SHIMADZU
Excellence in Science

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

Water and Environmental Analysis

LCMS

https://www.shimadzu.com/an

Publish Date:
10 January 2019

Authors:
Brahm Prakash[1], Cindy Lee[2], Gerard Byrne[1], Tairo Ogura[1]

[1]Shimadzu Scientific Instruments, USA.
[2]Marketing Innovation Centre, Singapore.

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.

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.

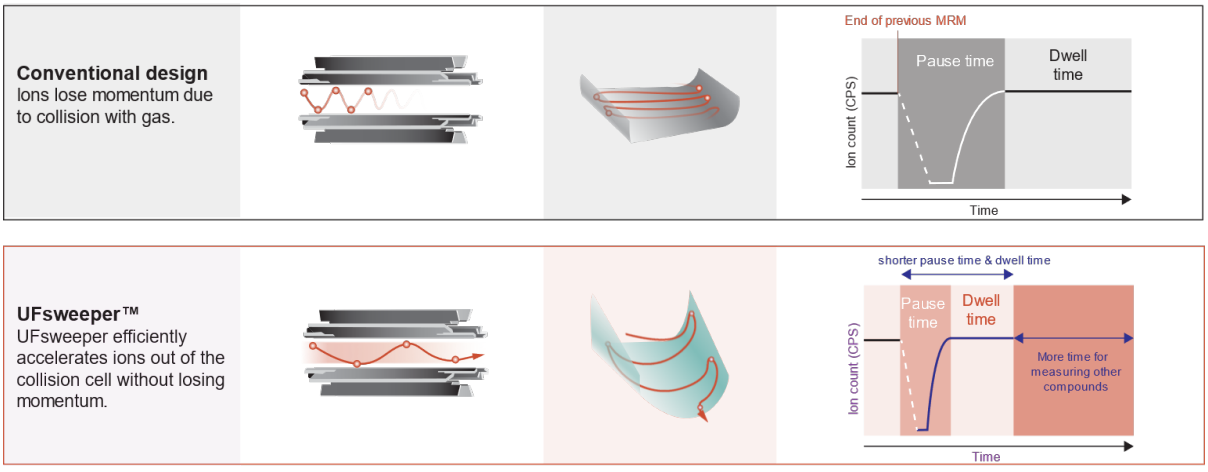
With the release of EPA's Health Advisory for PFAS in 2017, the availability of validated methods and increase of public awareness, PFAS monitoring and testing is becoming routine. Together with this trend of using similar compounds as alternatives, the list of PFAS that are of concern may continue to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



[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.

LCMS Instrument	Shimadzu LCMS-8060
Analytical Column	Shim-pack™ GIST Phenyl-Hexyl, 2.1 mm ID × 100 mm, 3 µm particle size
Solvent Delay Column	Shim-pack™ XR-ODS, 3 mm ID × 50 mm, 2.2 µm particle size
Column Temperature	40 °C
Injection Volume	10 µL
LC Flow Rate	0.4 mL/min
Mobile Phase A	20 mM Ammonium Acetate in LCMS-grade Water
Mobile Phase B	Acetonitrile
Gradient Conditions	<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>
Run / Acquisition Cycle Time	20 minutes (all 49 PFAS compounds are eluted in 13 minutes)
Interface	Electrospray Ionization (ESI)
Interface Temperature	300 °C
Desolvation Line Temperature	100 °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	74

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.

