL) and high (100 ng/mL) concentrations by 4 repeat injections over the course of

Table 5. Calibration curve linearity (1.25-100 ng/mL and %RSD of CCC (n = 4) using LCMS-8045

Compound	Linearity (R^2)	Low Concentration (20 ng/mL)		Mid Concentration (50 ng/mL)		High Concentration (100 ng/mL)	
		Conc.	%RSD	Conc.	%RSD	Conc.	%RSD
PFBS	0.9977	21	2	46	3	103	2
4:2FTS^	0.9928	22	2	45	7	94	1
PFHxA	0.9968	21	4	48	6	102	3
PFPeS^	0.9985	21	2	46	2	100	1
PFHpA	0.9974	21	5	46	5	101	2
PFHxS	0.9968	21	3	46	5	104	3
6:2 FTS^	0.9968	21	4	44	4	95	2
PFOA	0.9967	21	5	47	7	103	3
PFHpS^	0.9982	21	4	45	8	104	6
PFOS	0.9986	20	6	44	7	103	12
PFNA	0.9975	21	10	47	2	100	3
8:2 FTS^	0.9940	23	14	46	13	94	13
PFNS^	0.9978	21	2	46	6	100	5
PFDA	0.9969	21	3	47	3	98	2
N-MeFOSAA	0.9979	21	3	47	1	100	3
N-EtFOSAA	0.9980	22	4	48	2	102	5
PFDS^	0.9970	21	4	45	11	103	5
PFUnA	0.9973	21	4	48	4	100	6
PFDoA	0.9975	21	4	48	3	103	6
PFTriA	0.9967	20	5	45	5	101	5
PFTreA	0.9966	21	5	47	4	103	3

^Additional PFAS compounds not listed in EPA Method 537.

two weeks' investigation. The recovery of all PFAS compounds at the three concentration levels were well within the EPA's CCC criteria (i.e. 70–130% of the true value). The data demonstrated that both the LCMS-8045 and LCMS-8050 were capable of reliably covering the concentration range required by EPA 537, though the LCMS-8050 has a superior signal-to-noise ratio as illustrated in Figure 3 (LCMS-8045) and Figure 4 (LCMS-8050).

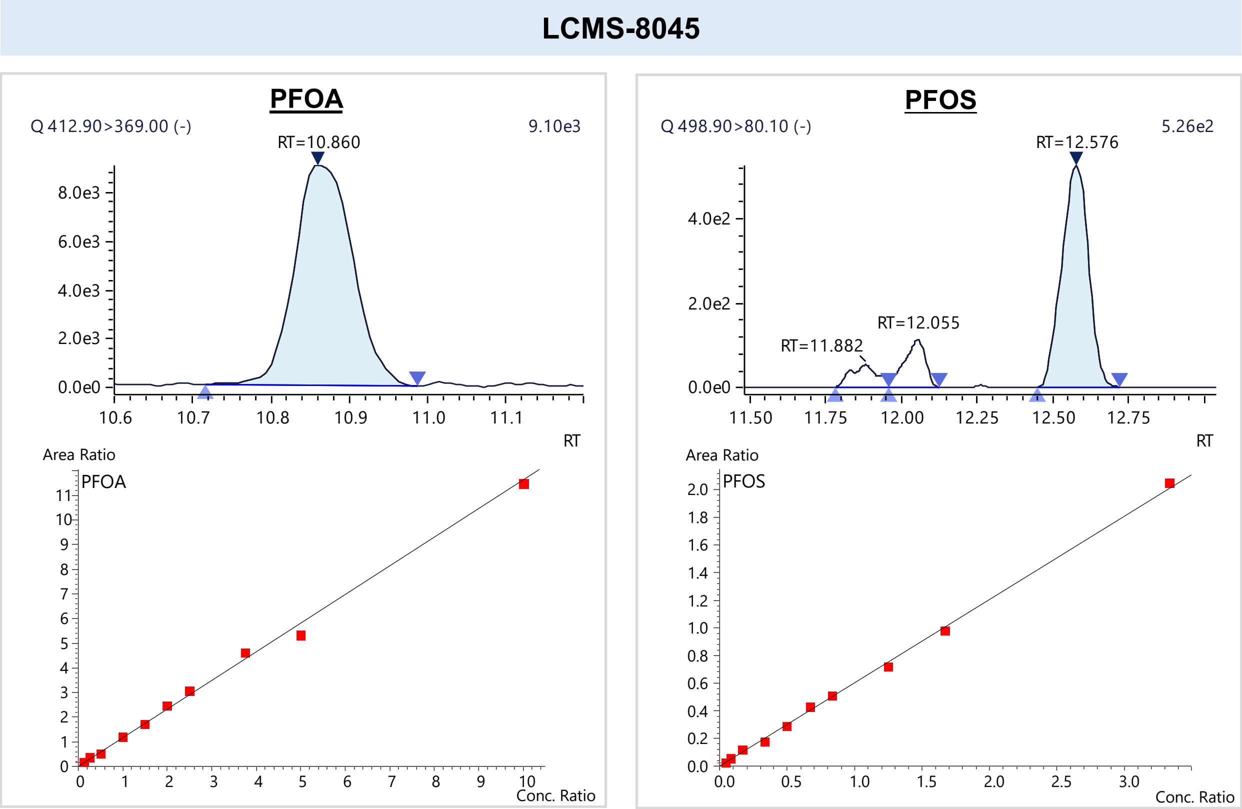

Figure 3. MRM chromatogram (for 1.25 ng/mL) and calibration curve for PFOA and PFOS using LCMS-8045

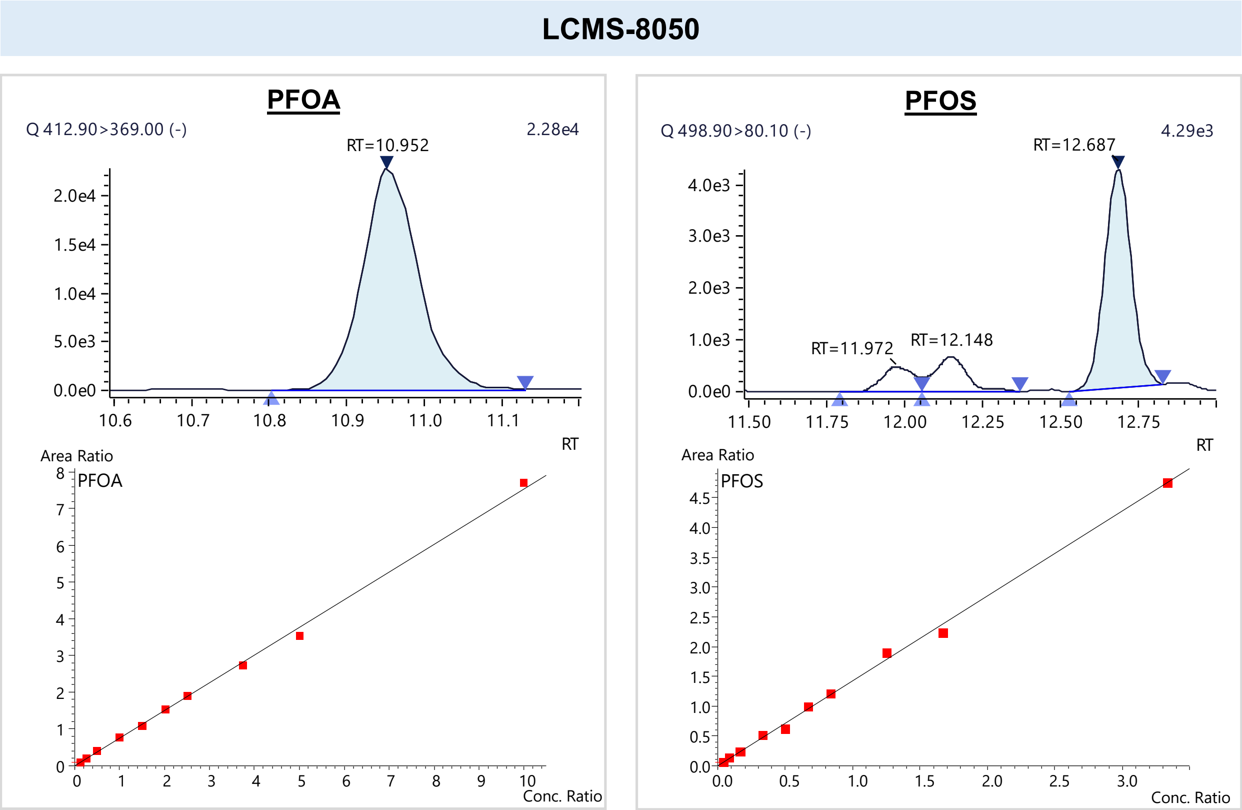

Figure 4. MRM chromatogram (1.25 ng/L) and calibration curve for PFOA and PFOS using LCMS-8050

Method Detection Limit

A Method Detection Limit (MDL) study was conducted by spiking the 250 mL water samples to obtain a spiked concentration of 5 ng/L (5 ppt) for each PFAS. These samples were then pretreated and concentrated to a final volume of 1 mL in 96:4 % methanol:water. Nine such samples were pretreated over the course of three days. The results of the MDL study using the LCMS-8045 and LCMS-8050 are tabulated (Table 6), MDLs ranging from 0.7–3.3 ng/L and 0.7–1.6 ng/L, respectively, were achieved.

Table 6. Results for Method Detection Limits (MDL) study using LCMS-8045 and LCMS-8050

Compound	Spiked Conc. (ng/L)	LCMS-8045				LCMS-8050			
		Calculated Conc. (ng/L), n = 9	% Recovery	% RSD	MDL (ng/L)	Calculated Conc. (ng/L), n = 9	% Recovery	%RSD	MDL
PFBS	5	4.2	83	12	1.5	5.1	102	8	1.2
4:2FTS^	5	5.2	104	14	2.1	4.9	98	9	1.3
PFHxA	5	4.1	81	10	1.2	4.7	94	7	1.0
PFPeS^	5	4.1	81	13	1.5	4.8	96	9	1.4
PFHpA	5	4.2	84	8	1.1	4.7	94	7	1.0
PFHxS	5	4.3	85	6	0.7	4.8	96	8	1.2
6:2 FTS^	5	4.6	92	17	2.3	4.8	96	7	1.1
PFOA	5	4.6	92	12	1.6	4.7	94	7	1.0
PFHpS^	5	4.0	80	9	1.0	4.7	95	11	1.6
PFOS	5	4.0	81	15	1.7	4.6	92	6	0.8
PFNA	5	4.0	80	7	0.8	4.8	97	5	0.7
8:2 FTS^	5	5.0	100	22	3.3	5.3	106	11	1.7
PFNS^	5	4.0	81	9	2.1	4.4	91	8	1.1
PFDA	5	4.1	83	8	1.0	4.8	95	10	1.4
N-MeFOSAA	5	3.9	78	15	1.7	4.6	91	9	1.2
N-EtFOSAA	5	3.8	77	11	1.2	4.4	88	10	1.3
PFDS^	5	4.1	82	18	2.2	4.6	92	10	1.4
PFUnA	5	4.1	82	12	1.5	4.4	88	11	1.4
PFDoA	5	4.0	79	14	1.6	4.3	86	9	1.2
PFTriA	5	3.9	78	13	1.4	4.4	87	10	1.3
PFTreA	5	4.0	79	15	1.8	4.3	86	11	1.3

^Additional PFAS compounds not listed in EPA Method 537.

Accuracy and Precision

The initial demonstration of accuracy and precision was carried out using seven replicate LCMS-grade water blanks fortified with each PFAS at 60 ng/L (ppt). Table 7 shows the average measured concentrations of the seven replicates and the results of accuracy and precision evaluation expressed as percentage recovery and relative standard deviation (RSD). The recoveries obtained using the LCMS-8045 and LCMS-8050 were all within ± 20% of the true value, meeting the criteria listed by EPA.

Table 7. Accuracy (% Recovery) and precision (% RSD) of target PFAS at 60 ng/L for LCMS-8045 and LCMS-8050

Compound	LCMS-8045			LCMS-8050		
	Average Conc. (ng/L), n = 7	% Recovery	% RSD	Average Conc. (ng/L), n = 7	% Recovery	% RSD
PFBS	52	87	13	54	90	6
4:2FTS^	54	90	13	56	94	8
PFHxA	52	87	12	52	87	9
PFPeS^	54	90	14	54	90	9
PFHpA	53	88	16	52	87	10
PFHxS	54	89	13	54	90	8
6:2 FTS^	55	92	15	55	92	9
PFOA	52	86	14	53	88	11
PFHpS^	54	90	13	53	89	9
PFOS	53	89	17	51	85	12
PFNA	51	86	16	64	107	21
8:2 FTS^	51	86	19	56	93	9
PFNS^	54	89	15	55	92	11
PFDA	52	87	13	52	87	10
N-MeFOSAA	53	88	15	53	88	9
N-EtFOSAA	54	90	15	56	93	10
PFDS^	52	86	17	53	89	9
PFUnA	51	85	11	53	88	10
PFDoA	51	86	14	51	85	9
PFTriA	49	82	14	51	85	9
PFTreA	49	82	14	49	81	8

^Additional PFAS compounds not listed in EPA Method 537.

Table 8. Average conc. (n = 7), % recovery and % RSD of surrogates in spiked samples using LCMS-8045 and LCMS-8050

Compound	Fortified Conc. (ng/L)	LCMS-8045			LCMS-8050		
		Average Conc (ng/L), n=7	% Recovery	% RSD	Average Conc (ng/L), n=7	% Recovery	% RSD
M2PFHxA	40	43	107	14	40	101	10
M2PFDA	40	44	109	12	42	106	13
M-N-EtFOSAA	160	175	109	14	160	100	12

Surrogate Recovery

Surrogate recovery was similarly investigated by first spiking the water samples with surrogates, prior to sample extraction. The spiked water samples undergo the sample preparation procedures and LCMS analysis. The calculated recovery of the surrogates must be in the range of 70–130% (EPA, Section 9.3.5) to demonstrate good method performance.

Seven water samples were spiked with 10 ng of M2PFHxA, 10 ng of M2PFDA and 40 ng of M-N-EtFOSAA giving a concentration of 40 ng/L for M2PFHxA and M2PFDA and 160 ng/L for M-N-EtFOSAA in the 250 mL water sample. The calculated recoveries obtained using LCMS-8045 and LCMS-8050 are shown in Table 8 using a Mean Response Factor. All recoveries were within ± 10%, well achieving EPA requirements.

Summary and Conclusions

This application note described and demonstrated the use, performance and compatibility of Shimadzu UFMS™ for EPA Method 537 with seven additional PFAS targets. In this study, all samples and blanks were extracted by the same SPE procedure and analyzed using the same LC-MS/MS method on different instrument models. Method detection limits of 0.7–1.7 ng/L (LCMS-8050) and 0.7–3.3 ng/L (LCMS-8045) were obtained and both systems fulfilled all of the EPA's requirements for PFAS analysis in drinking water. This was achieved with a 1 µL injection volume, in contrast to 10 µL as described in the original EPA M537. The smaller injection volume (less burden on the LCMS) would make the method more robust and reduce the long-term cost of ownership. Moreover, Shimadzu's high-speed and high-sensitivity UFMS™ instruments allow users to further increase productivity by running multiple EPA methods on the same system, in which case using the LCMS-8050 is recommended.

References

[1] U.S. EPA, "EPA Method 537: Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by SPE and LC/MS/MS," Washington D.C., 2009.

[2] ASTM International, "ASTM D7979-17: Standard Test Method for Determination of Perfluorinated Compounds in Water, Sludge, Influent, Effluent and Wastewater by LC/MS/MS," Conshohocken PA, 2017.

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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 note 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 note 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 App Note 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 note, 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 LCMS 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.

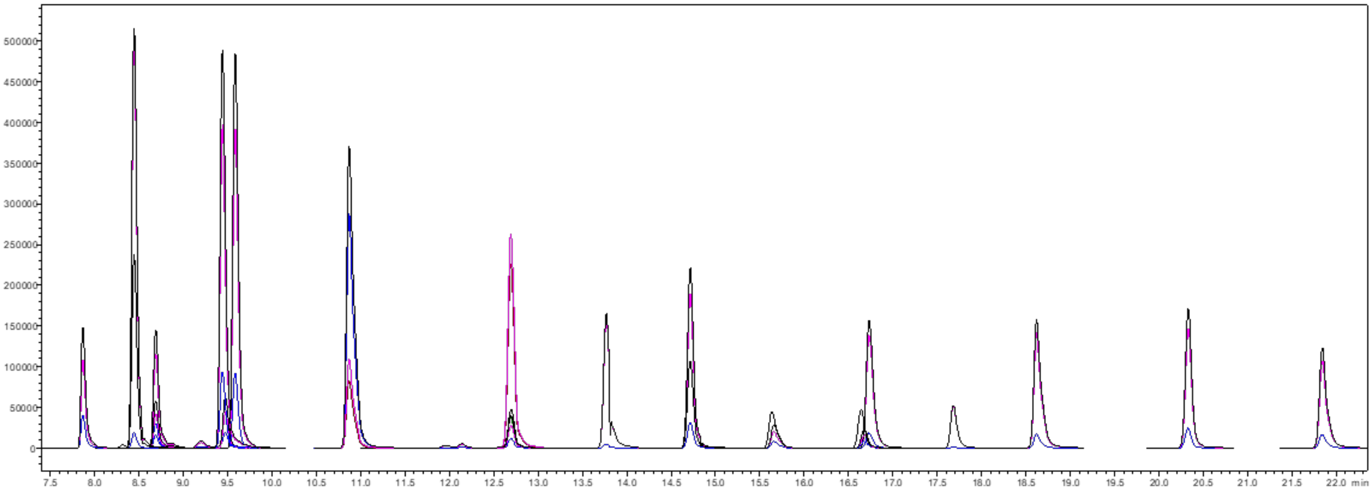

Figure 1: MRM (Pink and Blue) and TIC (black) chromatograms of all PFAS in EPA 537.1 at 80 ppt sample concentration

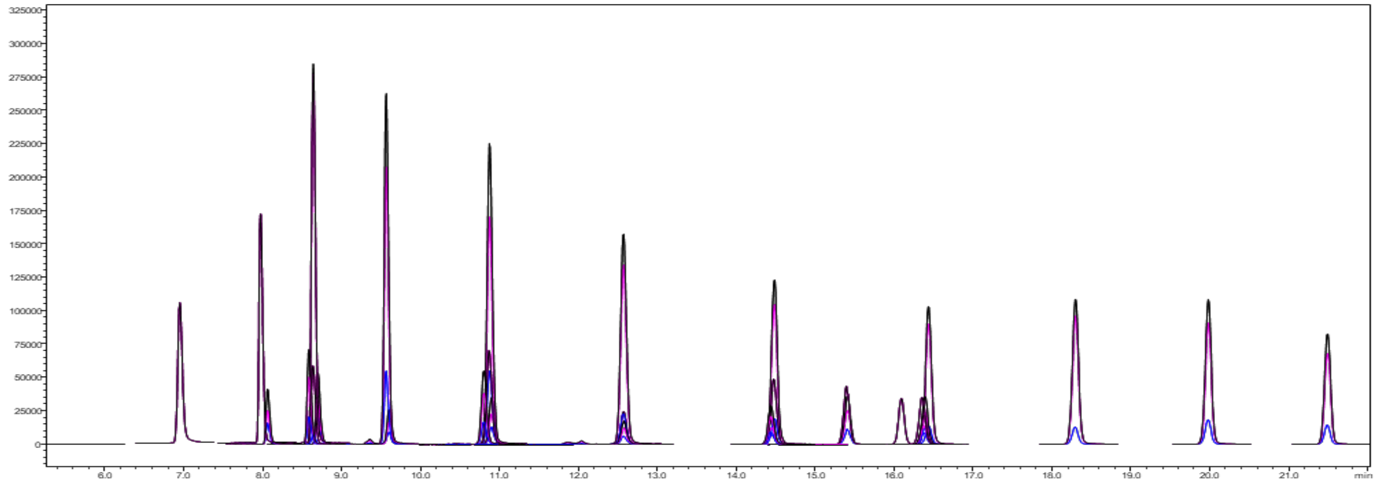

Figure 2: MRM (Pink and Blue) and TIC (black) chromatograms of all PFAS in EPA 537 at 80 ppt sample concentration

