

Analysis of Per- and Polyfluoroalkyl Substances (PFASs) in Non-Drinking Water Matrices Using the LC-Triple Quadrupole Mass Spectrometer

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Introduction

In June 2019, Method 8327 was posted at the EPA SW-846 validated methods website for the analysis of PFAS in groundwater, surface water, and wastewater. Currently, no other EPA method for PFAS analysis in complex matrices is available; therefore, this method in its final version will provide a tool for monitoring selected PFAS in non-potable waters. This poster demonstrates that the Shimadzu 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 method provides a fast and robust solution for addressing the challenges in the quantitation of low levels of PFAS in non-potable waters.

This poster summarizes this new fast and robust method using the Shimadzu LCMS-8050. Results demonstrate that the instrument obtained lower method reporting limits and better precision than listed in the draft EPA method. Most importantly, the results confirm that laboratories currently analyzing samples by ASTM Method D7979 can easily update their workflow to implement EPA Method 8327.

Experimental - Instrument Operating Conditions

The SW-846 draft Method 8327 analyzes 24 target PFAS compounds and 19 surrogates in reagent, ground, surface, and wastewater. 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. A detailed description of the LC/MS/MS parameters is included in Table 1. Table 2 lists the compounds tested, retention time, the MRM transitions and collision energies. At least two multiple reaction monitoring (MRM) transitions were optimized for most of the analytes.

Table 1: 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

Mobile Phase A consisted of 20 mM Ammonium acetate in 95:5 H₂O:ACN. Mobile Phase B consisted of 10 mM ammonium acetate in 95:5 ACN: H₂O. 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. The overall runtime for each injection was 21 minutes, including re-equilibration for both the delay and the analytical column. This run time of 21 minutes includes a final wash with concentrated acetonitrile to flush the column, remove background residuals contaminants and restore column performance before starting the next run. Since SW-846 methods are performance based, the method could easily be modified to include isotopic dilution or internal calibration for quantifying the concentrations.

Experimental - Sample Analysis

Calibration Standards

Standards available from Wellington Laboratories were used for this study (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 a matrix consisting of 50:50 water:methanol containing 0.1% acetic acid in order to match the matrix of the environmental samples. Filtration was not performed on the calibration standards. Figure 1 shows an extracted ion chromatogram of representative peak at 5 ng/L and calibration curves of PFHxS, PFOS and PFTrEA.

Sample Preparation

The SW-846 draft Method 8327 was tested using reagent water, surface water, ground water, and wastewater matrices. Five mL of water samples, procedural blanks, as well as an LCS containing known amounts of PFASs were collected in a 15 mL polypropylene centrifuge tube. Forty microliters of the surrogate spiking solution containing 19 isotopically labeled PFAS and 5 mL of methanol were added to each sample, blank, and control sample. The samples were shaken and mixed on a vortex mixer for 2 minutes then filtered through a polypropylene syringe filter. 10 microliters of acetic acid was added to all samples, and a portion transferred to an autosampler glass vial for analysis by LC/MS/MS.