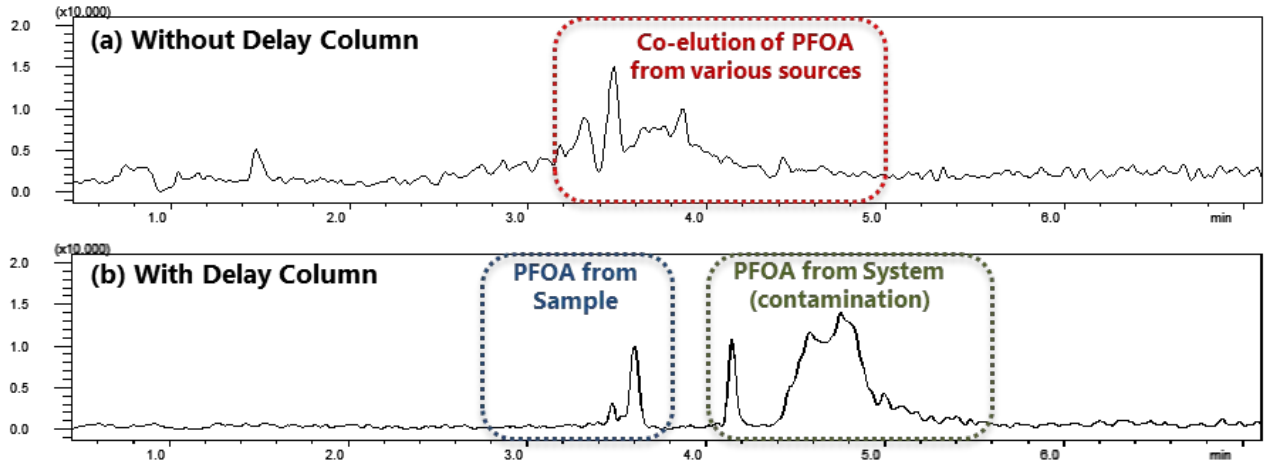


Figure 1. Chromatogram of PFOA: (a) without delay column and (b) with delay column.

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.

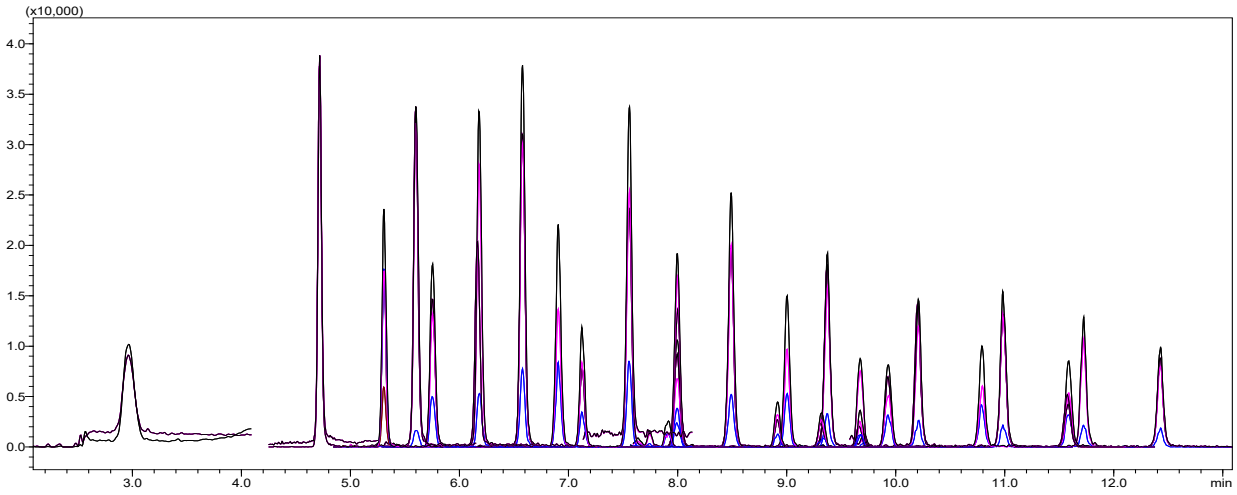


Figure 2. MRM (pink & blue) and TIC (black) chromatograms of all 49 PFAS in a mixed standard solution, with each PFAS at 100 ng/L.

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.