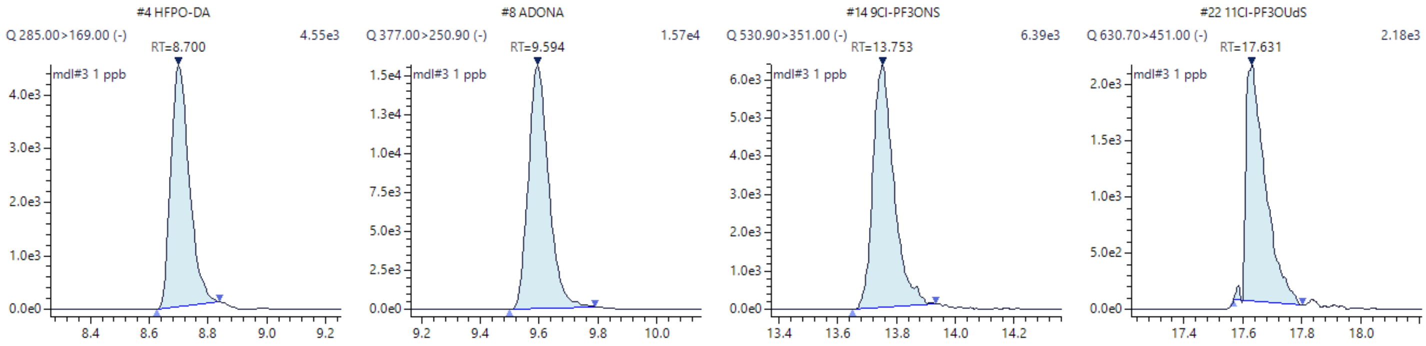

Figure 3: Chromatograms for all new compounds in EPA 537.1 at a representative MDL study

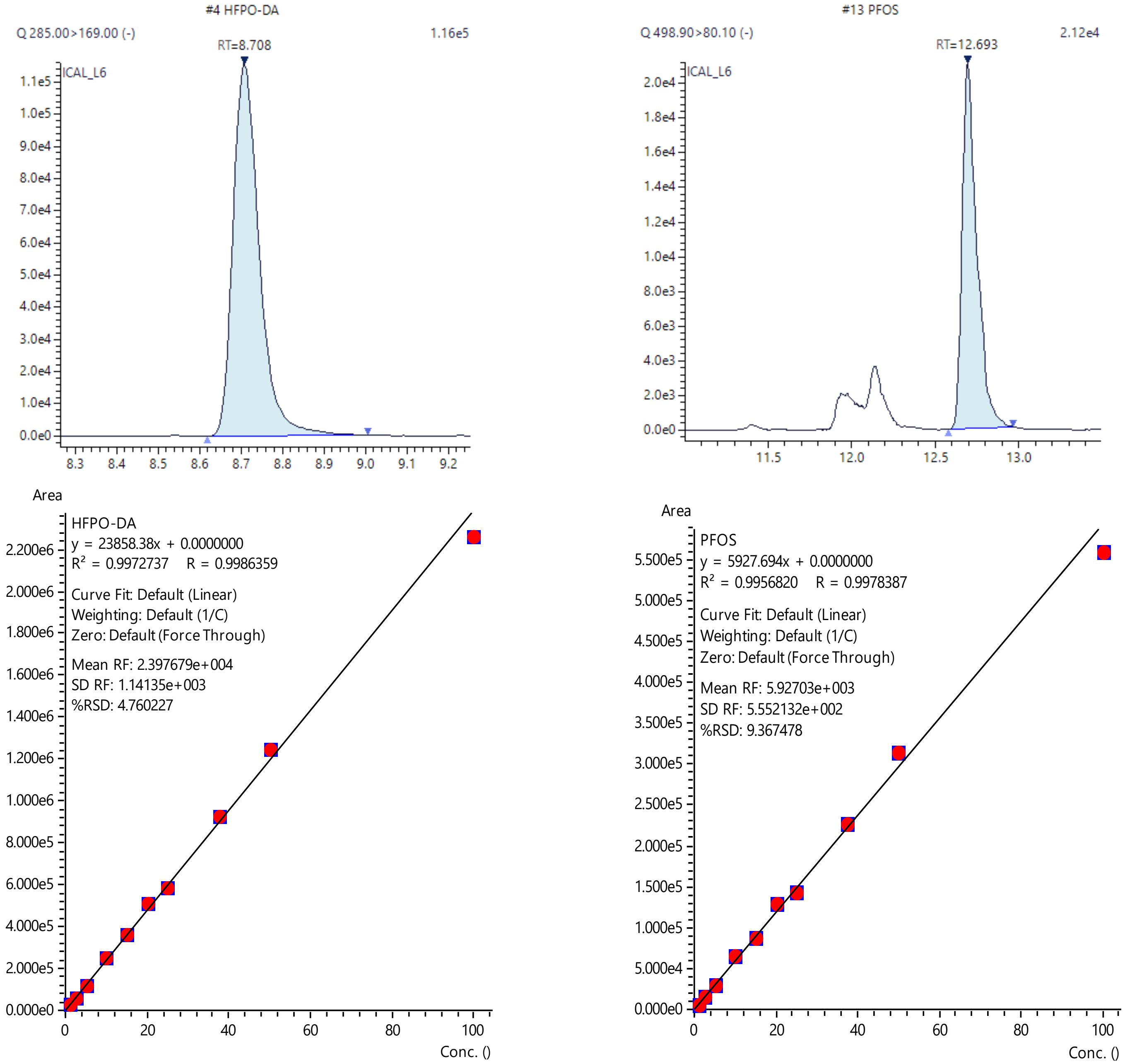

Figure 4: MRM chromatogram (for 80 ppt sample concentration) and calibration curve for HFPO-DA and PFOS using LCMS-8045

■ 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: LCMS 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

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Application News

No. LCMS-106

Liquid Chromatography Mass Spectrometry

Analysis of Per- and Polyfluoroalkyl Substances (PFAS) Specified in EPA M8327 using the LCMS-8050 Triple Quadrupole Mass Spectrometer

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■ Abstract

The Environmental Protection Agency (EPA) has recently published draft SW-846 Method 8327 for the analysis of PFAS in groundwater, surface water, and wastewater. No other EPA method for PFAS analysis in complex matrices was available; hence, this method in its final version will provide a tool for monitoring selected PFAS in non-potable waters. This application note demonstrates that the LCMS-8050 meets and exceeds the Quality Assurance and Quality Control criteria specified in the method. All analytes were reliably quantitated at or less than 5 ppt. Ultimately, this work provides a fast and robust solution for addressing the challenges in the quantitation of low levels of PFAS in non-potable waters.

■ 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[1], together with their ubiquitous use has resulted in the accumulation of PFAS in the environment.

The PFAS family encompasses over 4,000 chemicals, with the commonality of having a per- or poly-fluorinated carbon backbone compounds. Due to their potential deleterious effects on humans and ecosystems, PFOA and PFOS are no longer manufactured in the US; this has resulted in the introduction of replacement chemicals. There is a need of robust and fast analytical methods to ensure accurate quantitation of low levels (in low ng/L range) of legacy and replacement PFAS entering the environment and there are concerns about their effects on humans and ecosystems as well as the compounds ability to repel oil and water.

Research into the adverse health effects[2-6] of PFAS in humans is ongoing. Many studies have linked PFOA and PFOS to reproductive damage, liver and kidney damage, and weakened immune systems. PFAS exposure has also been linked to elevated cholesterol levels.

This application note provides a fast and robust solution based on the use of Shimadzu LCMS-8050 for all analytes listed in EPA Method 8327. Results demonstrate that the instrument's performance exceeds the requirements outlined in the draft EPA method. Most importantly, the results confirm that laboratories currently analyzing samples by ASTM Method D7979[7-8] using Ultra-fast LC-MS/MS (UFMS™) Analysis of PFAS in environmental samples can easily update their workflow to implement EPA Method 8327.

Keywords: Per- and Polyfluorinated Alkyl Substances, PFAS, Perfluorinated Compounds, PFCs, PFOA, PFOS, Persistent Organic Pollutants, POPs, Triple Quad, Wastewater, Ground Water, Surface Water, EPA Method 8327, ASTM D7979

■ Analyte List

EPA Method 8327 analyzes 24 target PFAS compounds and 19 surrogates in reagent, ground, surface, and wastewater. Target compounds and their respective acronyms, surrogate compounds, and their chemical classes are listed in Table 1. For the remainder of this application note, refer to the acronyms in Table 1.

Table 1: Target analytes, surrogates, acronyms and CAS # included in this method

Analyte	Acronym	CAS #	Surrogates
Sulfonic acids			
Perfluorobutyl sulfonic acid	PFBS	29420-49-3	13C3-PFBS
Perfluorohexyl sulfonic acid	PFHxS	3871-99-6	13C3-PFxS
Perfluorooctyl sulfonic acid	PFOS	1763-23-1	13C8-PFOS
1H,1H, 2H, 2H-perfluorohexane sulfonic acid	4:2 FTS	757124-72-4	13C2-4:2 FTS
1H, 1H, 2H, 2H-perfluorooctane sulfonic acid	6:2 FTS	27619-97-2	13C2-6:2 FTS
1H, 1H, 2H, 2H-perfluorodecane sulfonic acid	8:2 FTS	39108-34-4	13C2-8:2 FTS
Perfluoro-1-pentanesulfonic acid	L-PFPeS	706-91-4	-
Perfluoro-1-heptanesulfonic acid	L-PFHpS	375-92-8	-
Perfluoro-1-nonanesulfonic acid	L-PFNS	68259-12-1	-
Perfluoro-1-decanesulfonic acid	L-PFDS	2806-15-7	-
Carboxylic acids			
Perfluorobutanoic acid	PFBA	375-22-4	13C4-PFBA
Perfluoropentanoic acid	PFPeA	2706-90-3	13C5-PFPeA
Perfluorohexanoic acid	PFHxA	307-24-4	13C5-PFHxA
Perfluoroheptanoic acid	PFHpA	375-85-9	13C4-PFHpA
Perfluorooctanoic acid	PFOA	335-67-1	13C8-PFOA
Perfluorononanoic acid	PFNA	375-95-1	13C9-PFNA
Perfluorodecanoic acid	PFDA	335-76-2	13C6-PFDA
Perfluoroundecanoic acid	PFUnA	2058-94-8	13C7-PFUnA
Perfluorododecanoic acid	PFDoA	307-55-1	13C2-PFDoA
Perfluorotridecanoic acid	PFTriA	72629-94-8	-
Perfluorotetradecanoic acid	PFTreA	376-06-7	13C2-PFTreA
Sulfonamides and sulfonamidoacetic acids			
N-ethylperfluoro-1-octanesulfonamidoacetic acid	N-EtFOSAA	2991-50-6	D3-N-EtFOSAA
N-methylperfluoro-1-octanesulfonamidoacetic acid	N-MeFOSAA	2355-31-9	D3-N-MeFOSAA
Perfluoro-1-octanesulfonamide	FOSA	754-91-6	13C8-PFOSA

■ Method

This application news describes and demonstrates the use and performance of the Shimadzu LCMS-8050 for the analysis of 43 PFAS, 24 targets and 19 surrogates, in reagent, ground, surface and wastewater matrices as outlined in draft EPA M8327 (as of September 2019). EPA provided a set of supplies including 15 mL polypropylene (PP) tubes, analytical column, delay column, PFAS precision and recovery standard (Wellington), labeled PFAS extraction standard (Wellington), certified amber glass 2 ml vials, PP septumless caps for 2 ml vials, GXF/GHP syringe filters membrane 0.2 um filters and 10 ml metal luer-lock all glass syringe.

An equivalent to Shimadzu Shim-pack GIST Phenyl-Hexyl, 2.1×100 mm and 3.0 µm particle size analytical column was used to conduct the analysis for all PFAS compounds (Shimadzu part no. 227-30713-03) along with a Shimadzu Shim-pack XR-ODS 50mm x 3.0mm x 2.2 µm as delay column (Shimadzu part no 228-41606-92). Multiple Reaction Monitoring (MRM) transitions were optimized using Flow Injection Analysis (FIA) for all compounds.

Mobile Phase A consisted of 20 mM Ammonium acetate in 95:5 H_2O: ACN. Mobile Phase B consisted of 10 mM ammonium acetate in 95:5 ACN: H2O. A 30 µL injection volume was used for all calibration levels. A 0.3 mL/min flow rate was used. Chromatography was adjusted to obtain maximum resolution between peaks in the shortest time possible with minimum co-elution of isomers. Overall runtime for each injection was 21 minutes, including re-equilibration for both the delay and the analytical column. The total run time of 21 minutes includes a final wash out with concentrated acetonitrile to flush the column, remove background residuals contaminants and restore column performance before starting the next run. The method could easily be modified to include isotopic dilution or internal calibration if needed for quantifying the concentrations.

The LC/MS/MS analysis was performed using a Shimadzu Nexera UHPLC system coupled with LCMS-8050 triple quadrupole mass spectrometer. An injection volume of 30 µL was used in this study. A detailed description of the LC/MS/MS parameters is included in Table 2.

Table 2: Chromatography and mass spectrometer conditions

Parameter	**Value**	
LCMS	Shimadzu LCMS-8050	
Analytical Column	Shim-pack GIST Phenyl-Hexyl (2.1 mm ID. x 100 mm L., 3 µm) Part No 227-30713-03	
Solvent Delay Column	Shim-pack XR-ODS (3 mm ID. x 50 mm L., 2.2 µm) Part No. 228-41606-92	
Column Oven Temperature	40 °	
Injection Volume	30 µL	
Mobile Phase	A: 20 mmol Ammonium Acetate in 5 % (v/v) Acetonitrile in reagent water B: 10 mmol Ammonium Acetate in 95 % (v/v) Acetonitrile in reagent water	
Gradient Flow rate	0.3 mL/ Min	
Gradient	Time (minutes)	% B
	0	0
	1	20
	6	50
	14	100
	17	100
	18	0
	21	0
Run time	21 minutes	
Nebulizing gas flow	5 L/min	
Heating gas flow	15 L /Min	
Interface temperature	300 °C	
Desolvation Line temperature	100 °C	
Heat Block temperature	200 °C	
Drying gas flow	5 L /min	
Acquisition cycle time	21 min	
Total MRMs	66	

Fluorotelomer acids, observed as $[M-H]^-$ and $[M-HF-H]^-$ can result in an ion with the same m/z as the unsaturated fluorotelomer acid. Even under optimized chromatography, these compounds have near identical retention times. The lower ESI heater temperature reduces HF loss and minimizes false identification of fluorotelomer acids. Temperature conditions may vary depending on the type of applications performed[9].

All compound parameters, including precursor ion, product ion, and collision energies were optimized using FIA, bypassing the analytical column using Lab Solutions software. There are at least two MRM transitions for most of the analytes that are listed in Table 3.

Table 3: MRM transitions, retention times and collision energies

Component	**Retention Time (minutes)**	**Transition (m/z)**	**Collision energy (V)**
PFBA	3.341	213 > 169	9
MPFBA	3.341	217 > 172	9
PFPeA	3.941	263 > 219	8
M5PFPeA	3.940	268 > 223	8
4-2 FTS	4.444	327 > 307 327 >81	18 35
M4-2 FTS	4.442	329 > 309	20
PFHxA	4.683	313 > 269 313 >119	9 21
M5PFHxA	4.680	318 > 273	11
PFBS	4.709	299 > 80 299 >99	30 28
M3PFBS	4.813	302 > 80	34
PFHpA	5.401	363 > 319 363 >169	9 16
M4PFHpA	5.400	367 > 322	10
PFPeS	5.606	349 > 80 349 >99	42 30

6-2 FTS	5.797	427 > 407 427 >81	23 39
M6-2 FTS	5.799	429 >409	22
PFOA	6.048	413 > 369 413 >169	10 17
M8PFOA	6.051	421 > 376	10
PFHxS	6.305	399 > 80 399 >99	43 22
M3PFHxS	6.306	402 > 80 403 >84	49 49
PFNA	6.642	463 > 419 463 >219	11 16
M9PFNA	6.641	472 > 427	12
8-2 FTS	6.927	527 > 507 527 >81	26 49
M8-2 FTS	6.928	529 > 509 527 >81	26 49
PFHpS	6.928	449 > 80 449 >99	51 37
N-MeFOSAA	7.254	570 > 419 570 >483	21 16
d3M N-MeFOSAA	7.243	573 > 419	20
PFDA	7.189	513 > 468.9 413 >219	11 17
M6PFDA	7.188	519 > 474	11
N-EtFOSAA	7.469	584 > 419 584 >483	20 16
M N-EtFOSAA	7.463	589 > 419	21
PFOS	7.483	499 > 80 499 >99	54 38
M8PHOS	7.484	507 > 80	55
PFUdA	7.697	563 > 519 563 >269	12 16
M7PFUdA	7.695	570 > 525	12
PFNS	8.009	549 > 80 549 >99	54 44
PFDoA	8.181	613 > 569 613 >169	12 21
MPFDoA	8.179	615 > 570	11
FOSA	8.498	498 > 78	43
M8FOSA	8.498	506 > 78	48
PFDS	8.523	599 > 80 599 >99	55 50
PFTriA	8.662	663 > 619 663 >169	12 27
PFTeDA	9.155	713 > 669 713 >169	13 27
M2PFTeDA	9.130	715 > 670	15

Calibration Standards

Standards available from Wellington Laboratories were used for these studies (Catalog no. PFAC-24PAR and MPFAC-24ES). These standards were then diluted to working standards as outlined in Section 7.4 of EPA Method 8327 using 95:5 acetonitrile:water as the diluent. The working standards were used to create a calibration curve ranging from 5-200 ppt with the injection solvent consisting of 50:50 water:methanol with 0.1% acetic acid in order to match the injection solvent for the extracted samples. Filtration was not performed on the calibration standards

Sample Preparation

EPA Method 8327 was tested using reagent water, surface water, ground water, and wastewater as sample matrices. This report outlines data collected with representative chromatograms and tables for each matrix tested. Each sample was diluted 50:50 with MeOH and 0.1% acetic acid, spiked with isotopically labeled surrogates and vortexed for 2 min. The samples were then filtered through /0.2 µm syringe filters and analyzed by LC/MS/MS.