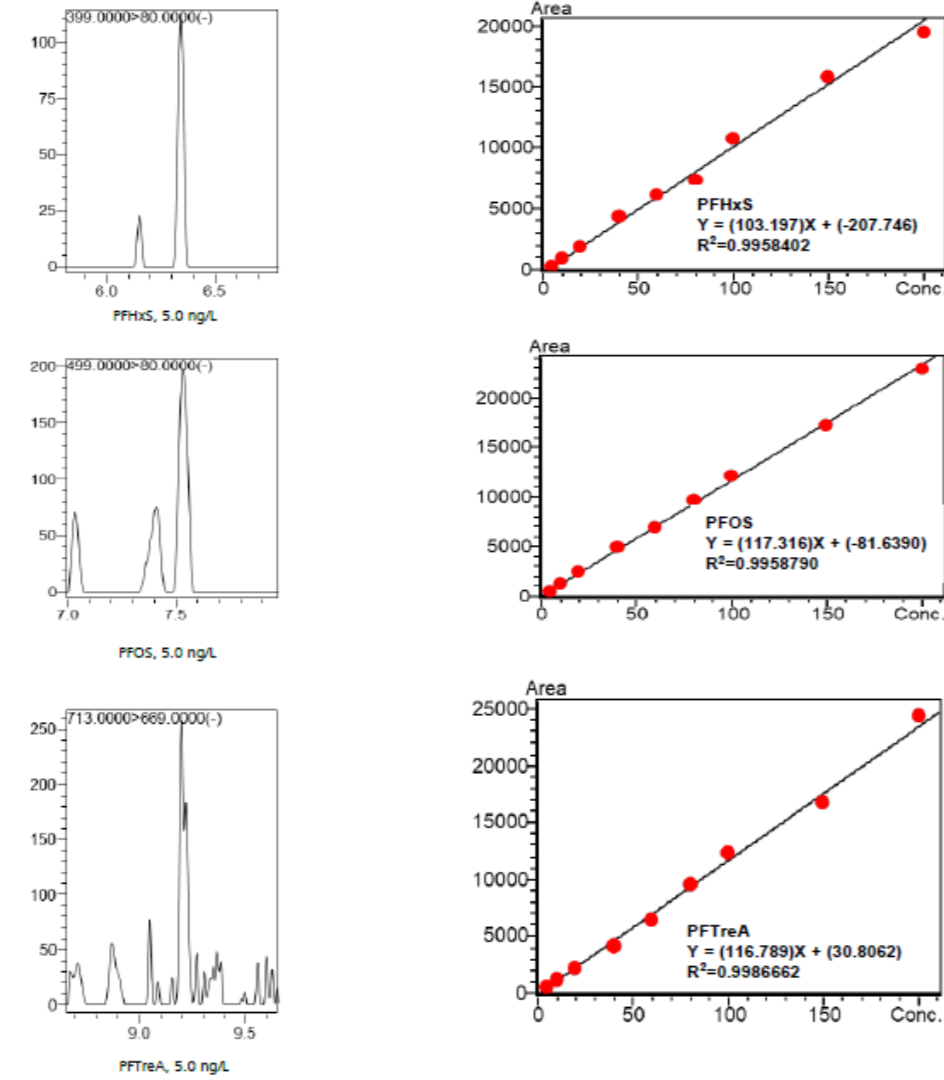


Figure 1: Representative Chromatograms and Calibration curves for compounds listed in EPA Method 8327

Table 2: MRM transitions, retention times, collision energies and %recoveries at 40 ppt and 80 ppt.