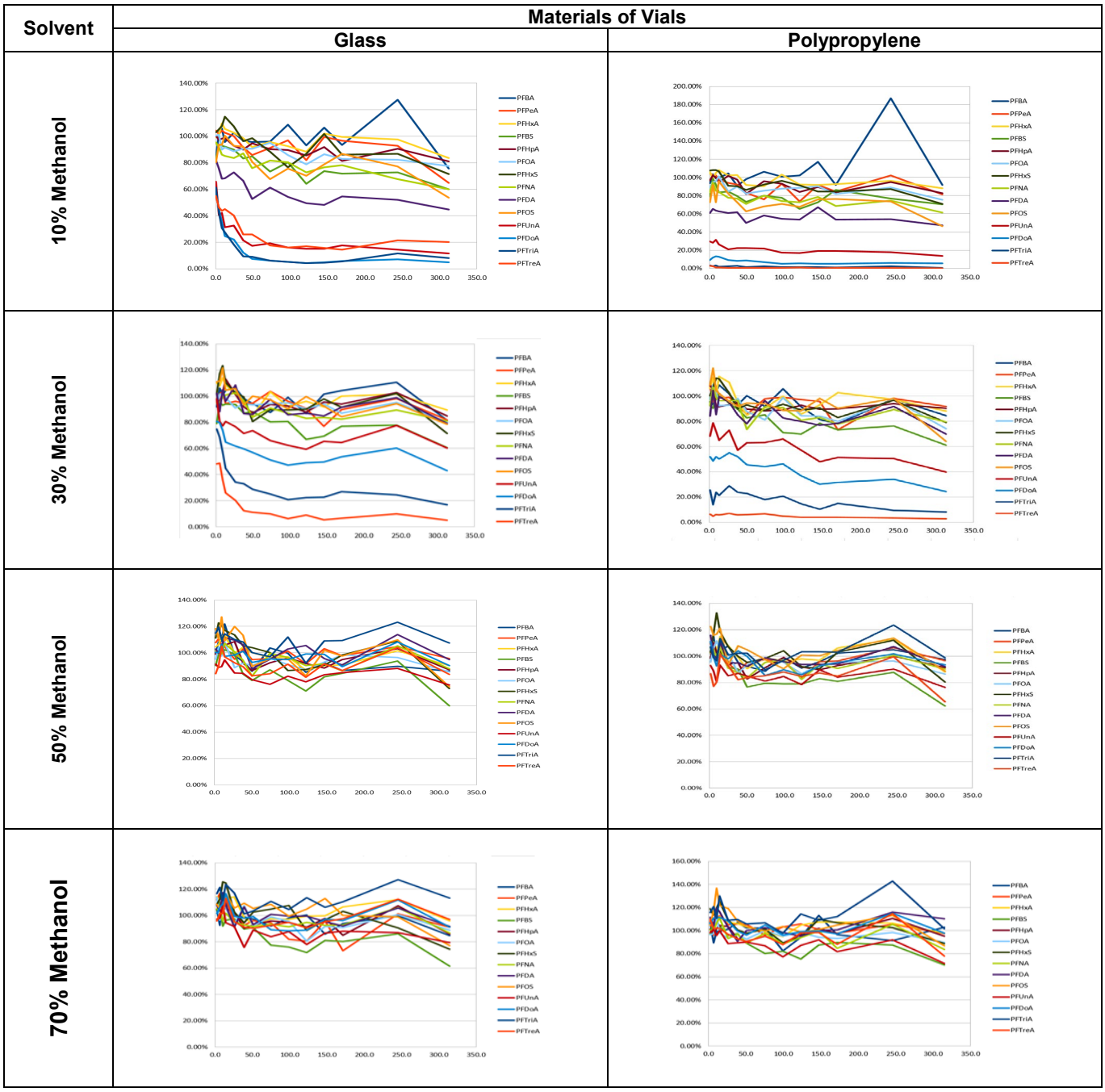


Figure 3. Plots of PFAS recovery against shelf life (time/hour) for the various solvents in glass and polypropylene LC vials.

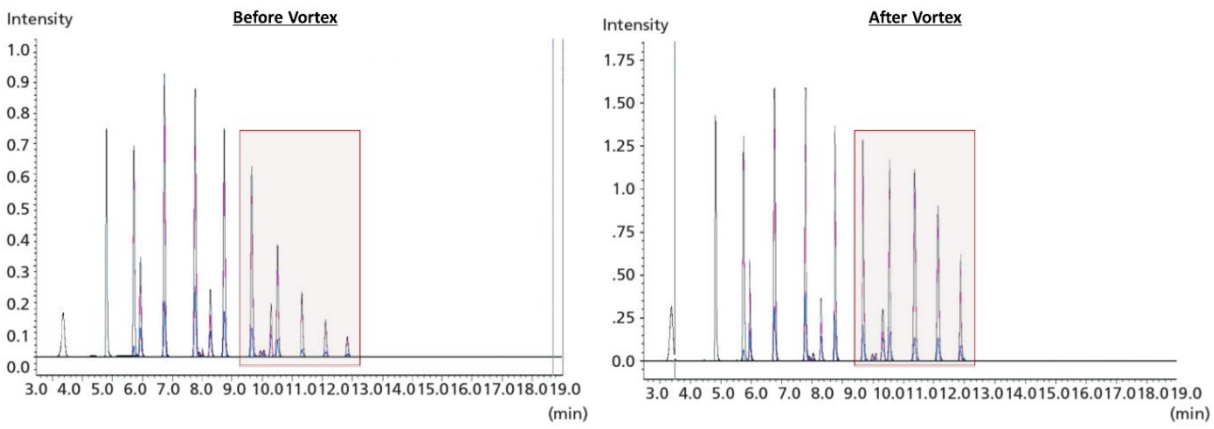


Figure 4. Recovery of PFAS before (left) and after (right) mixing the standard PFAS solution vial.