■ Results and Discussion

It is known that PFAS can be present in reagents, glassware, pipettes, tubing, degassers and other parts from the LC-MS/MS instruments. PFAS contamination coming from the LC system is eliminated using a delay column placed between the reagents and the sample valve. This separates PFAS in the sample from the PFAS in the LC system. All supplies used to conduct the study were free from PFAS contamination. To monitor the lack of contamination two blanks were injected at the beginning of each batch: system null injection (air injection, shown in Figure 1) and reagent blank (0.1% acetic acid in high purity water:methanol (50:50), shown in Figure 2). Data displayed in Figures 1 and 2 demonstrates the absence of PFAS in the instrument and the materials used for analysis, respectively.

Calibration was performed for all PFAS targets using a nine-point calibration curve, ranging from 5 ng/L - 200 ng/L. The linearity of the curve was determined using a 1/x weighting factor and not forcing through zero. Excellent linearity was obtained with correlation coefficients (r^2) greater than 0.99 for all analytes or transitions. Calibration residuals of each standards were within ±30%. Figure 3 shows a total ion chromatogram and MRMs from a 5 ng/L standard; this figure demonstrates the separation and peak shape of targets at the lowest concentration included in the calibration curve. Figure 4 shows a chromatogram of a mid-level standard at 80 ng/L for all PFAS targets and surrogate compounds included in draft EPA method 8327 and confirms that peak shape is maintained at higher concentrations.

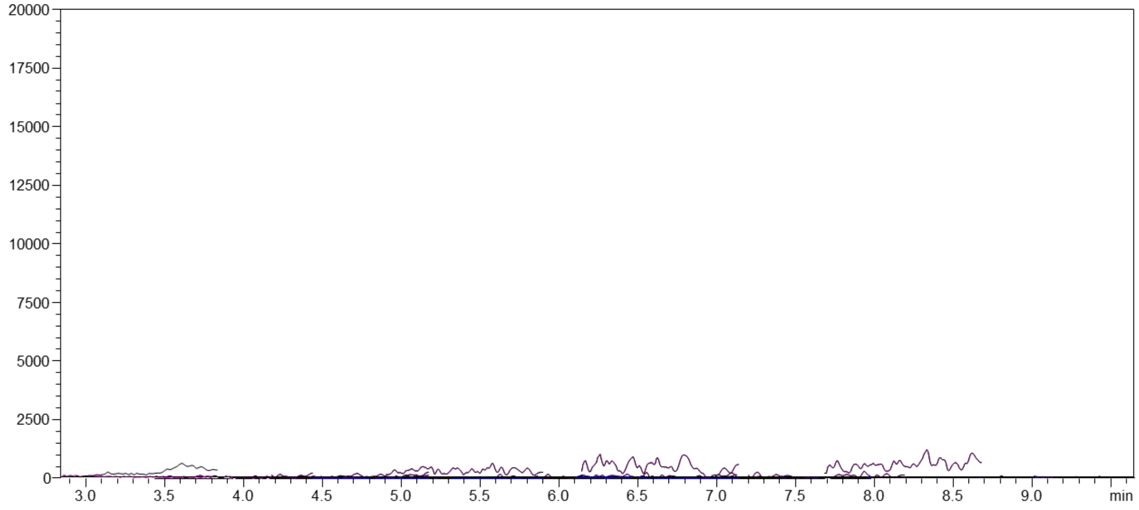


Figure 1: TIC Chromatogram of a Null Blank

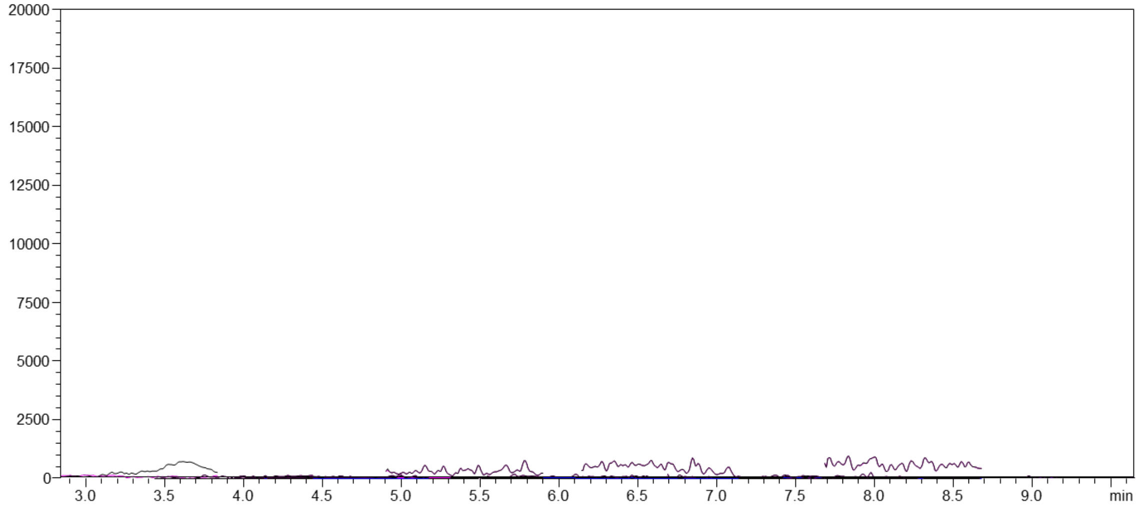


Figure 2: TIC Chromatogram of a reagent blank in 50:50 MeOH: H2O with 0.1% acetic acid

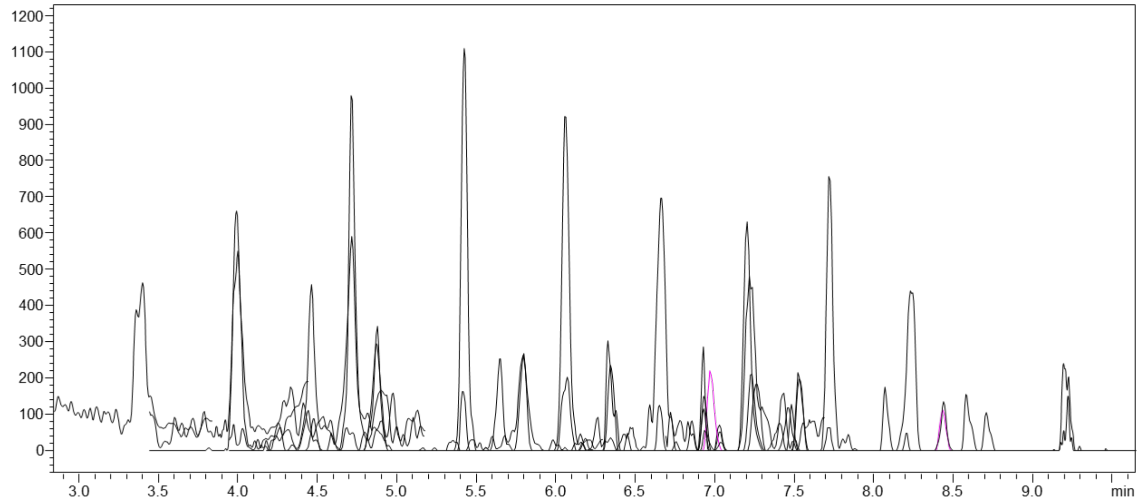


Figure 3: TIC (black) chromatograms and MRM transitions (other colors) of all PFAS in EPA Method 8327 at the low-level calibrator, 5 ppt

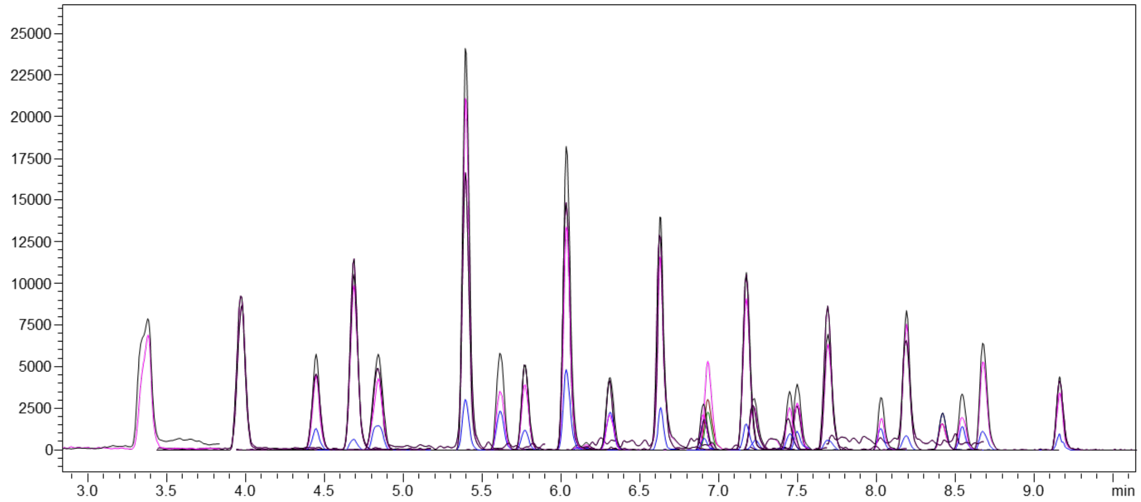
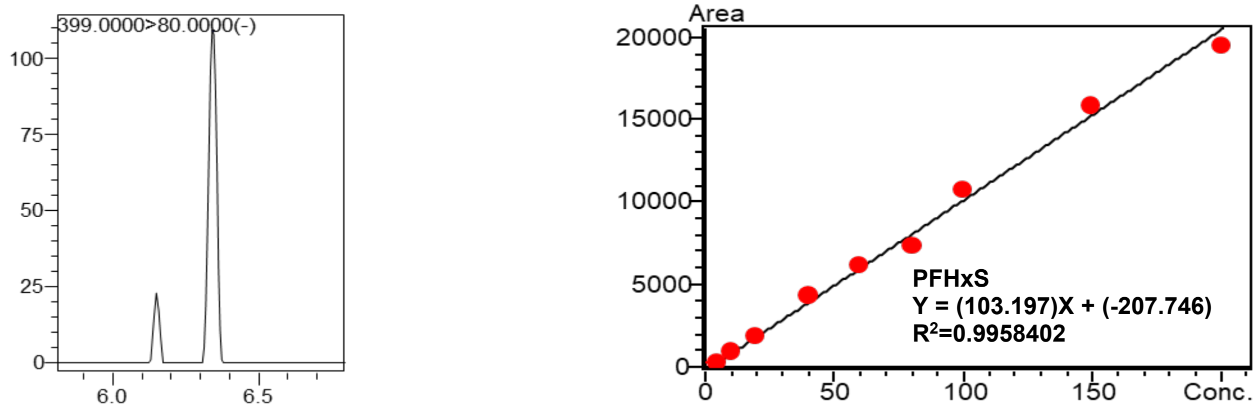


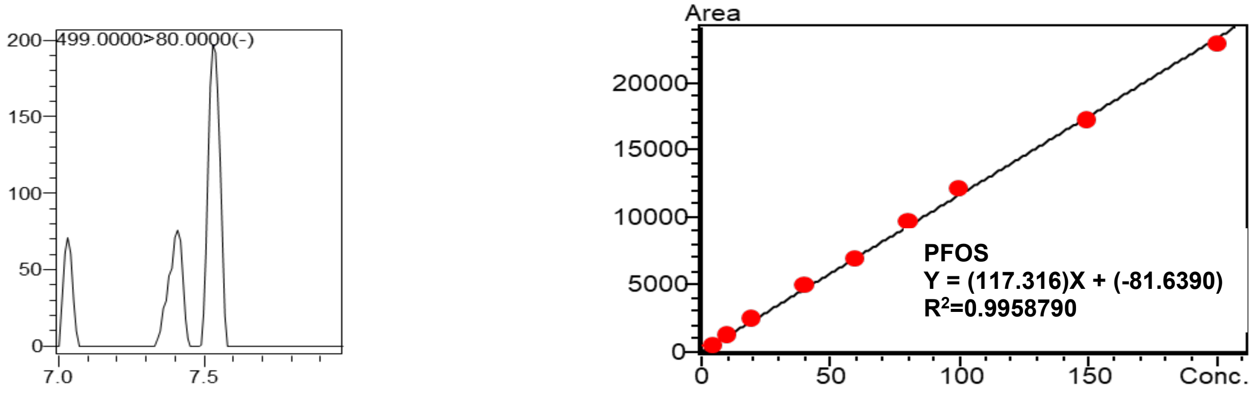
Figure 4 TIC (black) chromatograms and MRM transitions (other colors) of all PFAS in EPA Method 8327 at the mid-level, 80ppt calibrator

Figure 5 shows an extracted ion chromatogram of representative peak at 5 ng/L and calibration curves for PFHxS, PFOS and PFTreA. Table 4 lists the calculated concentrations, percent recovery for all targets in EPA Method 8327 at representative low, mid and high-level concentrations. All percent recoveries were within the limits established as acceptable in draft method EPA 8327 (50%-150% for the lowest calibration standard and 70%-130% for the remaining ones). Signal to Noise ratio for each target compound at 5 ng/L is also included in Table 4. All compounds except PFHxS presented S/N larger than 3these results suggest that for most of the compounds lower sensitivity could be achieved.

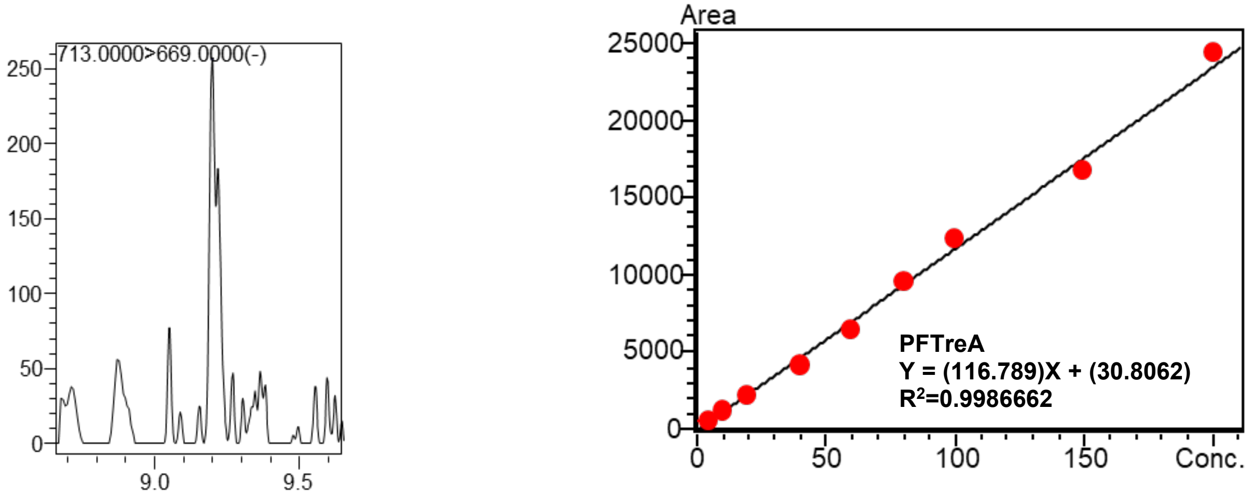
Figure 6 shows the chromatogram for 24 PFAS compounds spiked at 60 ppt in various matrices, including reagent water, ground water, surface water, and wastewater. Results show that despite the differences in the sample composition and presence of potential interferences, the separation and peak shape is maintained in all samples types analyzed.



PFHxS, 5.0 ng/L



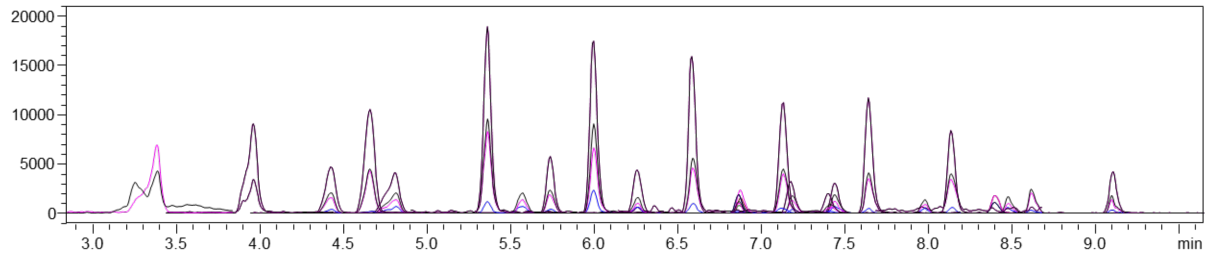
PFOS, 5.0 ng/L



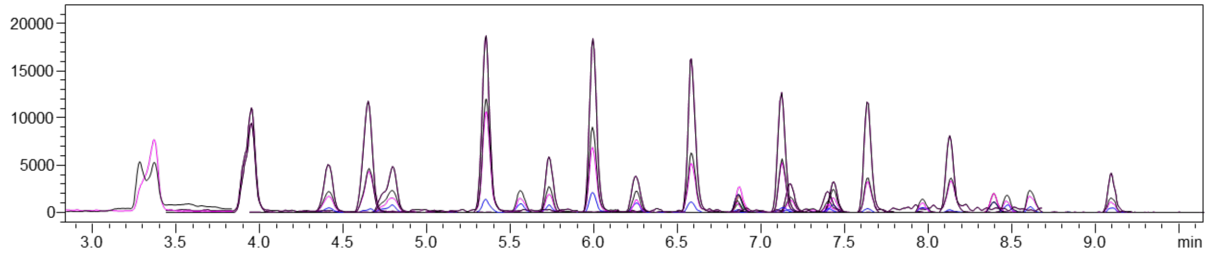
PFTreA, 5.0 ng/L

Figure 5: Representative Chromatograms and Calibration curves for compounds listed in EPA Method 8327

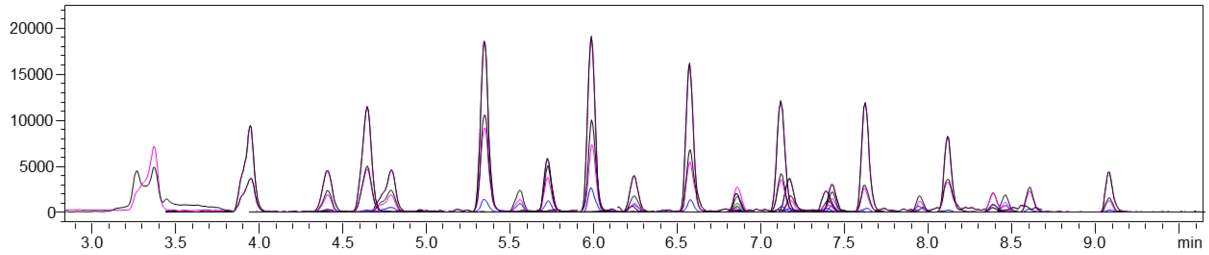
A. Reagent Water



B. Ground Water



C. Surface Water



D. Waste Water

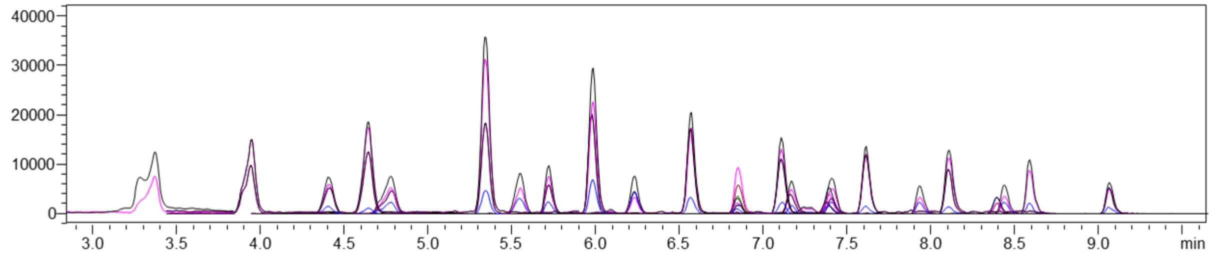


Figure 6: Chromatogram (TIC and MRMs) of 24 PFAS Compounds spiked at the 60 ng/L in: A) Reagent Water; B) Ground Water; C) Surface Water, and D) Waste Water

Table 4: Calculated concentrations for the low, mid, and high-level standards for all targets in EPA Method 8327.

