

PFAS in wastewater – Demonstration of performance for EPA 1633

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INTRODUCTION

The US Environmental Protection Agency (EPA) published the first method for the analysis of PFAS in drinking water in 2009. Since then, EPA has published methods EPA 537.1 and EPA 533 in 2018 and 2019, respectively, also for drinking water samples. It was not until 2021 that EPA published the first method (draft method 1633) for analyzing PFAS in wastewater and other environmental samples under the scope of the Clean Water Act. Currently, this is the only standardized method published by EPA available to environmental labs interested in monitoring PFAS in wastewater samples in anticipation of future regulation.

In this work, we optimized an analytical method on a Shimadzu's LCMS 8050 for the analysis of PFAS in accordance with EPA Draft Method 1633 and evaluated the individual recoveries from each step required in the preparation of wastewater samples (solid phase extraction and carbon clean-up). This poster summarizes the optimized instrumental method and its performance, based on sensitivity, linearity, repeatability, and the results from the analysis of ultra pure water and wastewater effluent samples.

EXPERIMENTAL APPROACH

Standards and calibration curve

The forty (40) target PFAS compounds, twenty-three (23) Extracted Internal Standards (EIS) and seven (7) Non-Extracted Internal Standards (NIS) included in EPA Draft Method 1633 were purchased from Wellington Laboratories as native mixes. Standard solutions were prepared to achieve the desired concentrations listed in the method (targets: 0.2 – 250 ng/mL; EIS: 1.25 – 25 ng/L; NIS: 1.25 – 5 ng/L).

Sample Preparation

500 mL of wastewater effluent or ultra pure water were collected into pre-cleaned polyethylene bottles and weighed. 25 µL of EIS stock solution was added to each sample. Pre-condition of SPE with 0.1% methanolic ammonium, methanol and reagent water was performed according to the product manual (Inert Sep mini MA-2: 5010-27235, 280mg). Samples were loaded onto the SPE cartridge at 5 mL/min. Sample bottles were rinsed with 10 mL of reagent water and those rinses were loaded onto the SPE cartridge. Subsequently, the cartridge was dried with nitrogen gas and then eluted with 5 mL of 0.1% methanolic ammonium. 25 µL of NIS was added to each extract.

Instrument and operational conditions

The LC/MS/MS analysis was performed using a Shimadzu Nexera UHPLC system coupled with a LCMS-8050 Triple Quadrupole Mass Spectrometer. A delay column, the essential modification of hardware for minimizing possible PFAS background contamination from LC and solvents, was installed in between the mixer and autosampler for perform this work (Figure 1).

The detailed description of the LC/MS/MS parameters is included in Table 1.

Table 1. HPLC Instrumental conditions

Parameter	Value
LCMS	Shimadzu LCMS-8050
Analytical Column	Shim-pack GIST-HP C18 2.1 mm i.d. x 50 mm L, 3 µm
Solvent Delay Column	Shim-pack GIST C18 3.0 mm i.d. x 50 mm L, 5 µm
Column Oven Temperature	40 °C
Injection Volume	2 µL
Mobile Phase	A: 2 mM Ammonium Acetate in 5% (v/v) Acetonitrile in reagent water B: Acetonitrile
Gradient Flow rate	0.4 mL/Min
Run time	20 minutes
Nebulizing gas flow	3 L/Min
Heating gas flow	15 L/Min
Interface temperature	190 °C
Desolvation Line temperature	200 °C
Heat Block temperature	300 °C
Drying gas flow	5 L/Min
Acquisition cycle time	16 min
Total MRMs	72