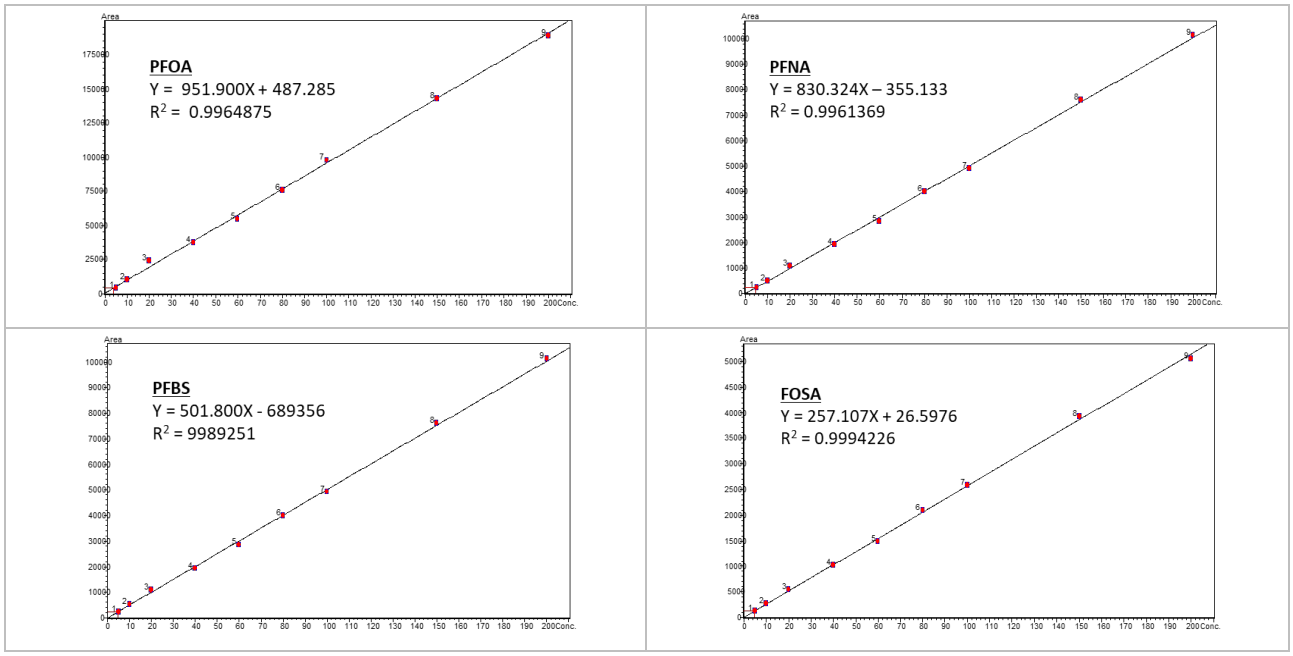


Figure 5. Representative calibration curves (PFOA, PFBS, PFNA and FOSA) at 10 µL injection using LCMS-8060.

References

[1] Agency for Toxic Substances and Disease Registry , "Per- and Polyfluoroalkyl Substances (PFAS) and Your Health," 31 October 2018. [Online]. Available: https://www.atsdr.cdc.gov/pfas/. [Accessed 11 December 2018].

[2] C. Lau, K. Anitole, C. Hodes, D. Lai, A. Pfahles-Hutchens and J. Seed, "Perfluoroalkyl Acids: A Review of Monitoring and Toxicological Findings," *Toxicological Sciences,* vol. 99, no. 2, pp. 366-394, 1 October 2007.

[3] Environmental Protection Agency, "Lifetime Health Advisories and Health Effects Support Documents for Perfluorooctanoic Acid and Perfluorooctane Sulfonate," *Federal Register ,* vol. 81, no. 101, pp. 33250-33251, 2016.

[4] United States Environmental Protection Agency (US EPA), "PFOA, PFOS and Other PFASs: Basic Information about PFAS," 20 August 2018. [Online]. Available: https://www.epa.gov/pfas/basic-information-pfas#exposed. [Accessed 5 December 2018].

[5] Sara Sahlin, Swedish Environmental Protection Agency, "PFAS in the Baltic Sea Region: Inventory of Awareness, Actions and Strategies Related to Highly Fluorinated Substances PFAS, including PFOS," 2017.