			5 ppt		40 ppt		200 ppt	
Compound	**RT (min)**	**Conc**	**% Recoveries**	**Signal/noise (S/N) (*)**	**Conc**	**% Recoveries**	**Conc**	**% Recoveries**
PFBA	3.382	4.48	90	3.28	42.37	106	196.7	98
M4PFBA	3.378	4.65	93	72.36	40.14	100	200.1	100
PFPeA	3.897	5.20	104	21.57	41.49	104	200.8	100
M5PFPeA	3.892	5.09	102	268.79	40.34	101	202.3	101
4-2 FTS	4.333	4.56	91	212.65	41.08	103	199.8	100
M2-4-2 FTS	4.319	4.82	96	71.11	41.48	104	200.8	100
PFHxA	4.544	4.95	99	44.95	41.10	103	198.3	99
M5PFHxA	4.542	4.99	100	830.68	40.57	101	198.5	99
PFBS	4.676	4.25	85	9.21	38.96	97	195.2	98
M3PFBS	4.674	5.15	103	172.98	39.32	98	202.2	101
PFHpA	5.219	4.99	100	37.17	39.01	98	196.1	98
M4PFHpA	5.217	4.93	99	1247.7	38.68	97	199.6	100
PFPeS	5.399	5.31	106	196.02	41.15	103	199.6	100
6-2 FTS	5.586	4.25	85	75.54	37.33	93	183.1	92
M2-6-2 FTS	5.591	4.94	99	61.36	39.19	98	205.0	103
PFOA	5.826	4.61	92	46.56	40.05	100	198.7	99
M8PFOA	5.827	4.50	90	611.9	41.73	104	195.5	98
PFHxS	6.062	5.69	114	(INF)	41.34	103	195.3	98
M3PFHxS	6.064	5.08	102	(INF)	41.46	104	204.1	102
PFNA	6.401	3.83	77	23.64	38.10	95	198.9	100
M9PFNA	6.397	5.13	103	292.26	39.58	99	195.4	98
8-2 FTS	6.681	4.04	81	(INF)	33.29	83	200.1	100
M2-8-2 FTS	6.673	4.92	98	31.79	35.90	90	198.6	99
PFHpS	6.663	4.35	87	(INF)	41.09	103	197.8	99
N-MeFOSAA	7.005	5.30	106	(INF)	39.93	100	208.6	104
d3-NMeFOSAA	7.001	5.98	120	(INF)	39.33	98	197.8	99
PFDA	6.93	5.45	109	64.37	40.68	102	201.1	101
M6PFDA	6.927	5.02	100	596.91	39.27	98	201.5	101
N-EtFOSAA	7.221	5.67	113	14.63	38.42	96	202.8	101
d5-NEtFOSAA	7.221	5.45	109	(INF)	44.72	112	200.8	100
PFOS	7.204	5.39	108	(INF)	34.56	86	196.8	98
M8PFOS	7.201	4.71	94	(INF)	36.86	92	195.4	98
PFUnA	7.426	5.42	108	21.82	41.21	103	197.1	99
M7PFUnA	7.423	5.34	107	545.68	43.51	109	203.8	102
PFNS	7.705	4.94	99	(INF)	44.30	111	198.2	99
PFDoA	7.893	5.14	103	54.66	37.82	95	205.8	103
M2PFDoA	7.889	5.11	102	(INF)	39.36	98	202.2	101
FOSA	8.207	4.95	99	(INF)	41.83	105	200.8	100
M8FOSA	8.215	4.94	99	1663.83	41.12	103	201.9	101
PFDS	8.188	4.94	99	(INF)	41.55	104	200.1	100
PFTriA	8.359	4.40	88	43.58	42.18	105	198.1	99
PFTreA	8.816	4.66	93	21.34	39.44	99	199.8	100
M2PFTreA	8.82	4.48	99	1703.08	37.43	94	198.0	99

(*) INF: S/N value when background noise is zero for a compound.

Table 5 outlines the Accuracy (spike %recovery) and precision (%RSD) of targets and surrogates spiked at 80 ng/L in reagent water. The mean recovery for all compounds were within 70 to 130% and the precision (%RSD) were ≤ 20%, well within the QA criteria outlined in drafted EPA method 8327.

Tables 6-9 outline the surrogate percent recoveries and precision (%RSD) spiked at 160 ng/L in, reagent water, ground water, surface water and wastewater samples. Surrogate recoveries for all PFASs tested were within 70 to 130% as required by the method acceptance criteria and the precision (RSD%) were ≤ 20%.

Table 5: Accuracy (spike %recovery) and precision (%RSD) 24 PFASs and 19 mass-labeled surrogates at 80 ng/L, spiked in reagent water.

Component	**#1**	**#2**	**#3**	**#4**	**Average Concentration (ng/L)**	**%Average Recovery**	**%RSD**
PFBA	81.5	83.9	84.1	83.1	83.1	103.9	1.4
MPFBA	79.3	81.4	81.3	81.3	80.8	101.0	1.3
PFPeA	78.2	78.3	81.5	82.8	80.2	100.3	2.8
M5PFPeA	77.9	77.8	80.6	80.6	79.2	99.0	2.0
4-2 FTS	78.5	84.1	81.8	84.1	82.1	102.6	3.2
M4-2 FTS	78.5	82.0	78.3	83.1	80.5	100.6	3.1
PFHxA	80.0	80.3	79.9	81.7	80.5	100.6	1.1
M5PFHxA	80.3	82.3	80.9	81.0	81.1	101.4	1.1
PFBS	78.0	81.0	79.2	83.6	80.5	100.6	3.0
M3PFBS	77.7	81.0	81.2	81.8	80.4	100.5	2.3
PFHpA	81.1	81.8	81.6	82.4	81.7	102.1	0.6
M4PFHpA	80.8	81.3	80.5	78.0	80.1	100.2	1.8
PFPeS	78.2	78.9	79.7	82.4	79.8	99.8	2.3
6-2 FTS	80.3	90.8	90.1	80.5	85.4	106.8	6.7
M6-2 FTS	79.0	86.3	79.7	75.9	80.2	100.3	5.5
PFOA	80.7	80.9	80.0	82.8	81.1	101.4	1.4
M8PFOA	79.0	82.4	84.3	83.9	82.4	103.0	2.8
PFHxS	71.6	74.3	75.6	76.1	74.4	93.0	2.7
M3PFHxS	78.4	78.3	81.9	79.6	79.5	99.4	2.1
PFNA	78.9	74.8	84.4	79.5	79.4	99.3	4.9
M9PFNA	79.0	79.8	79.8	77.7	79.1	98.9	1.3
8-2 FTS	82.3	75.3	88.1	68.6	78.6	98.3	10.7
M8-2 FTS	87.0	80.1	81.8	84.4	83.3	104.1	3.6
PFHpS	81.3	81.0	79.2	79.8	80.3	100.4	1.26
N-MeFOSAA	79.5	76.7	94.3	80.7	82.8	103.5	9.5
d3M N- MeFOSAA	74.5	83.1	83.5	78.3	79.9	99.8	5.4
PFDA	81.3	80.4	79.1	84.5	81.3	101.7	2.8
M6PFDA	81.1	78.6	81.7	83.2	81.2	101.4	2.4
N-EtFOSAA	66.8	78.1	83.0	69.0	74.2	92.8	10.2
M N-EtFOSAA	74.3	69.6	75.1	82.0	75.3	94.1	6.7
PFOS	74.2	74.4	71.5	80.9	75.2	94.0	5.3
M8PHOS	77.8	78.7	73.9	79.7	77.5	96.9	3.3
PFUdA	77.5	81.6	87.3	79.1	81.4	101.7	5.3
M7PFUdA	75.8	80.1	82.7	85.4	81.0	101.3	5.1
PFNS	77.0	82.5	95.6	85.4	85.1	106.4	9.2
PFDoA	74.4	79.2	80.5	78.8	78.2	97.8	3.4
MPFDoA	75.8	78.1	79.3	78.9	78.0	97.6	2.0
FOSA	75.4	80.9	85.6	81.8	80.9	101.2	5.2
M8FOSA	80.0	83.1	81.6	83.0	81.9	102.4	1.7
PFDS	78.1	83.2	78.6	82.7	80.7	100.8	3.3
PFTriA	76.0	79.4	78.9	82.7	79.2	99.1	3.4
PFTeDA	71.3	85.8	83.9	78.8	80.0	100.0	8.1
M2PFTeDA	67.1	76.7	78.5	82.3	76.2	95.2	8.5

Table 6: Ground Water - Surrogates Spike Recoveries: Accuracy (%recovery) and precision (%RSD) at 160 ng/L.

Sample ID	160 ng/L #1	160 ng/L #2	160 ng/L #3	160 ng/L #4	%Average Recovery (ng/L)	%RSD
d3-NMeFOSAA	182.7	170.8	219.4	173.5	116.7	12.0
d5-NEtFOSAA	165.1	188.6	174.0	169.9	109.0	5.8
M2-4-2 FTS	144.6	163.7	153.0	146.9	95.0	5.6
M2-6-2 FTS	164.9	157.6	168.4	141.3	98.8	7.6
M2-8-2 FTS	152.7	194.6	177.2	172.0	108.9	9.9
M2PFDoA	185.9	197.6	215.0	187.3	122.8	6.8
M2PFTreA	219.0	223.5	232.1	208.4	138.0	4.5
M3PFBS	174.0	175.5	180.2	175.6	110.2	1.5
M3PFHxS	184.5	202.9	196.5	176.1	118.8	6.3
M4PFBA	181.0	195.4	189.1	186.9	117.6	3.2
M4PFHpA	180.3	188.0	190.1	180.2	115.4	2.8
M5PFHxA	186.2	199.9	193.6	168.7	117.0	7.2
M5PFPeA	182.4	192.4	193.8	182.1	117.3	3.4
M6PFDA	182.5	179.5	194.2	176.7	114.6	4.2
M7PFUnA	185.4	191.9	204.3	196.0	121.5	4.1
M8FOSA	193.4	194.6	215.3	184.7	123.1	6.6
M8PFOA	182.2	187.9	188.9	179.7	115.5	2.4
M8PFOS	184.2	188.9	198.3	185.5	118.3	3.4
M9PFNA	173.9	186.0	195.7	182.8	115.4	4.9

Table 7: Reagent Water -Surrogates Spike Recoveries: Accuracy (%recovery) and precision (%RSD) at 160 ng/L.

Sample ID	160 ng/L #1	160 ng/L #2	160 ng/L #3	160 ng/L #4	%Average Recovery (ng/L)	%RSD
d3-NMeFOSAA	152.5	158.2	152.3	155.7	96.7	1.8
d5-NEtFOSAA	145.8	144.1	139.2	153.2	91.0	4.0
M2-4-2 FTS	129.5	146.5	136.2	130.7	84.8	5.7
M2-6-2 FTS	139.5	145.2	136.5	131.2	86.3	4.2
M2-8-2 FTS	124.3	139.7	156.5	145.1	88.4	9.5
M2PFDoA	149.2	152.6	152.2	148.4	94.2	1.4
M2PFTreA	143.2	140.9	148.6	136.8	89.0	3.5
M3PFBS	133.1	152.9	138.7	141.2	88.4	5.9
M3PFHxS	137.6	146.1	149.4	142.9	90.0	3.5
M4PFBA	140.2	126.2	140.7	138.7	85.3	5.0
M4PFHpA	147.8	154.2	152.1	153.3	94.9	1.9
M5PFHxA	151.3	152.2	154.5	146.5	94.5	2.2
M5PFPeA	145.6	152.1	147.4	148.7	92.8	1.8
M6PFDA	150.2	151.3	148.8	154.1	94.5	1.5
M7PFUnA	146.0	149.6	150.3	144.7	92.3	1.8
M8FOSA	143.3	171.0	149.2	134.3	93.4	10.4
M8PFOA	145.7	157.8	153.7	145.5	94.2	4.0
M8PFOS	139.2	141.6	140.6	140.9	87.9	0.7
M9PFNA	153.3	149.2	156.6	157.5	96.4	2.4

Table 8: Surface Water -Surrogates Spike Recoveries: Accuracy (%recovery) and precision (%RSD) at 160 ng/L.

Sample ID	160 ng/L #1	160 ng/L #2	160 ng/L #3	160 ng/L #4	%Average Recovery (ng/L)	%RSD
d3-NMeFOSAA	159.9	134.1	139.7	132.6	88.5	8.9
d5-NEtFOSAA	133.1	144.2	140.6	111.3	82.7	11.1
M2-4-2 FTS	149.9	134.2	122.9	132.3	84.3	8.3
M2-6-2 FTS	141.3	124.5	134.4	132.6	83.3	5.2
M2-8-2 FTS	143.2	131.1	128.0	116.8	81.1	8.4
M2PFDoA	157.3	146.4	146.2	137.8	91.8	5.4
M2PFTreA	155.9	138.4	135.4	137.4	88.6	6.7
M3PFBS	153.7	136.2	143.5	132.2	88.4	6.7
M3PFHxS	153.5	128.0	143.6	131.4	87.0	8.4
M4PFBA	155.8	140.6	141.6	132.9	89.2	6.7
M4PFHpA	155.9	139.4	140.2	130.7	88.5	7.4
M5PFHxA	162.8	144.8	142.2	129.2	90.5	9.6
M5PFPeA	158.2	144.1	140.1	136.8	90.5	6.5
M6PFDA	148.1	137.5	138.5	138.1	87.9	3.6
M7PFUnA	151.2	145.2	143.9	143.2	91.2	2.5
M8FOSA	155.3	149.2	131.9	135.2	89.3	7.8
M8PFOA	156.7	138.5	146.7	136.6	90.4	6.3
M8PFOS	141.2	139.1	136.7	120.8	84.1	6.9
M9PFNA	157.2	136.0	144.3	132.3	89.1	7.7

Table 9: Wastewater- Surrogates Recoveries: Accuracy (%recovery) and precision (%RSD) at 160 ng/L.

Sample ID	160 ng/L #1	160 ng/L #2	160 ng/L #3	160 ng/L #4	%Average Recovery (ng/L)	%RSD
d3-NMeFOSAA	158.1	145.7	150.1	138.8	92.6	5.4
d5-NEtFOSAA	161.7	153.8	147.5	141.7	94.5	5.7
M2-4-2 FTS	170.6	147.6	161.9	159.5	100.0	5.9
M2-6-2 FTS	146.9	157.1	146.2	143.0	92.7	4.1
M2-8-2 FTS	151.2	151.7	166.9	146.3	96.3	5.8
M2PFDoA	160.1	160.5	168.6	143.3	98.9	6.7
M2PFTreA	153.4	150.3	157.4	136.7	93.4	6.0
M3PFBS	179.4	165.4	163.8	151.9	103.2	6.8
M3PFHxS	169.9	151.6	160.2	144.6	97.9	7.0
M4PFBA	173.8	172.4	155.5	149.5	101.8	7.5
M4PFHpA	169.1	164.5	156.1	148.4	99.7	5.7
M5PFHxA	174.3	171.4	164.2	148.5	102.9	7.0
M5PFPeA	174.6	168.7	158.5	149.5	101.8	6.8
M6PFDA	154.4	154.1	155.1	134.8	93.5	6.6
M7PFUnA	156.5	156.9	167.9	139.5	97.0	7.6
M8FOSA	156.2	169.7	159.3	146.6	98.8	6.0
M8PFOA	166.2	156.4	162.5	150.2	99.3	4.4
M8PFOS	147.4	146.3	150.7	136.2	90.7	4.3
M9PFNA	159.8	157.6	164.5	142.3	97.6	6.2

■ Summary and Conclusions

The app note evaluated EPA SW-846 method 8327 for the direct injection analysis of 24 PFASs and 19 mass-labeled surrogates in non-potable waters (namely ground water, surface water and wastewater) using Shimadzu UFMS™ LCMS-8050. The data referenced in this article shows excellent performance of the LCMS-8050 for PFAS analysis in challenging environmental matrices with minimal sample preparation.

Good linearity, accuracy, and precision for all PFAS compounds included in draft EPA Method 8327 were achieved. Hence, the Shimadzu LCMS-8050 could achieve rapid, reliable and highly-sensitive quantitative results in non-potable waters, allowing for high-throughput and fast turnaround times.

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9. Analysis of Per-and Polyfluoroalkyl Substances (PFAS) Specified in EPA M537.1 Using LCMS-8045. Brahm Prakash, Gerard Byrne II, Ruth Marfil-Vega, Yuka Fujito, Christopher Gilles, Shimadzu Scientific Instruments, Inc., Columbia, MD 21046

ULTRA FAST MASS SPECTROMETRY


LCMS-8040


LCMS-8045


LCMS-8050


LCMS-8060


LCMS-2020


Q-TOF LCMS-9030

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Application News

No. LCMS-121

Liquid Chromatography Mass Spectrometry

Analysis of Per- and Polyfluoroalkyl Substances (PFAS) Specified in EPA M533 Using the Triple Quadrupole LC-MS/MS

■ Introduction

EPA published a new method for testing short chain per- and polyfluoroalkyl substances (PFAS) in drinking water. Method 533[1] measures PFAS by isotope dilution anion exchange solid phase extraction and liquid chromatography/tandem mass spectrometry (LC-MS/MS). The lowest concentration minimum reporting levels (LCMRLs) for the method analytes range from 1.4 to 16 ng/L. Shimadzu Scientific Instruments was one of eight laboratories that participated in providing EPA with outside laboratory validation data along with a review of the method draft. This document summarizes Shimadzu Scientific Instruments data from the validation study.

■ Analytical Method

Sample Preparation

Solid Phase Extraction (SPE) with a WAX sorbent (500 mg) was used for the extraction, as outlined in EPA method 533 (section 6.8.1). Each cartridge was cleaned and conditioned first, following EPA 533 (section 11.4.1). A vacuum manifold with a high-volume sampling kit outfitted with large bore PEEK tubing was used to reduce potential contamination.

All sample bottles were rinsed with the elution solvent prior to use. Each water sample (250 mL) was adjusted to pH 6-8 and fortified with PFAS analyte and isotope dilution analogues, mixed, and loaded onto the conditioned cartridge. Compounds were eluted at a high pH from the solid phase with two 5 mL aliquots of methanol containing 2% ammonium hydroxide (v/v) and evaporated to dryness using nitrogen. Extracted samples were reconstituted to a final volume of 1 mL in 80:20 methanol:H_2O with internal standards added.