Component	Retention Time (minutes)	Transition (m/z)	Collision energy (V)	40 ppt Recovery	% Recovery 40 ppt	80 ppt (n=3) Recovery	% Recovery 80 ppt	%RSD 40 ppt	%RSD 80 ppt
PFBA	3.341	213 > 169	9	42.37	106	83.1	103.9	1.4	
MPFBA	3.341	217 > 172	9	40.14	100	80.8	101.0	1.3	
PFPeA	3.941	263 > 219	8	41.49	104	80.2	100.3	2.8	
MSPFPeA	3.940	268 > 223	8	40.34	101	79.2	99.0	2.0	
4-2 FTS	4.444	327 > 307 327 > 81	18 35	41.08	103	82.1	102.6	3.2	
M4-2 FTS	4.442	329 > 309	20	41.48	104	80.5	100.6	3.1	
PfHxA	4.683	313 > 269 313 > 119	9 21	41.10	103	80.5	100.6	1.1	
MSPFHxA	4.680	318 > 273	11	40.57	101	81.1	101.4	1.1	
PFBS	4.709	299 > 80 299 > 99	30 28	38.96	97	80.5	100.6	3.0	
M3PFBS	4.813	302 > 80	34	39.32	98	80.4	100.5	2.3	
PfHpA	5.401	363 > 319 363 > 169	9 16	39.01	98	81.7	102.1	0.6	
M4PFHpA	5.400	367 > 322	10	38.68	97	80.1	100.2	1.8	
PFPeS	5.606	349 > 80 349 > 99	42 30	41.15	103	79.8	99.8	2.3	
6-2 FTS	5.797	427 > 407 427 > 81	23 39	37.33	93	85.4	106.8	6.7	
M6-2 FTS	5.799	429 > 409	22	39.19	98	80.2	100.3	5.5	
PFOA	6.048	413 > 369 413 > 169	10 17	40.05	100	81.1	101.4	1.4	
M8PFOA	6.051	421 > 376	10	41.73	104	82.4	103.0	2.8	
PfHxS	6.305	399 > 80 399 > 99	43 22	41.34	103	74.4	93.0	2.7	
M3PFHxS	6.306	402 > 80 403 > 84	49 49	41.46	104	79.5	99.4	2.1	
PFNA	6.642	463 > 419 463 > 219	11 16	38.10	95	79.4	99.3	4.9	
M9PFNA	6.641	472 > 427	12	39.58	99	79.1	98.9	1.3	
8-2 FTS	6.927	527 > 507 527 > 81	26 49	33.29	83	78.6	98.3	10.7	
M8-2 FTS	6.928	529 > 509 527 > 81	26 49	35.90	90	83.3	104.1	3.6	
PfHpS	6.928	449 > 80 449 > 99	51 37	41.09	103	80.3	100.4	1.26	
N- MeFOSAA	7.254	570 > 419 570 > 483	21 16	39.93	100	82.8	103.5	9.5	
d3 N- MeFOSAA	7.243	573 > 419	20	39.33	98	79.9	99.8	5.4	
PFDA	7.189	513 > 468.9 413 > 219	11 17	40.68	102	81.3	101.7	2.8	
M6PFDA	7.188	519 > 474	11	39.27	98	81.2	101.4	2.4	
N-EiFOSAA	7.469	584 > 419 584 > 483	20 16	38.42	96	74.2	92.8	10.2	
M N- EiFOSAA	7.463	589 > 419	21	44.72	112	75.3	94.1	6.7	
PFOS	7.483	499 > 80 499 > 99	54 38	34.56	86	75.2	94.0	5.3	
M8PHOS	7.484	507 > 80	55	36.86	92	77.5	96.9	3.3	
PFUdA	7.697	563 > 519 563 > 269	12 16	41.21	103	81.4	101.7	5.3	
M7PFUdA	7.695	549 > 525	12	43.51	109	81.0	101.3	5.1	
PNFS	8.009	549 > 80 549 > 99 613 > 569	54 44 12	44.30	111	85.1	106.4	9.2	
PFDoA	8.181	613 > 169	21	37.82	95	78.2	97.8	3.4	
MPFDoA	8.179	615 > 570	11	39.36	98	78.0	97.6	2.0	
FOSA	8.498	498 > 78	43	41.83	105	80.9	101.2	5.2	
M8FOSA	8.498	506 > 78	48	41.12	103	81.9	102.4	1.7	
PFDS	8.523	599 > 80 599 > 99	55 50	41.55	104	80.7	100.8	3.3	
PFTriA	8.662	663 > 619 663 > 169	12 27	42.18	105	79.2	99.1	3.4	
PFTeDA	9.155	713 > 669 713 > 169	13 27	39.44	99	80.0	100.0	8.1	
M2PFTeDA	9.130	715 > 670	15	37.43	94	76.2	95.2	8.5	

Results and Discussion

Since PFAS can be present in reagents, glassware, pipettes, tubing, degassers and other parts from the LC-MS/MS instruments, potential 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 detectable PFAS contamination. To verify 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), shown in Figure 2). Data displayed in Figure 2 demonstrates the absence of PFAS in the materials used for analysis, respectively. Results from the null injection (not included here) confirmed the absence of background contamination originating from the instrument.

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 (r²) greater than 0.99 for all analytes or transitions. In addition, calibration residuals of each standard were verified to be 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 method EPA 8327 and confirms that peak shape is maintained at higher concentrations. Figure 5 shows the chromatogram for 24 PFAS compounds spiked at 60 ppt in various matrices, including reagent water, groundwater, surface water, and wastewater. This figure shows that despite the differences in the sample composition and presence of potential interferences, the separation and peak shape is maintained in all sample types analyzed.