[6] W. H. O. (WHO), Keeping our water clean: the case of water contamination in the Veneto Region, Italy, Copenhagen, Denmark: World Health Organization (WHO) Regaional Office for Europe, 2016.

[7] K. M. Rappazzo, E. Coffman and E. P. Hines, "Exposure to Perfluorinated Alkyl Substances and Health Outcomes in Children: A Systematic Review of the Epidemiologic Literature," *International Journal of Environmental Research and Public Health,* vol. 14, no. 7, p. 691, 2017.

[8] United States Environmental Protection Agency, "Supporting Documents for Drinking Water Health Advisories for PFOA and PFOS," November 2016. [Online]. Available: https://www.epa.gov/ground-water-and-drinking-water/supporting-documents-drinking-water-health-advisories-pfoa-and-pfos. [Accessed 4 December 2018].

[9] United States Environmental Protection Agency (US EPA), "U.S. State Resources about PFAS," [Online]. Available: https://www.epa.gov/pfas/us-state-resources-about-pfas. [Accessed 4 December 2018].

[10] C. Alder, "Analysis of State-by-State Differences in PFAS Regulation," Northeastern University Social Science Environmental Health Research Institute, 2 October 2018. [Online]. Available: https://pfasproject.com/2018/10/02/analysis-of-state-by-state-differences-in-pfas-regulation/. [Accessed 11 December 2018].

[11] California Water Boards, State Water Resources Control Board, "Perfluorooctanoic acid (PFOA) and Perfluorooctanesulfonic acid (PFOS)," 13 July 2018. [Online]. Available: https://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/PFOA_PFOS.html. [Accessed 13 December 2018].

[12] X. C. Hu, D. Q. Andrews, A. B. Lindstrom, T. A. Bruton, L. A. Schaider, P. Grandjean, R. Lohmann, C. C. Carignan, A. Blum, S. A. Balan, C. P. Higgins and E. M. Sunderland, "Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Areas and Wastewater Treatment Plants," *Environmental Science & Technology Letters,* vol. 3, no. 10, pp. 344-350, 2016.

[13] H. A. Kabore, S. Vo Duy, G. Munoz, M. Ladji, M. Desrosiers, J. Liu, T. K. Sory and S. Sauve, "Worldwide drinking water occurrence and levels of newly-identified perfluoroalkyl and

polyfluoroalkyl substances," *Science of The Total Environment,* Vols. 616-617, pp. 1089-1100, 2018.

[14] U.S. Environmental Protection Agency, "US EPA Method 537: Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography / Tandem Mass Spectrometry (LC/MS/MS)," Washington D.C., 2009.

[15] United States Environmental Protection Agency, "US EPA - PFAS Research and Development," 14 August 2018. [Online]. Available: https://www.epa.gov/sites/production/files/2018-08/documents/r4_combined_presentations_.pdf. [Accessed 5 December 2018].

[16] ASTM International, "ASTM D7979-17: Standard Test Method for Determination of Perfluorinated Compounds in Water, Sludge, Influent, Effluent and Wastewater by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)," West Conshohocken, 2017.

[17] ASTM International, "ASTM D7968-17a: Standard Test Method for Determination of Perfluorinated Compounds in Soil by LIquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)," West Conshohocken, 2017.

[18] United States Environmental Protection Agency (US EPA), "Assessing and Managing Chemicals under TSCA, Fact Sheet: 2010/2015 PFOA Stewardship Program," [Online]. Available: https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/fact-sheet-20102015-pfoa-stewardship-program. [Accessed 23 December 2018].

[19] Secretariat of the Basel, Rotterdam and Stockholm Conventions (UNEP), "Two More Toxic Chemicals Recommended to be Eliminated as UN Scientific Committee Paves Way for Ban on Widely-Used PFOA [Press Release]," 18 September 2018. [Online]. Available: http://www.brsmeas.org/Implementation/MediaResources/PressReleases/POPRC14PressReleases/tabid/7685/language/en-US/Default.aspx. [Accessed 3 December 2018].

[20] S. A. Meiburg, "Emerging Contaminants and Environmental Health," *North Carolina Medical Journal,* vol. 79, no. 5, pp. 315-316, 2018.

[21] U.S. Environmental Protection Agency, "US 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)," Washington D.C., 2018.

SHIMADZU
Excellence in Science

Shimadzu Corporation
www.shimadzu.com/an/