Extraction for Precision & Accuracy study was performed by fortifying five replicates of reagent water and tap water samples at 10 ng/L. For LCMRL calculations (results not shown here) samples were extracted at eight concentration levels ranging from 0.2 ppt and 14 ppt. Four replicates were prepared at each concentration level and a minimum of four laboratory reagent blanks (LRB) were also included in the extraction batches.

■ Instrumental Method

The analysis of 25 PFAS compounds, with16 isotope dilution analogues and 3 post extraction internal standards was performed using a UHPLC system coupled with a triple quadrupole mass spectrometer. MRM transitions were optimized using Flow Injection Analysis for all compounds[2]. Source parameters were optimized to reduce fragmentation and increase sensitivity. Fluorotelomer acids, observed as [M-H]- and [M-HF-H]- can result in an ion with the same m/z as the unsaturated fluorotelomer acid. Even under optimized chromatography, these compounds have near identical retention times. The lower ESI heater temperature reduces HF loss and minimizes false identification of fluorotelomer acids. The chromatographic parameters are based on the chromatographic method used in EPA Method 533. A Shim-pack XR-ODS 50 x 3.0 mm column was used as a delay column, and a Phenomenex Gemini™ C18, 2.0 mm ID × 50 mm, 3.0 µm particle size column was used as the analytical column. Quantitation was performed using MRM on tandem mass spectrometer (LC-MS/MS). Figure 1 shows the LCMS system used for this work (LCMS-8045); instrumental conditions are included in Table 1 and retention times, MRM transitions and collision energies are listed in Table 2.

Figure 1: LCMS-8045 triple quadrupole mass spectrometer

Table 1: Instrumental conditions

LCMS Instrument	Shimadzu LCMS-8045
Analytical Column	Gemini 3µm C18 110A LC Column 50 x 2mm
Solvent Delay Column	Shim-pack XR-ODS 2.2-micron, 3.0 x 50mm
Injection Volume	10 µL
LC Flow Rate	0.25 mL/min
Mobile Phase A	20 mM Ammonium Acetate in LCMS-grade Water
Mobile Phase B	Methanol
Run / Acquisition Cycle Time	35 minutes (all 44 PFAS compounds are eluted in 20 minutes)

LCMS-8045	
Interface	ESI, Negative Mode
Interface Temperature	100 °C
Desolvation Line Temperature	160 °C
Heat Block Temperature	200 °C
Heating Gas Flow	15 L/min
Drying Gas Flow	5 L/min
Nebulizing Gas Flow	3 L/min
Total MRMs	66
Minimum Dwell Time	19 msec
Maximum Dwell Time	124 msec

	Time (min)	**% A**	**%B**
Gradient Conditions	0	95	5
	3	60	40
	16	20	80
	20	5	95
	22	5	95
	25	95	5

Table 2: Target and labelled PFAS m/z, retention times, and correlation coefficients from the aggregate curve (Days 1-5)

ID#	**Compound**	**Type**	**ISTD Group#**	**m/z**	**RT**	**Collision Energy, V**	**MRL in vial (ng/mL)**	**MRL in sample (ng/L)**	**R2**
1	M3PFBA	ISTD	3	216.00>172.00	5	10	----	----	----
2	MPFBA	Surrogate	1	217.00>172.00	5	10	----	----	----
3	PFBA	Target	1	212.90>168.90	5.18	10	0.05	0.2	0.9945
4	PFMPA	Target	1	229.00>85.00	6.2	10	0.025	0.1	0.9947
5	PFPeA	Target	1	263.00>219.00	7.95	8	0.05	0.2	0.9947
6	M5PFPeA	Surrogate	1	268.00>223.00	7.94	8	----	----	----
7	M3PFBS	Surrogate	1	302.00>80.00	8.54	34	----	----	----
8	PFBS	Target	2	298.90>80.10	8.55	30	0.1	4	0.9949
9	PFMBA	Target	1	279.00>85.00	8.72	20	0.025	0.1	0.994
10	PFEESA	Target	1	314.90>134.85	9.54	25	0.025	0.1	0.9958
11	NFDHA	Target	1	295.00>201.15	10.08	8	5	20	0.9982
12	M2-4-2 FTS	Surrogate	2	329.00>309.00	10.22	20	----	----	----
13	4-2 FTS	Target	2	327.00>307.00	10.2	18	1	4	0.9938
14	PFHxA	Target	1	312.90>269.00	10.48	8	0.05	0.2	0.9947
15	PFPeS	Target	2	349.00>80.00	10.82	9	0.1	0.4	0.9949
16	HFPO-DA	Target	1	285.00>169.00	11.21	42	0.025	0.1	0.9953
17	13C-HFPO-DA	Surrogate	1	287.00>169.20	11.21	8	----	----	----
18	PFHpA	Target	1	362.90>319.00	12.57	9	0.025	0.1	0.9942
19	M4PFHpA	Surrogate	1	367.00>322.00	12.57	10	----	----	----
20	M3PFHxS	Surrogate	2	402.00>80.00	12.75	9	----	----	----
21	PFHxS	Target	2	398.90>80.10	12.08	49	0.1	0.4	0.9965
22	ADONA	Target	1	377.00>250.90	12.8	43	0.025	0.1	0.9948
23	6-2 FTS	Target	2	427.00>407.00	14.12	11	0.5	2	0.9955
24	M2-6-2 FTS	Surrogate	2	429.00>409.00	14.14	22	----	----	----
25	M8PFOA	Surrogate	1	421.00>376.00	14.27	23	----	----	----
26	PFOA	Target	1	412.90>369.00	14.25	10	0.1	0.4	0.9944
27	M2PFOA	ISTD	1	415.00>370.00	14.28	10	----	----	----
28	PFHpS	Target	2	449.00>80.00	14.33	10	0.1	0.4	0.9952
29	PFNA	Target	1	462.90>418.90	15.76	51	0.05	0.2	0.9942

ID#	Compound	Type	ISTD Group#	m/z	RT	Collision Energy, V	MRL in vial (ng/mL)	MRL in sample (ng/L)	R2
30	M8PFOS	Surrogate	3	507.00>80.00	15.75	12	----	----	----
31	M9PFNA	Surrogate	1	472.00>427.00	15.73	11	----	----	----
32	PFOS	Target	2	498.90>80.10	15.23	45	0.05	0.2	0.9952
33	M4PFOS	ISTD	2	503.00>80.00	15.76	45	----	----	----
34	9Cl-PF3ONS	Target	1	530.90>351.00	16.5	54	0.025	0.1	0.9954
35	8-2 FTS	Target	2	527.00>507.00	16.97	27	1	4	0.997
36	M2-8-2 FTS	Surrogate	2	529.00>509.00	16.98	26	----	----	----
37	PFDA	Target	1	512.90>468.90	17.04	26	0.025	0.1	0.9952
38	MPFHxA	Surrogate	1	318.00>273.00	10.48	12	----	----	----
39	PFUnA	Target	1	562.90>519.00	18.14	11	0.025	0.1	0.9948
40	M7PFUnA	Surrogate	3	570.00>525.00	18.11	12	----	----	----
41	11Cl-PF3OUdS	Target	1	630.70>451.00	18.63	12	0.025	0.1	0.9953
42	PFDoA	Target	1	612.90>568.90	19.06	30	0.025	0.1	0.9951
43	M2PFDoA	Surrogate	3	615.00>570.00	19.06	10	----	----	----
44	MPFDA	Surrogate	1	519.00>474.10	17.04	12	----	----	----

Calibration

Standards available from Wellington Laboratories were used for these studies (EPA method analyte stock 2 mL volume in methanol at 1 ug/L, Internal standard in methanol Wellington Catalog No. 533-IS and Isotope Dilution Analogue PDS in Methanol Wellington Catalog No. 533-ES). These standards were then diluted to working standards as outlined in Section 7.17.5 of EPA Method 533 using 20% water in methanol as diluent to match the extract solvent composition. The working standards were used to create a calibration curve ranging from 1 ng/L to 1000 ng/L for NFDHA, and from 0.1 ng/L to 100 ng/L for all other analytes.

During this study, an Initial Calibration curve was ran 5 consecutive days. Figure 2 shows an aggregate calibration curve for PFMPA and PFPeA and Figure 3 shows an aggregate calibration curve for PFDA and example MRL 0.1 ng/L chromatogram. The chromatogram shown in Figure 4 is from a level 7, 6 ng/L calibrator. Figure 5 shows a clean instrument blank (80:20 MeOH:H_2O), indicating that the system is free from PFAS contamination as no PFAS was detected.

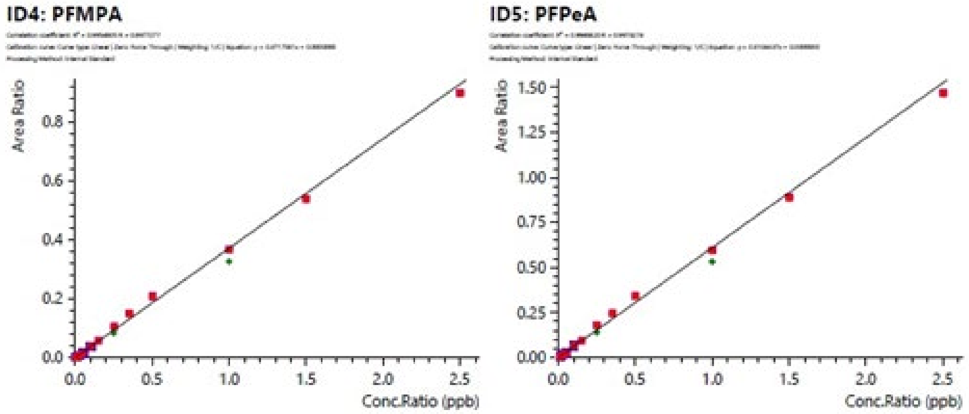

Figure 2: Aggregate calibration curves for PFMPA, and PFPeA.

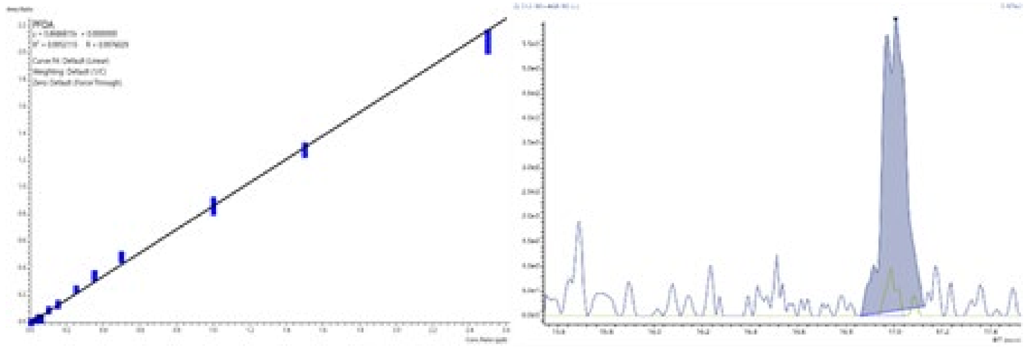

Figure 3: Aggregate calibration curve for PFDA and example MRL 0.1 ng/L chromatogram.

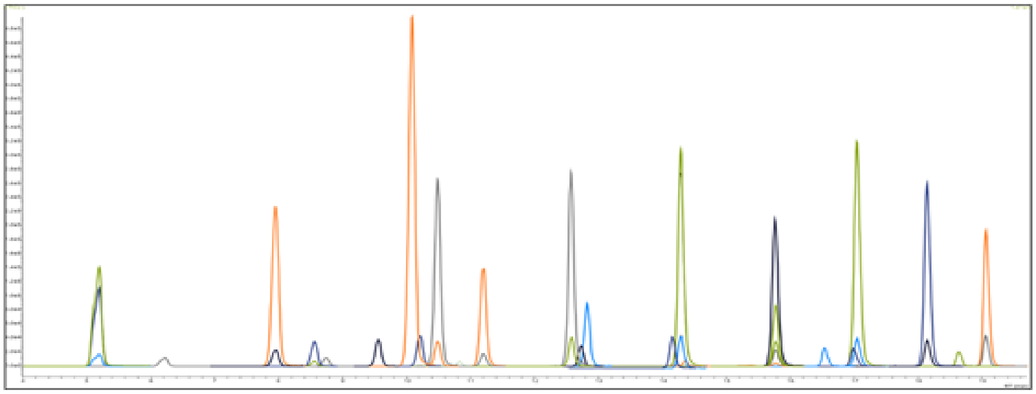

Figure 4: TIC of all 44 compounds at Level 7, 6 ng/L.

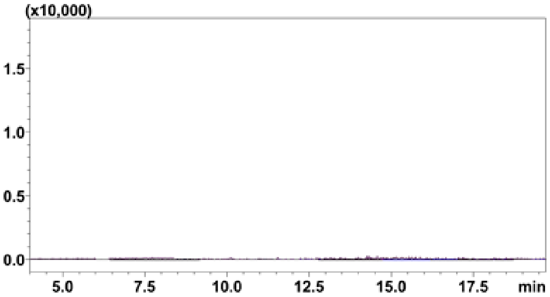

Figure 5: Blank: 80:20 MeOH: H2O.

■ Results

The use of a Phenomenex Gemini™ C18, 2.0 mm ID × 50 mm, 3.0 µm particle size analytical column and a Shim-Pack XR-ODS 50 x 3.0 mm column as a delay column provided a good chromatographic separation for all compounds including branched and linear isomers. Calibration curves for PFAS analytes were prepared in the range of 0.025 – 25 ng/mL, representing pre-SPE sample concentrations of 0.1 – 100 ng/L (except for NFDHA which was analyzed from 0.25 – 250 ng/L). All calibration curves (aggregate curve and 5 individual curves analyzed 15 consecutive days) demonstrated r^2 values greater than 0.99; the results are included in Table 2.

All RSD results for the aggregate curve were less than 20%. All MRL level accuracies were between 50 – 150%. Accuracies at the MRL for each day (against the aggregate curve), and %RSDs are shown in Figure 6. Precision and accuracy studies in reagent water (RW) and tap water (TW) were performed at 10 ng/L and recoveries of majority of analytes were within 70-130% with %RSDs below 20% for all method analytes. The P & A study results were within EPA method 533 requirements; the data is included in Figure 7.

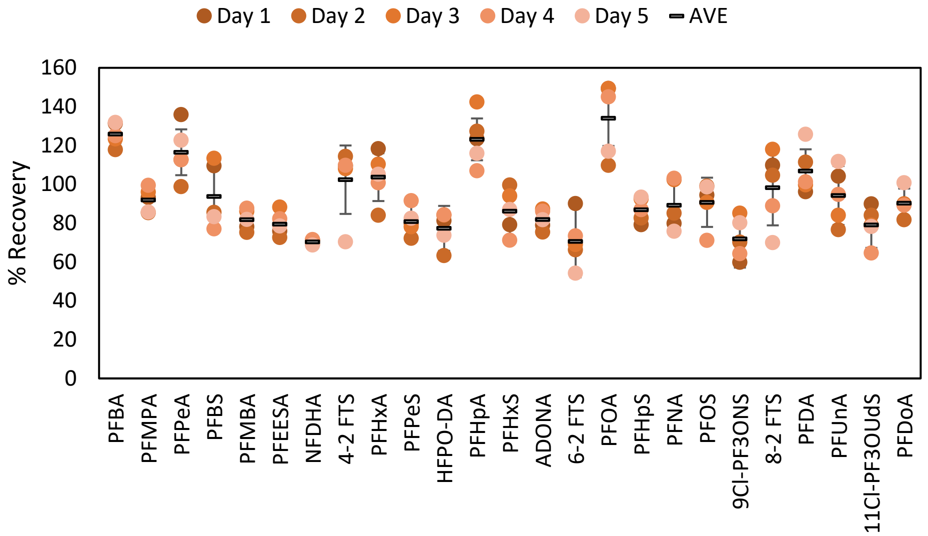

Figure 6: %recovery (individual injections from five consecutive days and average) at MRL concentration.

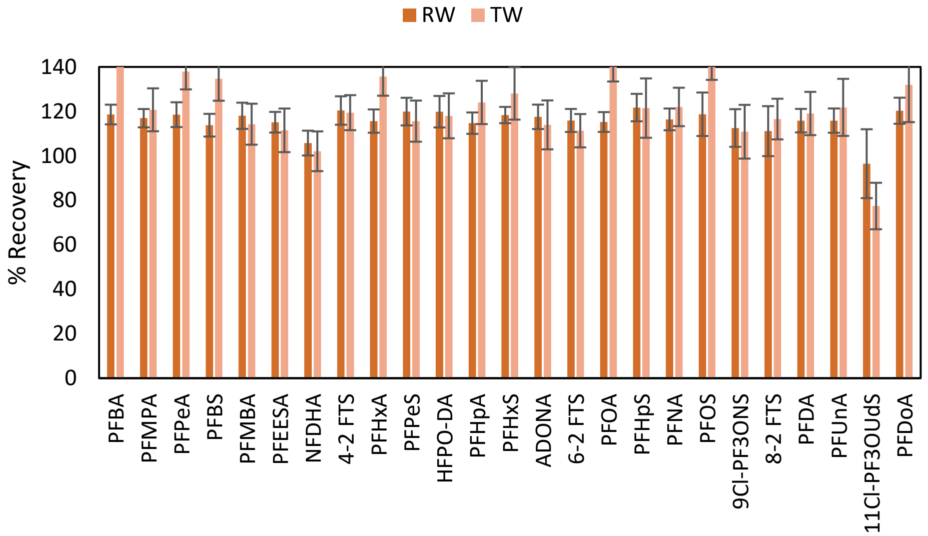

Figure 7: Precision and accuracy results.

■ Conclusions

This study showed good chromatographic separation for all compounds listed in the method using the delay and analytical columns recommended by EPA. Recoveries for most target compounds and precision and accuracy data for all target analytes in reagent water and tap water were within EPA requirements of 70 -130%, with %RSD below 20% for all method analytes.

This data was generated as part of the EPA method 533 second laboratory validation organized by EPA. Shimadzu participated in this validation, as acknowledged in the final method.

■ References

1. EPA method 533: Determination of Per- and Polyfluoroalkyl Substances in Drinking Water by Isotope Dilution anion exchange Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry(U.S. Environmental Protection Agency, Washington, D.C., December 2019).
2. Shimadzu Application News No. C184, “Analysis of PFAS Specified in EPA Method 537 and Beyond Using Shimadzu UFMS”, 2019.

UFMS

ULTRA FAST MASS SPECTROMETRY


LCMS-8040


LCMS-8045


LCMS-8050


LCMS-8060NX


LCMS-2020


Q-TOF LCMS-9030

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First Edition: October 2020

Application News

No. HPLC-037

High Performance Liquid Chromatography

Analysis of PFAS Compounds in Fish Tissue Using Offline Supercritical Fluid Extraction and LC-MS/MS

■ Introduction

Per and Poly-fluoroalkyl substances (PFAS) are synthetic compounds that are found in a wide range of industrial and consumer products. Due to the strong nature of the carbon-fluorine bond, these compounds are resistant to degradation and have been found to accumulate in fish, wildlife and multiple environmental samples (ex. water, soil…), posing a significant health risk to humans. Current sample preparation techniques for PFAS analysis are laborious and not easily automated. In this study, supercritical fluid extraction (SFE) was evaluated as an alternative sample preparation technique for the extraction of eighteen PFAS compounds from fish tissue, as a preconcentration step prior to their analysis by LC-MS/MS.