Table 2 lists the calculated concentrations, percent recovery for all targets in EPA Method 8327 at mid and high-level concentrations (40 and 80 ppt). All percent recoveries were within the limits established as acceptable in draft method (50%-150% for the lowest calibration standard and 70%-130% for the remaining ones). Table 3 outline the surrogate percent recoveries and precision (%RSD) spiked at 160 ng/L in reagent water, groundwater, surface water and wastewater samples. All results (except those from M2PFTeA in groundwater) were within 70 to 130% as required by the method acceptance criteria and precision (%RSD) were ≤ 20%.

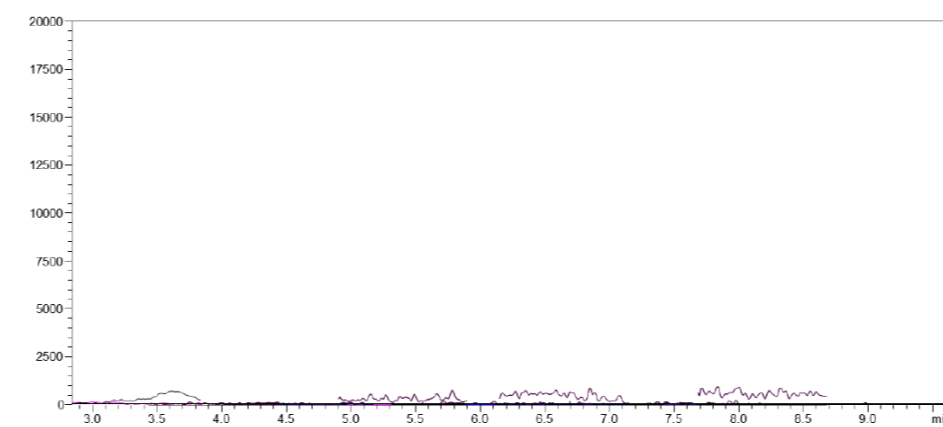


Figure 2: TIC Chromatogram of a reagent blank in 50:50 MeOH:H2O with 0.1% acetic acid

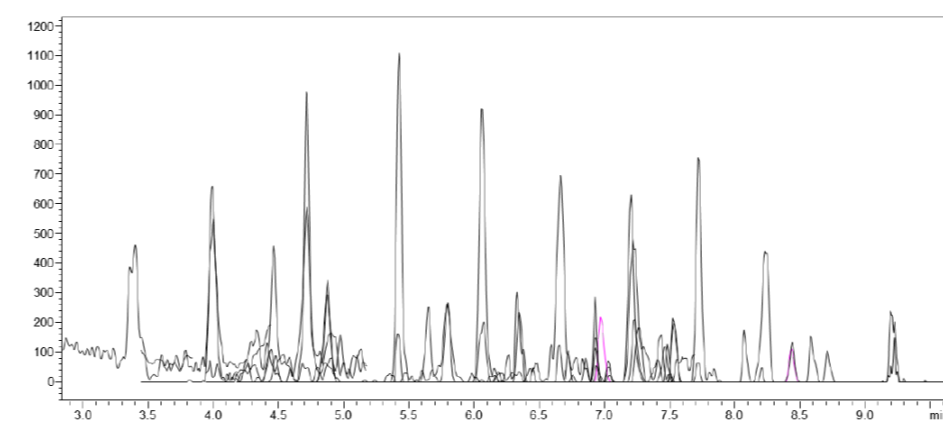


Figure 3: TIC (black) chromatograms and MRM transitions (other colors) of all PFAS in EPA Method 8327 at the low-level calibrator (5 ppt).