■ Experimental Approach

For this study, the Shimadzu Nexera UC offline SFE system (configuration shown in Figure 1) was employed. 0.5 grams of freeze-dried fish tissue was milled and mixed with 1 packet (1 gram) of Miyazaki Hydro-Protect and placed into a 5 mL extraction vessel for extraction.

Optimized extraction conditions to maximize PFAS recoveries are shown in Table 1. After extraction, the sample was dried down under nitrogen and reconstituted with 1 mL of methanol. The sample was centrifuged and the supernatant was transferred to an LC vial. 1 uL of the supernatant was injected for LC-MS/MS analysis. Table 2 shows the LC-MS/MS conditions used for the Shimadzu LCMS-8050 for this study; a representative chromatogram is included in Figure 2.

Table 1: SFE optimized method conditions

Item	Value
Mobile phase	CO_2/MeOH
Modifier concentration	20% MeOH
Flow rate	5 mL/min
Vessel temperature	60 ℃
Extraction cycles	3
Back pressure	20 MPa
Extraction time	45 minutes

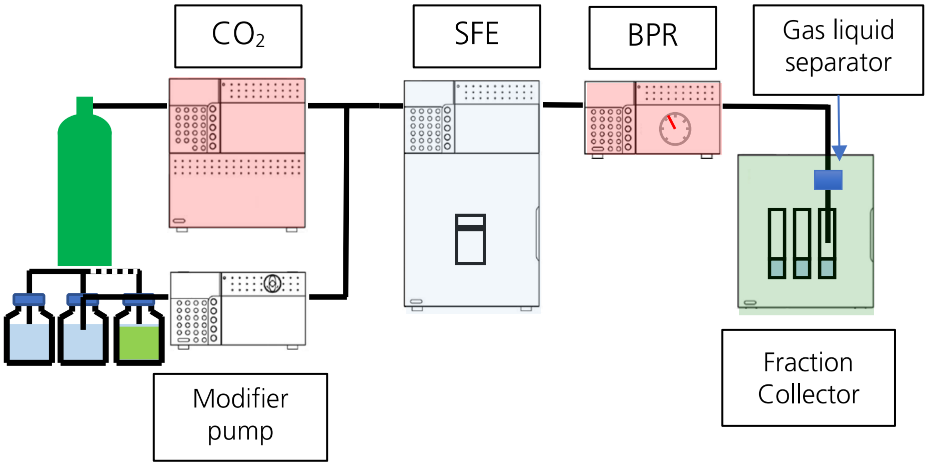


Figure 1: System Configuration of offline SFE system for direct collection method.
CO2: CO2 pump; SFE: Supercritical Fluid Extraction Module; BPR: Back pressure regulator

Table 2: LC-MS/MS method conditions used in Shimadzu LCMS-8050

Item	Value
Column	Shim-pack GIST C18 2.7 um 100 x 2.1 mm
Delay column	XR-ODSII 3 x 75 mm
Mobile phase	A: 10 mM ammonium acetate in H_2O; B: MeOH
Flow rate	0.5 mL/min
Gradient	0 min: 20% B 9 min: 90% B 11 min: 90% B 11.5 min: 20% B 15 min: 20% B
Oven temperature	35 °C
Injection volume	1 µL
Ionization mode	ESI (-)

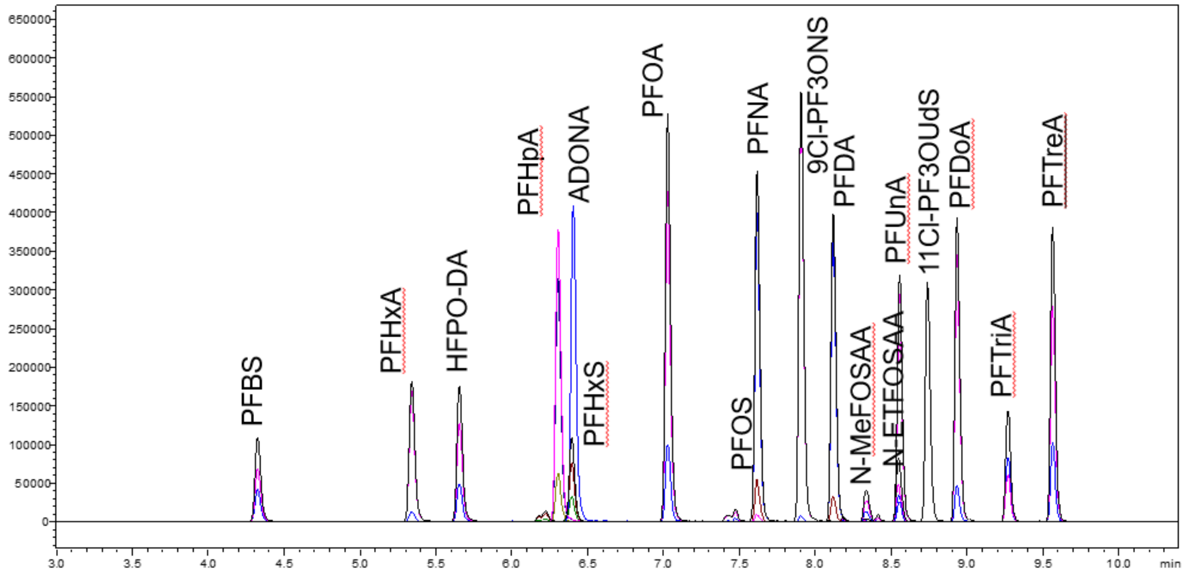


Figure 2: LC-MS/MS chromatogram of target PFAS in a commercial standard diluted in MeOH (50 pg each on column)

■ Results and Discussion

Recovery, Linearity, Reproducibility

A set of experiments to identify the combination of CO_2's modifier and additives that maximized the extraction efficiency of 18 PFAS was first conducted in this work. While 100% CO_2 can be effective in extracting nonpolar compounds, the addition of a cosolvent is often required in SFE to extract more polar compounds. Optimum extraction conditions were found to be 20% methanol without the need for additives. The 18 targets from this study showed recoveries over 95% with these conditions, as shown in Table 3.

Linearity of a matrix matched calibration curve, to minimize the impact from coextracted matrix components, was evaluated. Concentrations from 0.5 to 100 ng/g were spiked to a freeze-dried farm-raised trout fish tissue sample found to be free from PFAS contamination.

Linearity results are shown in Table 4 along with the determined limit of quantitation for each compound; r^2 for all compounds was >0.9995 except for N-MeFOSAA (r^2: 0.9994). Linearity results show accurate determinations for PFAS compounds can be obtained regardless of concentration levels.

Reproducibility results for supercritical fluid extractions were determined at three PFAS concentration levels: 2 ng/g, 20 ng/g and 100 ng/g. Extractions were performed in triplicated samples. Table 5 summarizes the variability of the extraction at each of the concentrations evaluated. %RSDs at 20 and 100 ng/g were less than 12% for all compounds evaluated. At 2 ng/g, %RSD was less than 25%, except for PFTriA (27%) and N-MeFOSAA (45%). These results demonstrate the reproducibility of SFE as a sample preparation technique.

Table 3: % recovery of target PFAS

Compound	% recovery
PFBS	98.7
PFHxA	105.9
HFPO-DA	97.4
PFHxS	102.7
PFHpA	100.5
ADONA	100.7
PFOA	104.2
PFNA	101.9
PFOS	98.1
9Cl-PF3ONS	100.5
PFDA	99.9
N-MeFOSAA	102.2
N-EtFOSAA	97.6
PFUnA	94.6
11Cl-PF3OUds	102.2
PFDoA	96.3
PFTriA	99.8
PFTreA	97.2

Quantitative analysis of fish samples

Three fish samples with unknown PFAS concentrations were then evaluated with this method. The samples were wild caught Walleye, wild caught Large Mouth Bass, and farm raised Trout. Figure 3 shows the LC-MS/MS chromatogram of an extracted sample from each fish's type. Table 6 shows the concentration of PFAS determined in each type of fish. The wild caught Walleye and Large Mouth Bass were found to contain the largest amounts of PFOS, PFDA, and PFUnA. No PFAS compounds were detected above the LOQ in the farm raised Trout sample.

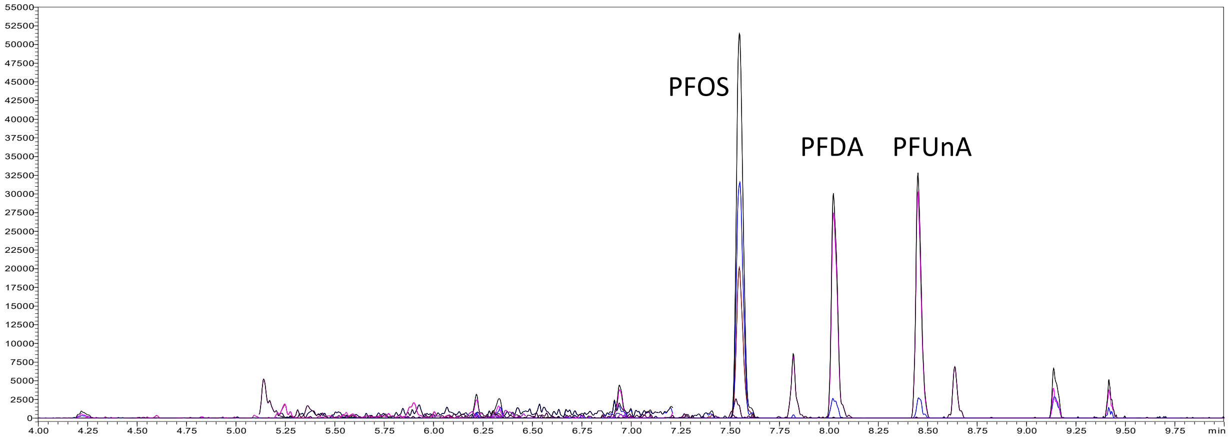
Table 4: Linearity of PFAS compounds spiked onto fish tissue

	Lowest Calibration Standard (LOQ)	Highest Calibration Standard	Linearity (R^2)
	ng/g spiked on fish	ng/g spiked on fish	
PFBS	0.5	100	0.9999
PFHxA	0.5	100	0.9995
HFPO-DA	1	100	0.9997
PFHpA	1	100	0.9996
PFHxS	0.5	100	0.9999
ADONA	0.5	100	0.9997
PFOA	0.5	100	0.9997
PFNA	0.5	100	0.9997
PFOS	2	100	0.9999
9Cl-PF3ONS	1	100	0.9995
PFDA	0.5	100	0.9998
N-MeFOSAA	2	100	0.9994
N-ETFOSAA	1	100	0.9999
PFUnA	1	100	0.9997
11Cl-PF3OUdS	0.5	100	0.9999
PFDoA	1	100	0.9996
PFTriA	2	100	0.9997
PFTreA	1	100	0.9995

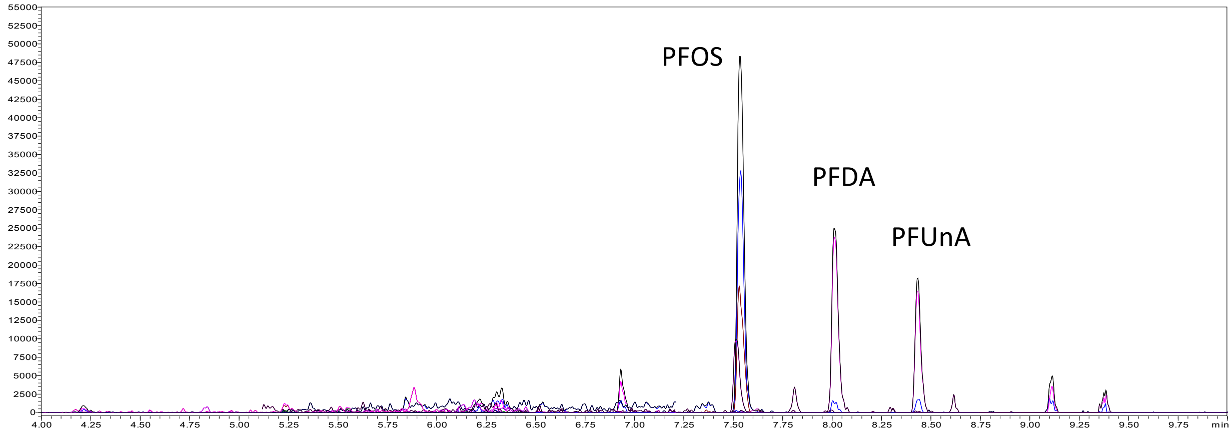
Table 5: Reproducibility of PFAS SFE extractions (n=3)

	%RSD		
	100 ng/g	20 ng/g	2 ng/g
PFBS	2.3	7.9	21.7
PFHxA	4.9	4.1	15.6
HFPO-DA	3.9	4.4	9.9
PFHxS	4.2	4.4	19.9
PFHpA	2.6	4.9	2.4
ADONA	3.9	3.2	13.2
PFOA	2.9	3.1	13.1
PFNA	3.5	3.6	18.1
PFOS	4.1	3.9	22.1
9Cl-PF3ONS	2.5	1.3	3.6
PFDA	1.6	7.4	20.9
N-MeFOSAA	9.5	9.6	44.7
N-EtFOSAA	8.4	6.2	10.7
PFUnA	2.3	2.8	18.4
11Cl-PF3OUds	4.1	4.9	7.8
PFDoA	4.7	5.8	15.9
PFTriA	4.4	11.6	26.8
PFTreA	2.3	3.6	11.5

(a) Wild caught Large Mouth Bass



(b) Wild caught Walleye



(c) Farm raised Trout

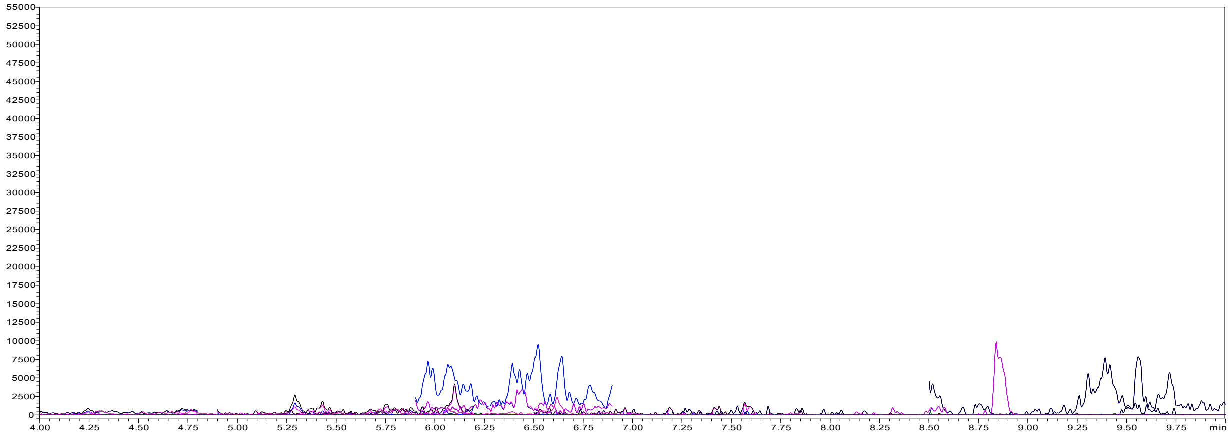


Figure 3: SFE extracted sample chromatograms from (a) Wild caught Large Mouth Bass, (b) Wild caught Walleye, and (c) Farm raised Trout

Table 6: Concentration of 18 PFAS in unknown fish samples

	Walleye ng/g	Large Mouth Bass ng/g	Farm raised Trout ng/g
PFBS	1.0	1.6	n.d.
PFHxA	n.d.	n.d.	n.d.
HFPO-DA	n.d.	n.d.	n.d.
PFHxS	n.d.	n.d.	n.d.
PFHpA	n.d.	n.d.	n.d.
ADONA	n.d.	n.d.	n.d.
PFOA	1.0	1.4	n.d.
PFNA	2.4	1.1	n.d.
PFOS	51.7	77.3	n.d.
9Cl-PF3ONS	1.0	2.7	n.d.
PFDA	6.7	10.5	n.d.
N-MeFOSAA	n.d.	n.d.	n.d.
MN-MeFOSAA	n.d.	n.d.	n.d.
N-EtFOSAA	n.d.	n.d.	n.d.
PFUnA	5.7	14.2	n.d.
11Cl-PF3OUds	0.7	3.0	n.d.
PFDoA	2.8	4.5	n.d.
PFTriA	4.1	7.3	n.d.
PFTreA	1.4	2.3	n.d.

■ Conclusion

A novel supercritical fluid extraction method, using the Shimadzu Nexera UC offline SFE system, for the extraction of PFAS compounds from fish tissue was evaluated and provided excellent results for recovery, linearity, and reproducibility. The results summarized here demonstrate the suitability of SFE as a sample preparation technique for PFAS analysis.

This sample preparation technique can be automated to allow the processing of up to 48 samples per batch to help reduce manual labor in testing laboratories.

■ Acknowledgement

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First Edition: July 2020

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Application News

No. LCMS-119

Liquid Chromatography Mass Spectrometry

Are there PFAS in my water? A detailed look into bottled water

■ Introduction

The presence of Per- and Polyfluorinated Alkyl Substances (PFAS) in drinking water is being thoroughly studied due to the persistence of these compounds in the environment and their potential health effects. However, there is limited knowledge about the occurrence of these chemicals in bottled water, despite the increasing concerns about PFAS in the food supply. This work presents results from a fast and simple direct injection method similar to EPA method 8237, using the Shimadzu LCMS-8050 to analyze seven commercially available samples of bottled water for 24 PFAS. The results demonstrate that the instrument's performance exceeds the requirements in FDA draft method C-010.01 for other matrices, including milk (which is the most similar to water), as well as the limits established by the EPA for drinking water.

While the origin of the water itself maybe the source of PFAS in bottled water, we also wanted to investigate the importance of the type of materials. Migration of PFAS from Food Contact Materials (FCM) is known to occur in all kinds of food containers. In this study, we procured bottled water in several different bottle materials, as well as two types of water source. These included spring and purified water, and bottles made from 5 different kinds of container materials: plastic (virgin and recycled), glass, metal, and cardboard. Preliminary results indicate that observed PFAS levels seem to depend on both the bottle material and the water source.

■ Methodology

We analyzed 24 target PFAS compounds and 19 surrogates in various types of water. The analysis of PFAS was performed using a Shimadzu Nexera X2 SIL-30AC autosampler and a LCMS-8050 triple quadrupole mass spectrometer. An injection volume of 30 µL was used in this study. A detailed description of the LC/MS/MS parameters is included in Table 1.

Chromatography was adjusted to obtain maximum resolution between peaks in the shortest time possible with minimum co-elution of isomers. The total run time of 21 minutes includes a final wash out with concentrated acetonitrile to flush the column, remove background residuals contaminants and restore column performance before starting the next run. The method could easily be modified to include isotopic dilution or internal calibration if needed for quantifying the concentrations.

Calibration Standards

Standards available from Wellington Laboratories were used for these studies (Catalog no. PFAC-24PAR and MPFAC-24ES). These standards were then diluted to working standards using 95:5 acetonitrile:water as the diluent. The working standards were used to create a calibration curve ranging from 5-200 ppt with the injection solvent consisting of 50:50 water:methanol with 0.1% acetic acid in order to match the injection solvent for the extracted samples. Filtration was not performed on the calibration standards.

Sample Preparation

Seven types of bottled water as sample matrices were tested using reagent water as the blank. Each sample was diluted 50:50 with MeOH and 0.1% acetic acid, spiked with isotopically labeled surrogates and vortexed for 2 min. The samples were then filtered through 0.2 µm syringe filters and analyzed by LC/MS/MS.

All compound parameters, including precursor ion, product ion, and collision energies, were optimized. There are at least two multiple reaction monitoring (MRM) transitions for most of the analytes.

Table 1: Chromatography and mass spectrometer conditions.

Parameter	Value	
LCMS	Shimadzu LCMS-8050	
Analytical Column	Restek Raptor C18 2.1 mm ID. x 150 mm L., 2.7 µm) Part No 9304A62	
Solvent Delay Column	Restek PFAS Delay Column (2.1 mm ID. x 50 mm L) Part No. 27854	
Column Oven Temperature	40 ° C	
Injection Volume	30 µL	
Mobile Phase	A: 20 mmol Ammonium Acetate in 5 % (v/v) Acetonitrile in reagent water B: 10 mmol Ammonium Acetate in 95 % (v/v) Acetonitrile in reagent water	
Gradient Flow rate	0.3 mL/ Min	
Gradient	Time (minutes)	% B
	0	0
	1	20
	6	50
	14	100
	17	100
	18	0
	21	0
Run time	21 minutes	
Nebulizing gas flow	5 L/min	
Heating gas flow	15 L /Min	
Interface temperature	300 °C	
Desolvation Line temperature	100 °C	
Heat Block temperature	200 °C	
Drying gas flow	5 L /min	
Acquisition cycle time	21 min	
Total MRMs	66	

■ Results and Discussion

It is known that PFAS can be present in reagents, glassware, pipettes, tubing, degassers and other parts from the LC-MS/MS instruments. PFAS contamination coming from the LC system is eliminated using a delay column placed between the reagents and the sample valve. This separates PFAS in the sample from the PFAS in the LC system. All supplies used to conduct the study were free from PFAS contamination.

To monitor the lack of contamination two blanks were injected at the beginning of each batch: system null injection (air injection) and reagent blank (0.1% acetic acid in high purity water:methanol (50:50)). Figure 1 shows the schematic of the delay column set up, and Figure 2 shows the importance of having a delay column and its impact on data quality.

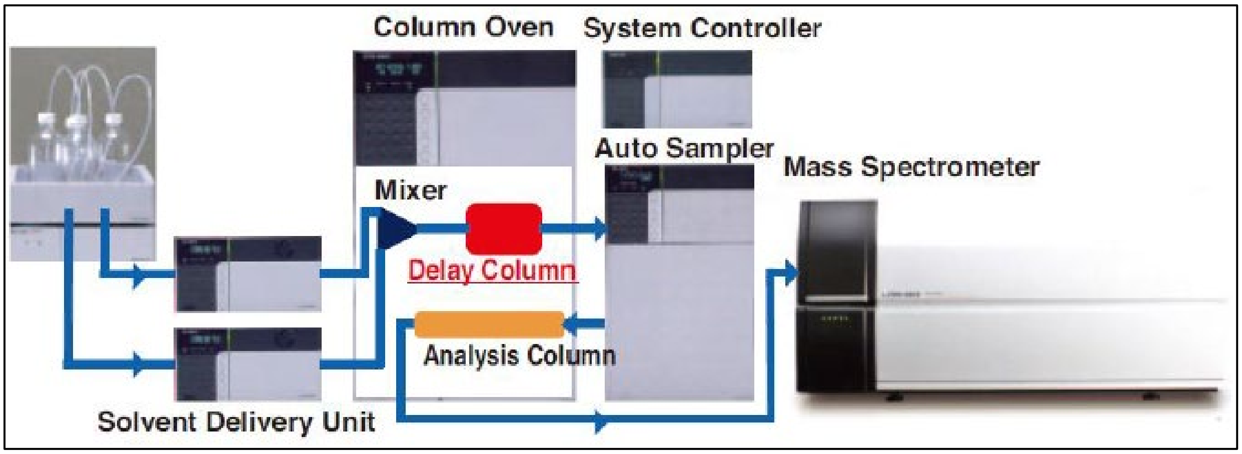

Figure 1: Schematic of Delay Column System to minimize background PFAS.

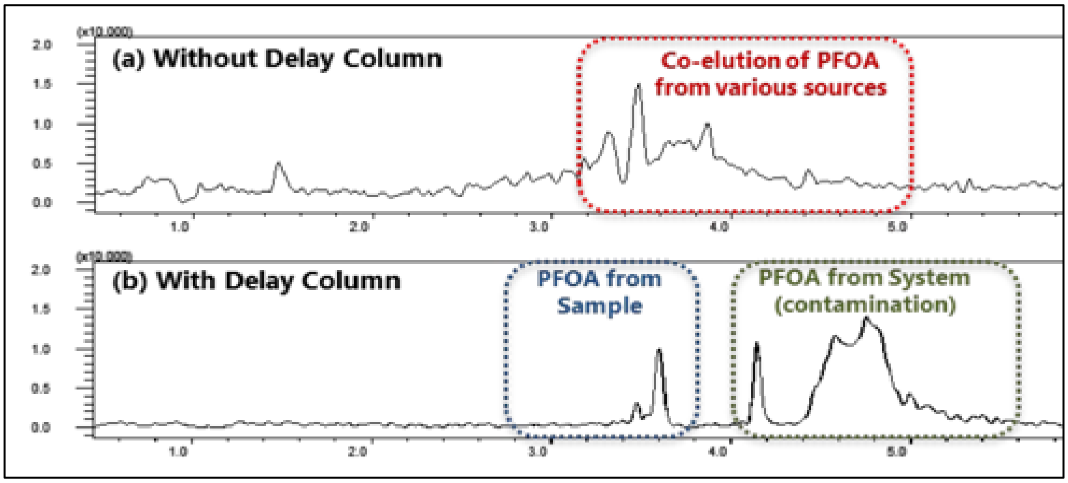

Figure 2: Comparison of Chromatograms with and without a Delay Column.

Recoveries of an 80 ppt standard are shown in Table 2. The data represent an average of three individual runs. This demonstrates the accuracy and reproducibility of the measurements. Recoveries ranged from 87.6% to 129.5%, and %RSD was below 10% for most compounds. The LOQ was determined at 10 ppt in the sample.

Table 2: Recoveries and Reproducibility of 80 ppt Standard.

	Average	%Recovery	%RSD
PFBA	103.64	129.55	21.17
MPFBA	81.87	102.34	2.33
PFPeA	79.29	99.12	2.52
M5PFPeA	83.49	104.36	1.39
4-2 FTS	85.54	106.92	6.39
M2-4-2 FTS	86.33	107.91	9.36
PFHxA	78.06	97.58	3.69
M5PFHxA	80.45	100.56	2.83
PFBS	79.55	99.44	3.38
M3PFBS	79.86	99.83	1.25
PFHpA	81.40	101.75	3.39
M4PFHpA	82.34	102.92	2.96
PFHxS	79.85	99.82	3.85
PFPeS	76.30	95.38	8.26
6-2 FTS	80.89	101.12	10.79
M2-6-2 FTS	77.43	96.78	22.96
PFOA	76.72	95.90	6.58
M8PFOA	82.68	103.35	4.87
M3PFHxS	77.67	97.09	5.21
PFOS	83.92	104.90	15.63
PFNA	76.42	95.53	2.82
M9PFNA	82.38	102.98	1.66
PFHpS	82.99	103.74	12.33
8-2 FTS	70.05	87.57	14.64
M2-8-2 FTS	74.27	92.83	3.76
N-EtFOSAA	73.15	91.44	2.87
N-MeFOSAA	79.25	99.06	2.75
PFDA	80.00	100.00	4.15
M6PFDA	76.99	96.23	2.86
d3-NMeFOSAA	73.57	91.96	6.99
M8PFOS	79.76	99.70	7.75
d5-NEtFOSAA	81.58	101.97	15.65
PFUnA	78.98	98.73	4.58
M7PFUnA	77.83	97.28	3.79
PFNS	80.60	100.75	19.61
PFDoA	76.57	95.72	4.70
M2PFDoA	74.04	92.55	2.81
PFDS	84.19	105.24	9.99
PFTriA	73.30	91.63	1.88

	Average	%Recovery	%RSD
FOSA	80.25	100.31	6.54
M8FOSA	73.51	91.89	4.03
PFTreA	76.45	95.57	3.85
M2PFTreA	73.54	91.92	4.97
HFPO-DA	82.41	103.01	4.22
13C-HFPO-DA SURR	79.29	99.12	5.91
ADONA	79.94	99.92	3.23
9Cl-PF3ONS	77.92	97.40	3.74
11Cl-PF3OUdS	79.39	99.24	9.23

Our method screened for 24 PFAS compounds, but only two were found in any of the samples – PFBA (perfluoro butanoic acid) and 6-2 FTS (fluorotelomer sulfonate). The highest levels were found in plastic bottles. Much of the attention in PFAS analysis has been on the longer chain analogs, especially PFOS and PFOA. We did not see either one of these in the samples tested. There is little information about the ones that we did see regarding their effect on human health.

Table 3 shows a summary of the PFAS residues in each water sample. The sample “Plastic 2” was labelled as “purified water” on the bottle, while all other bottles claimed “spring water” as their water source.

Only two of the samples had no detectable PFAS concentration – the glass bottle and the cardboard container. The other containers had at least one PFAS above the levels recommended by The International Bottled Water Association (IBWA). This organization has guidelines for its members of 5 ppt for any individual PFAS, and 10 ppt for total PFAS concentration. The EPA has set guidelines of total PFAS concentration below 70 ppt, while the FDA is currently testing many types of foods for PFAS contamination and will use this data to set exposure limits.

Table 3: PFAS Data by Water Bottle Material.

PFAS	Blank	Glass	Cardboard	Metal	Plastic 1	Plastic 2	Plastic 3	Recycled Plastic
PFBA	NQ	NQ	NQ	23.8	NQ	15.3	104.3	18.1
PFPeA	ND	ND	ND	ND	ND	ND	ND	ND
4-2 FTS	ND	NQ	NQ	NQ	NQ	NQ	NQ	NQ
PFHxA	ND	ND	ND	ND	ND	ND	ND	ND
PFBS	NQ	ND	ND	NQ	ND	ND	ND	ND
PFHpA	ND	NQ	NQ	ND	NQ	NQ	ND	ND
PFHxS	ND	ND	ND	ND	ND	ND	ND	ND
PFPeS	ND	ND	ND	ND	ND	ND	ND	ND
6-2 FTS	NQ	NQ	ND	NQ	81.5	NQ	ND	253.9
PFOA	ND	NQ	NQ	NQ	NQ	NQ	NQ	NQ
PFOS	ND	ND	ND	ND	ND	ND	ND	ND
PFNA	ND	NQ	NQ	NQ	NQ	NQ	NQ	NQ
PFHpS	ND	ND	ND	ND	ND	ND	ND	ND
8-2 FTS	NQ	ND	ND	ND	ND	ND	ND	ND
N-EtFOSAA	ND	ND	ND	ND	ND	ND	ND	ND
N-MeFOSAA	ND	ND	ND	ND	ND	ND	ND	ND
PFDA	NQ	ND	NQ	NQ	ND	NQ	NQ	NQ
PFUnA	ND	ND	ND	ND	ND	ND	ND	ND
PFNS	ND	ND	ND	ND	ND	ND	ND	ND
PFDoA	NQ	NQ	NQ	ND	NQ	ND	ND	NQ
PFDS	ND	ND	ND	ND	ND	ND	ND	ND
PFTriA	ND	ND	ND	ND	ND	ND	ND	ND
FOSA	ND	ND	ND	NQ	ND	ND	ND	ND
PFTreA	ND	ND	ND	ND	ND	ND	ND	ND
HFPO-DA	ND	ND	ND	NQ	ND	ND	ND	ND
ADONA	ND	ND	ND	ND	ND	ND	ND	ND
9Cl-PF3ONS	ND	ND	ND	ND	ND	ND	ND	ND
11Cl-PF3OUdS	ND	ND	ND	ND	ND	ND	ND	ND

ND = not detected; NQ = not quantitated

■ Summary and Conclusions

This study evaluated the direct injection analysis of 24 PFASs and 19 mass-labeled surrogates in bottled water using Shimadzu UFMS™ LCMS-8050. The data shows excellent performance of the LCMS-8050 for PFAS analysis in bottled water matrices with minimal sample preparation. Of the seven types of bottled water containers tested, plastic had the highest amount of PFAS present. In particular, the bottle made from recycled plastic showed by far the highest amount of PFAS.

Glass and cardboard bottles had no detectable PFAS levels. While this data would suggest that the plastic recycling process introduces additional PFAS into the water bottles, it is too early to draw that conclusion with any certainty. The data also suggests that the source of the water can contribute PFAS to the bottled water. More experiments are necessary to confirm these preliminary results.

■ References

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- FDA Makes Available Results from Second Round of Testing for PFAS in Foods from the General Food Supply
  https://www.fda.gov/food/cfsan-constituent-updates/fda-makes-available-results-second-round-testing-pfas-foods-general-food-supply
- 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
- International Bottled Water Association – Recommended PFAS Levels in bottled water
  https://www.bottledwater.org/and-polyfluoroalkyl-substances-pfas-and-bottled-water
- US EPA. Basic Information about Per- and Polyfluoroalkyl Substances (PFAS).
  https://www.epa.gov/pfas/basic-information-about-and-polyfluoroalkyl-substances-pfass

ULTRA FAST MASS SPECTROMETRY


LCMS-8040


LCMS-8045


LCMS-8050


LCMS-8060NX


LCMS-2020


Q-TOF LCMS-9030

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Application News

No. LCMS-120

Liquid Chromatography Mass Spectrometry

Analysis and Quantitation of Per- and Polyfluorinated Alkyl Substances (PFAS) in EPA Method 537.1 Using High Resolution Accurate Mass Spectrometry

■ Introduction

EPA Method 537 was expanded to EPA Method 537.1 in November 2018 to include four new per- and polyfluoroalkyl substances (PFAS). While EPA Method 537.1 focuses on well-known PFAS, such as PFOA, PFOS, and GenX[1], there are thousands of unknown PFAS that can potentially contaminate drinking water. Analysis of unknown contaminants requires high resolution and accurate mass capabilities in order to positively identify the molecular formula. This work demonstrates that the quantitation of all PFAS outlined in EPA Method 537.1 can be performed on a quadrupole time-of-flight mass spectrometer (QTOF) at low parts per trillion concentrations in environmental drinking water samples. Quantitation limits on the QTOF are compared to a triple quadrupole mass spectrometer (QQQ). Additionally, the workflow to tentatively identify untargeted PFAS is also included.

■ Methods

Electrospray source conditions were optimized on a QQQ (Shimadzu LCMS-8045) and applied to the QTOF (Shimadzu LCMS-9030). MRM transitions were determined on a QQQ, and accurate mass precursor/product ions were determined on a QTOF. The chromatographic parameters are based on the chromatographic method used in EPA Method 537.1. A Shim-pack XR-ODS 50 x 3.0 mm column was used as a delay column, and a Shim-pack ™ Velox 150 mm x 2.1 mm x 2.7 µm column was used as the analytical column. Quantitation was performed using MRM on the QQQ and high-resolution MRM on the QTOF. Detailed information of the method conditions is included in Tables 1 and 2.

Table 1: LC parameters

LC System	Nexera-X2 UHPLC System
Analytical Column	Shim-pack ™ Velox , 150mm x 2.1mm x 2.7µm, Part No. 227-320094-04
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

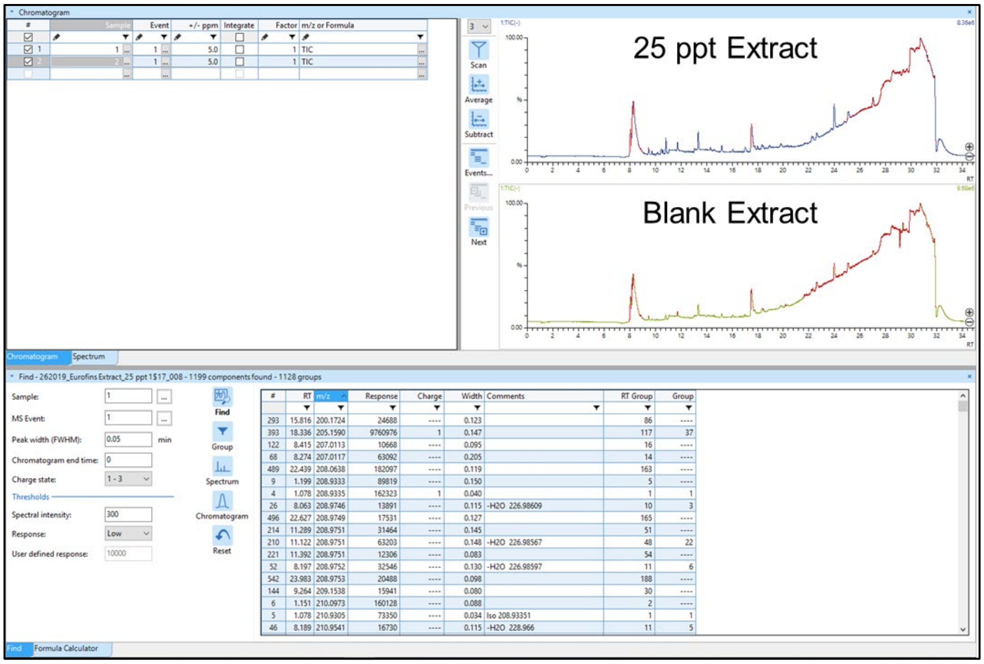
Table 2: LCMS parameters

MS Instrument	LCMS-8045 and LCMS-9030
Interface	Electrospray Ionization (ESI) Negative mode
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

■ Qualitative Analysis

The overall workflow for identifying unknown PFAS in environmental samples can be broken down into four steps. One representative ion was chosen to outline the workflow for tentatively identifying an unknown compound using Insight Explore.

Step 1: Load the .lcm and .lcd files into Insight Explore, then use **Find** to identify features of interest.