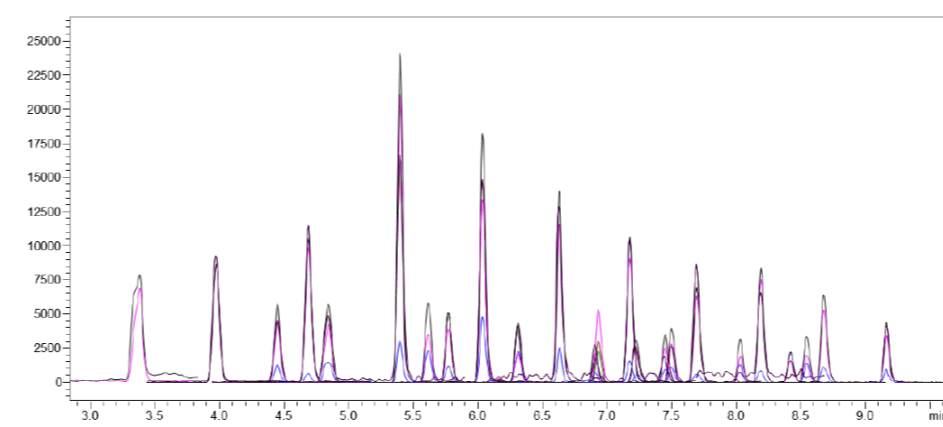


Figure 4: TIC (black) chromatograms and MRM transitions (other colors) of all PFAS in EPA Method 8327 at the mid-level calibrator (80ppt).