Chromatogram

#	Sample	Event	+/- ppm	Integrate	Factor	m/z or Formula
☑ 1	1	1	5.0	☐	1	TIC
☑ 2	2	1	5.0	☐	1	TIC

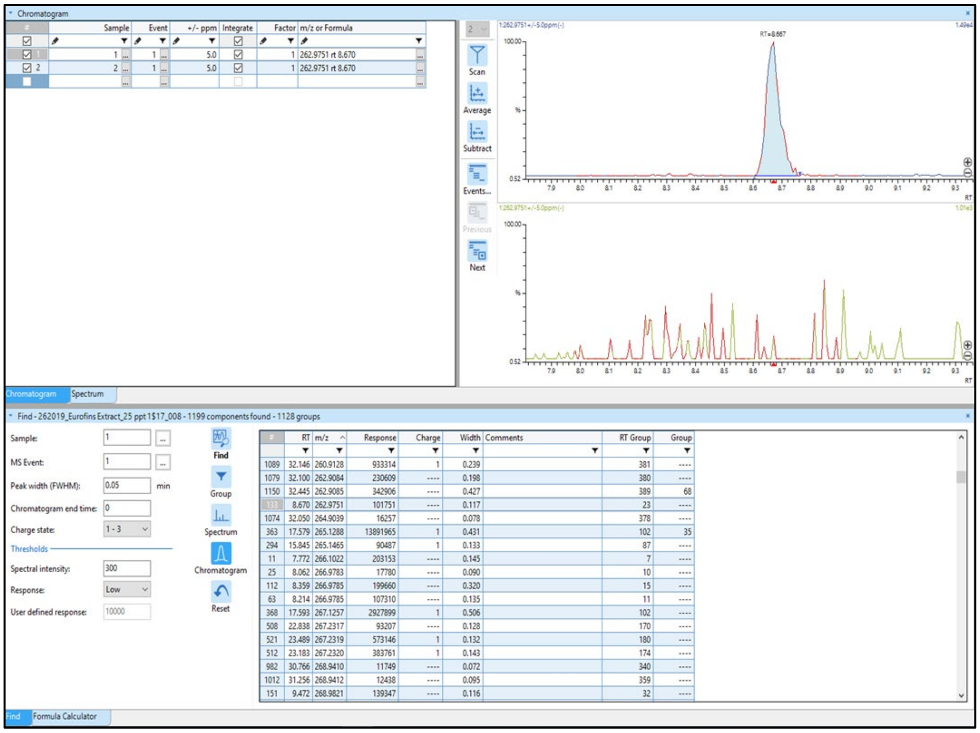
Find - 262019_Eurofins Extract_25 ppt 1$17_008 - 1199 components found - 1128 groups

Sample: 1
MS Event: 1
Peak width (FWHM): 0.05 min
Chromatogram end time: 0
Charge state: 1 - 3
Thresholds
Spectral intensity: 300
Response: Low
User defined response: 10000

#	RT	m/z	Response	Charge	Width	Comments	RT Group	Group
293	15.816	200.1724	24688	----	0.123		86	----
393	18.336	205.1590	9760976	1	0.147		117	37
122	8.415	207.0113	10668	----	0.095		16	----
68	8.274	207.0117	63092	----	0.205		14	----
489	22.439	208.0638	182097	----	0.119		163	----
9	1.199	208.9333	89819	----	0.150		5	----
4	1.078	208.9335	162323	1	0.040		1	1
26	8.063	208.9746	13891	----	0.115	-H2O 226.98609	10	3
496	22.627	208.9749	17531	----	0.127		165	----
214	11.289	208.9751	31464	----	0.145		51	----
210	11.122	208.9751	63203	----	0.148	-H2O 226.98567	48	22
221	11.392	208.9751	12306	----	0.083		54	----
52	8.197	208.9752	32546	----	0.130	-H2O 226.98597	11	6
542	23.983	208.9753	20488	----	0.098		188	----
144	9.264	209.1538	15941	----	0.080		30	----
6	1.151	210.0973	160128	----	0.088		2	----
5	1.078	210.9305	73350	----	0.034	Iso 208.93351	1	1
46	8.189	210.9541	16730	----	0.115	-H2O 228.966	11	5

Step 2: Find the feature compounds that are present in the sample but not in the blank.

An unknown compound with the accurate mass of 262.9751 *m/z* was found at retention time 8.670 min. This compound appeared in an extract, however it is not present in the blank extract.



Chromatogram

#	Sample	Event	+/- ppm	Integrate	Factor	m/z or Formula
☑ 1	1	1	5.0	☑	1	262.9751 rt 8.670
☑ 2	2	1	5.0	☑	1	262.9751 rt 8.670

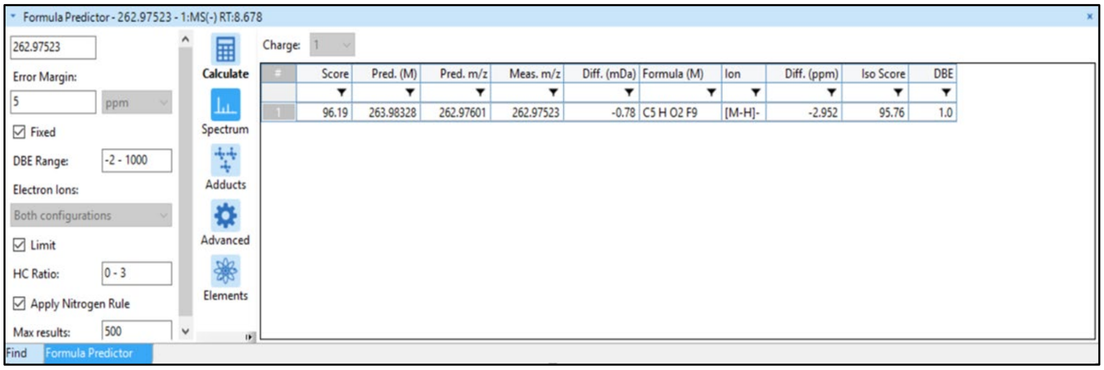
Find - 262019_Eurofins Extract_25 ppt 1$17_008 - 1199 components found - 1128 groups

Sample: 1
MS Event: 1
Peak width (FWHM): 0.05 min
Chromatogram end time: 0
Charge state: 1 - 3
Thresholds
Spectral intensity: 300
Response: Low
User defined response: 10000

#	RT	m/z	Response	Charge	Width	Comments	RT Group	Group
1089	32.146	260.9128	933314	1	0.239		381	----
1079	32.100	262.9084	230609	----	0.198		380	----
1150	32.445	262.9085	342906	----	0.427		389	68
133	8.670	262.9751	101751	----	0.117		23	----
1074	32.050	264.9039	16257	----	0.078		378	----
363	17.579	265.1288	13891965	1	0.431		102	35
294	15.845	265.1465	90487	1	0.133		87	----
11	7.772	266.1022	203153	----	0.145		7	----
25	8.062	266.9783	17780	----	0.090		10	----
112	8.359	266.9785	199660	----	0.320		15	----
63	8.214	266.9785	107310	----	0.135		11	----
368	17.593	267.1257	2927899	1	0.506		102	----
508	22.838	267.2317	93207	----	0.128		170	----
521	23.489	267.2319	573146	1	0.132		180	----
512	23.183	267.2320	383761	1	0.143		174	----
982	30.766	268.9410	11749	----	0.072		340	----
1012	31.256	268.9412	12438	----	0.095		359	----
151	9.472	268.9821	139347	----	0.116		32	----

Step 3: Identify the possible formula using Formula Predictor included in Insight Explore using accurate mass and isotopic pattern.

Using the *Formula Predictor* function, Insight Explore predicted the most likely formula for 262.9751 m/z to be $C_5HO_2F_9$.



Formula Predictor - 262.97523 - 1:MS(-) RT:8.678

262.97523

Error Margin: 5 ppm

☑ Fixed

DBE Range: -2 - 1000

Electron Ions: Both configurations

☑ Limit

HC Ratio: 0 - 3

☑ Apply Nitrogen Rule

Max results: 500

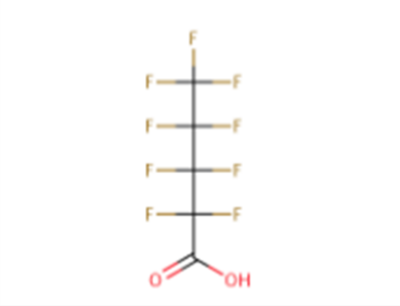
Charge: 1

#	Score	Pred. (M)	Pred. m/z	Meas. m/z	Diff. (mDa)	Formula (M)	Ion	Diff. (ppm)	Iso Score	DBE
1	96.19	263.98328	262.97601	262.97523	-0.78	C5 H O2 F9	[M-H]-	-2.952	95.76	1.0

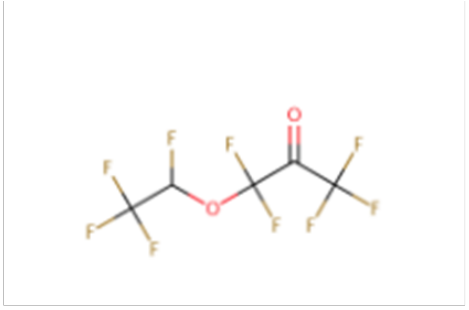
Step 4: Confirm the formula by comparing MS or MS/MS spectrum with a Database.

The predicted molecular weight of 263.98323 and the predicted molecular formula of C5HO2F9 was used to search DSSTox. A total of 10 candidates were found in the database, with four candidates being adduct ions of perfluoropentanoic acid.

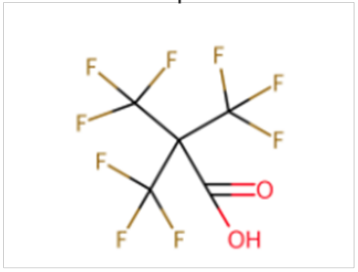
Further information can be acquired using MS/MS scans using 262.9751 as a precursor ion. Comparing *m/z*, formula, structures from DSSTox and MS/MS data, the potential structures were narrowed down to four potential candidates including PFPeA.



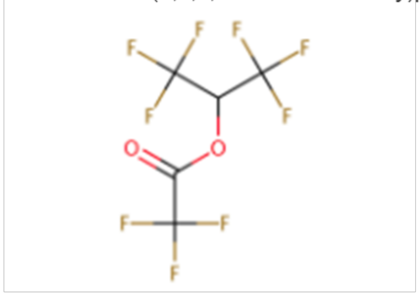
Perfluoropentanoic Acid



1,1,1,3,3-Pentafluoro-3-(1,2,2,2-tetrafluoroethoxy)propan-2-one



3,3,3-Trifluoro-2,2-bis(trifluoromethyl)propanoic acid



1,1,1,3,3,3-Hexafluoropropan-2-yl trifluoroacetate

Figure 1: Potential structures

■ Quantitative Analysis

Triple quadrupole instruments are typically the instruments of choice for quantitative analysis. The MRM optimization for the analysis of PFAS was conducted on a Shimadzu LCMS-8045 triple quadrupole instrument. The MRM method was then transferred from LCMS-8045 to LCMS-9030 QTOF instrument. The method transfer from triple quadrupole instrument to a QTOF instrument could be easily achieved due to similar front end for both the instruments. Both instruments comprise of a thermally assisted ESI probe where the sample is sprayed and ionized at atmospheric pressure. The ionized sample is then introduced through the sample introduction unit (desolvation line) into the vacuum chamber where the ion focusing units guide the ions to the quadrupoles. Effective use of triple quadrupole and QTOF MS provides a comprehensive and accurate data acquisition and analysis.

The quantitative capabilities of a QTOF for PFAS analysis were compared to a triple quadrupole mass spectrometer traditionally used for EPA Method 537.1. Since a TOF mass analyzer does not operate in the same fashion as a quadrupole mass analyzer, a MRM width of 20 ppm was used for all product ions. All calibration curves showed a r^2 value greater than 0.99 as required by EPA Method 537.1. Figure 2 compares the chromatograms at a sample concentration of 5 ppt for all new targets in EPA Method 537.1.

In order to assess TOF stability, a precision and accuracy study was conducted at 25 ppt. Table 3 and Table 4 show replicated 25 ppt injections for the QTOF and QQQ, respectively. Figure 3 compares the LOQs from QTOF and QQQ, with the results for the majority of compounds being less than 3 ng/L.

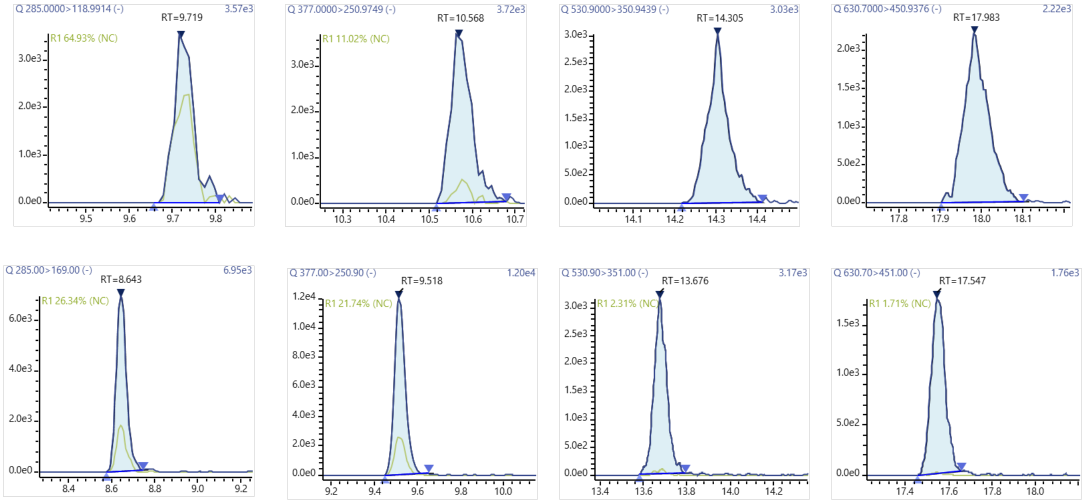


Figure 2: QTOF (top) vs QQQ (bottom) Chromatograms at 5ppt of GenX, ADONA, 9Cl-PF3ONS and 11Cl-PF3OUdS.

Table 3: Summary P&A with QTOF LCMS-9030.

QTOF 25 ppt P&A	True Value	Avg	Avg.%REC	%RSD	Std Dev
PFBS	22.2	23.7	107	7.6	1.80
PFHxA	25	29	116	4.8	1.39
HFPO-DA	62.5	80.4	129	7.3	5.89
PFHpA	25	27.6	110	7.8	2.16
PFHxS	22.8	25.9	113	14.4	3.73
ADONA	25	46.2	185	6.1	2.80
PFOA	25	28.7	115	5.8	1.65
PFOS	23.1	21.7	94	23.1	5.00
PFNA	25	28.2	113	6.3	1.78
9Cl-PF3ONS	23.2	28	121	6	1.68
PFDA	25	25	100	6.3	1.56
N-MeFOSAA	25	29.2	117	11.3	3.31
N-EtFOSAA	25	25.9	104	23.6	6.11
PFUnA	25	24.4	98	7.7	1.88
11Cl-PF3OUdS	23.5	44.5	189	6.6	2.94
PFDoA	25	22.1	88	6.5	1.43
PFTriA	25	22.8	91	6.3	1.44
PFTreA	25	22.8	91	6.8	1.55

Table 4: Summary P&A with QQQ LCMS-8045.

QQQ 25 ppt P&A	True Value	Avg	Avg.%REC	%RSD	Std Dev
PFBS	22.2	25.6	115	2.5	0.629
PFHxA	25	25.6	103	3.9	1.01
HFPO-DA	62.5	67.2	108	3.7	2.46
PFHpA	25	26.4	106	3.6	0.954
PFHxS	32.8	26.4	80	4.1	1.09
ADONA	25	39.7	159	3.2	1.29
PFOA	25	25.1	100	2.5	0.619
PFNA	23.1	25.8	112	3.1	0.797
PFOS	25	25.7	103	3.6	0.936
9Cl-PF3ONS	23.2	27.7	119	2.9	0.809
PFDA	25	23.4	94	2.9	0.686
N-MeFOSAA	25	31.4	126	5.6	1.75
N-EtFOSAA	25	34.8	139	5.5	1.90
PFUnA	25	24.1	96	3.6	0.875
11Cl-PF3OUdS	23.5	46	196	4	1.85
PFDoA	25	23.5	94	2.8	0.665
PFTriA	25	24.4	98	3.8	0.916
PFTreA	25	25.2	101	2.9	0.726

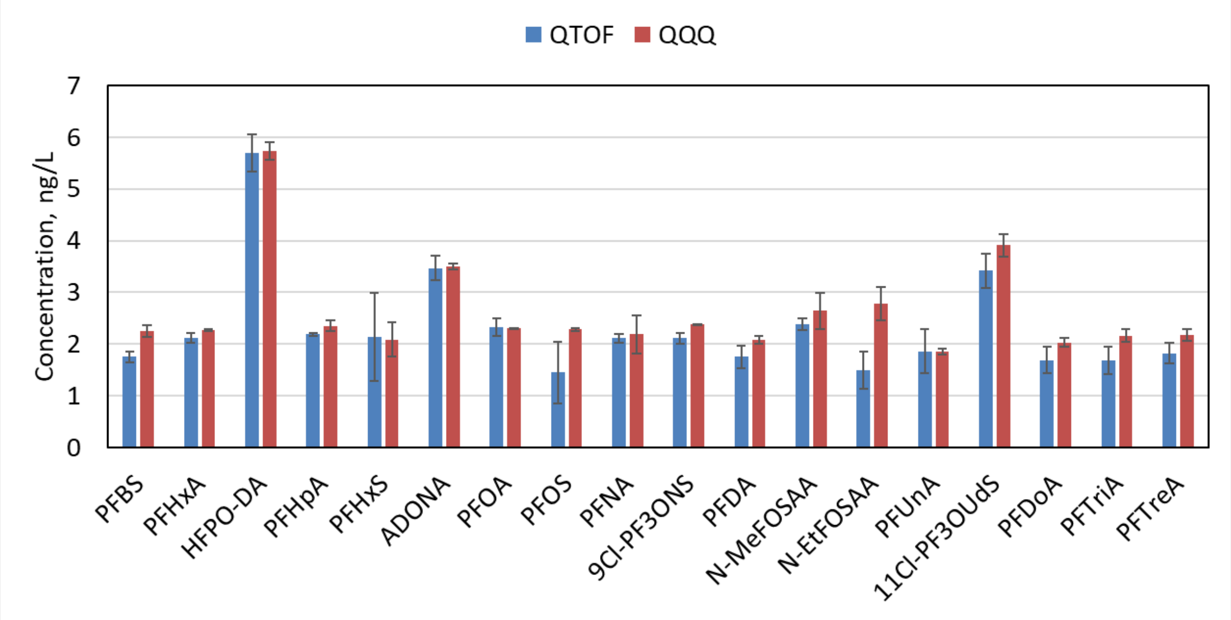


Figure 3: Comparison LOQ from QTOF LCMS-9030 and QQQ LCMS-8045.

■ Conclusions

Comparable quantitative results can be obtained by using either a LCMS QQQ or a LCMS QTOF, with the QTOF having the additional capability to simultaneously screen for potential unknown PFAS contaminants with a streamlined workflow using LabSolutions Insight Explore.

EPA Method 537.1 allows for additional compounds to be added to the method, as long as the QC requirements are met. Simultaneous qualitative and quantitative analysis allows for laboratories to constantly screen for PFAS not specifically in EPA Method 537.1, while quantifying known PFAS contaminants.

■ Reference

- EPA Method 537.1, Determination 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. (U.S. Environmental Protection Agency, Washington, D.C., Nov.2018).

UFMS
ULTRA FAST MASS SPECTROMETRY


LCMS-8040


LCMS-8045


LCMS-8050


LCMS-8060NX


LCMS-2020


Q-TOF LCMS-9030

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