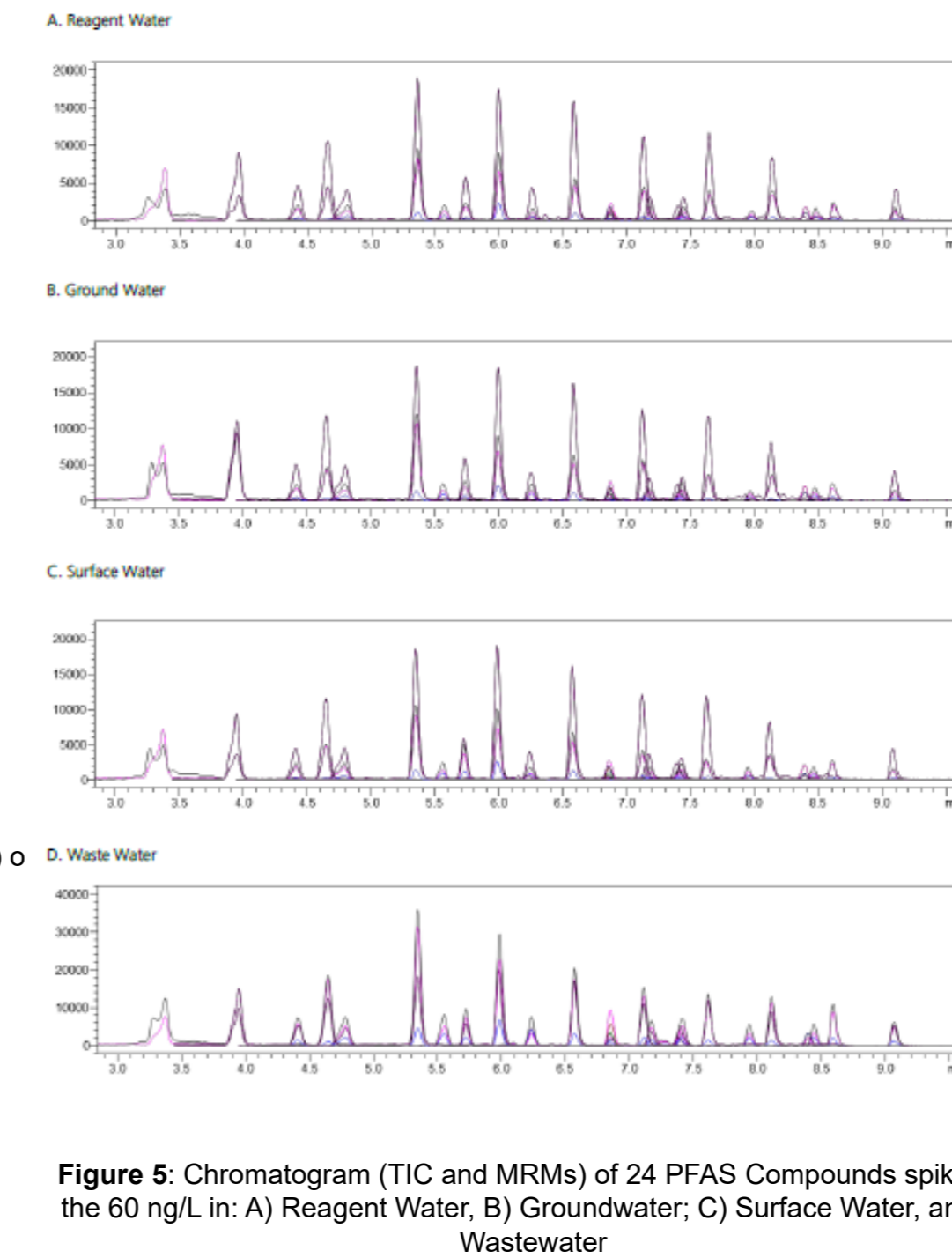


Figure 5: Chromatogram (TIC and MRMs) of 24 PFAS Compounds spiked at the 60 ng/L in: A) Reagent Water, B) Groundwater, C) Surface Water, and D) Wastewater

Compound	Reagent Water (n=4)		Groundwater (n=4)		Surface Water (n=4)		Wastewater (n=4)	
	%Average Recovery	%RSD	%Average Recovery	%RSD	%Average Recovery	%RSD	%Average Recovery	%RSD
M4PFBA	85.3	5	117.6	3.2	89.2	6.7	101.8	7.5
MSPFPeA	92.8	1.8	117.3	3.4	90.5	6.5	101.8	6.8
M2-4-2 FTS	84.8	5.7	95	5.6	84.3	8.3	100	5.9
MSPFHxA	94.5	2.2	117	7.2	90.5	9.6	102.9	7
M3PFBS	88.4	5.9	110.2	1.5	88.4	6.7	103.2	6.8
M4PFHpA	94.9	1.9	115.4	2.8	88.5	7.4	99.7	5.7
M2-6-2 FTS	86.3	4.2	86.8	7.6	83.3	5.2	92.7	4.1
M8PFOA	94.2	4	115.5	2.4	90.4	6.3	99.3	4.4
M3PFHxS	90	3.5	118.8	6.3	87	8.4	97.9	7
M9PFNA	96.4	2.4	115.4	4.9	89.1	7.7	97.6	6.2
M2-8-2 FTS	88.4	9.5	108.9	9.9	81.1	8.4	96.3	5.8
M6PFDA	94.5	1.5	114.6	4.2	87.9	3.6	93.5	6.6
d3-NMeFOSAA	96.7	1.8	116.7	12	88.5	8.9	92.6	5.4
d5-NEiFOSAA	91	4	109	5.8	82.7	11.1	94.5	5.7
M8PFOS	87.9	0.7	118.3	3.4	84.1	6.9	90.7	4.3
M7PFUdA	92.3	1.8	121.5	4.1	91.2	2.5	97	7.6
M2PFDoA	94.2	1.4	122.8	6.8	91.8	5.4	98.9	6.7
M8FOSA	93.4	10.4	123.1	6.6	89.3	7.8	98.8	6
M2PFTeA	89	3.5	138	4.5	88.6	6.7	93.4	6

Table 3: Surrogates Recoveries: Accuracy (%recovery) and precision (%RSD) at 160 ng/L in reagent water, ground water, surface water and wastewater samples.

Summary and Conclusions

The app note evaluated EPA SW-846 draft method 8327 for the 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. Linearity, minimum reportable levels, accuracy, and precision for all PFAS compounds met, or exceeded the criteria in draft EPA Method 8327. Thus, this data demonstrates that the Shimadzu LCMS-8050 could achieve rapid, reliable and highly-sensitive quantitative PFAS results in non-potable waters by SW-846 Method 8327, allowing for high-throughput and rapid turnaround.

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