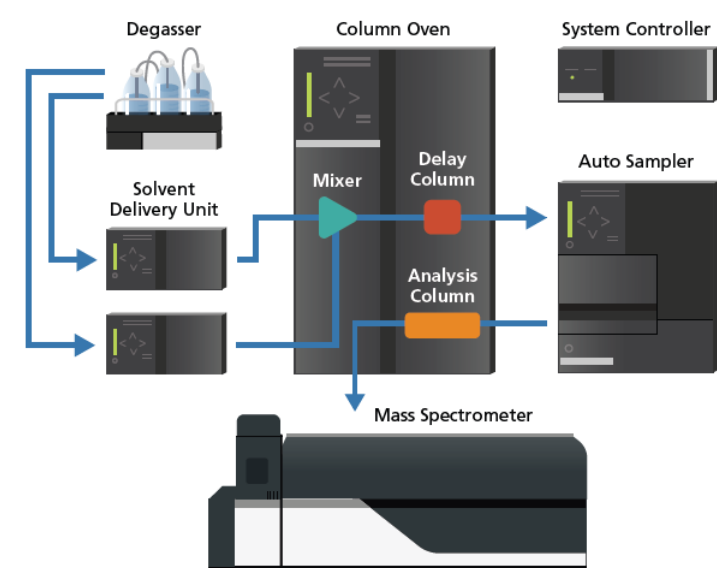


Figure 1. HPLC Configuration with Delay Column

RESULTS

Calibration was performed for all targeted PFAS using a seven-point weighted regression calibration curve following EPA draft method 1633 guidelines; concentration range for each target compound is summarized in Table 2. The linearity of the calibration curve was evaluated by calculating the Relative Standard Error (RSE); RSE for all target compounds was ≤20% (Table 2).

Accuracy for all target compounds in CS1 ranged between 80% and 116%, exceeding results reported and accepted in EPA draft 1633.

The instrument detection limit (IDL) and its %RSD for each target are shown in Table 2; they ranged between 1.9 ng/mL (7:3 FTCA) and 0.01 ng/mL (multiple analytes). The calculated limit of quantification (LOQ) for each target compound was determined to be equal to their concentration in CS1 and the LOQs listed in EPA draft 1633. S/N of CS1 ranged from 21 to 525 (Table 2); this demonstrates that lower LOQs could be easily achieved with the Shimadzu's LCMS-8050. For comparison purposes, IDLs using a higher sensitivity instrument (LCMS-8060) are also included in Table 2.

Repeatability was evaluated at CS1 (n=7), CS4 (n=6) and CS7 (n=6). In CS1, the lowest calibration standard, 75% of the targeted compounds showed %RSD ≤20%; the %RSD of 12.5% of the targets ranged between 20% and 30%, and it was >30% for the remaining 12.5% targets. In CS4 and CS7, %RSD for all targets was <20%, with most compounds showing %RSD of less than 10%. Figure 2 shows the %RSD of each targeted PFAS in CS4 and CS7.

Table 2. Retention time; calibration range; %accuracy CS1 (lowest calibration standard), RSE, average S/N; and instrument detection limit (average and %RSD).

Name	RT	Concentration CS1 (ng/mL)	Concentration CS7 (ng/mL)	% Accuracy CS1 (n=7)	RSE	CS1 Average S/N (n=7)	IDL ng/mL (n=7)	%RSD IDL (n=7)	IDL ng/mL (n=10)
PFBA	2.02	0.8	250	102.68	3.64	102.68	0.16	5.77	0.004
PFPeA	3.57	0.4	125	105.25	2.98	105.25	0.18	12.52	0.003
PFHxA	4.91	0.2	62.5	106.18	4.75	106.18	0.13	21.55	0.004
PFHpA	7.71	0.2	62.5	102.14	4.77	102.14	0.11	15.03	0.002
PFOA	8.64	0.2	62.5	103.79	8.42	103.79	0.08	11.19	0.008
PFNA	9.12	0.2	62.5	105.89	7.06	105.89	0.10	15.65	0.004
PFDA	9.51	0.2	62.5	105.47	9.36	105.47	0.07	11.79	0.038
PFUnA	9.90	0.2	62.5	104.42	7.51	104.42	0.10	15.78	0.007
PFDaA	10.46	0.2	62.5	99.14	6.67	99.14	0.15	20.17	0.007
PFTeDA	11.35	0.2	62.5	109.92	6.73	109.92	0.11	16.01	0.003
PFTeDA	12.24	0.2	62.5	86.49	7.07	86.49	0.08	10.89	0.004
PFBS	4.84	0.2	62.5	104.01	8.32	104.01	0.12	23.82	0.009
PFPeS	7.77	0.2	62.5	116.00	8.97	116.00	0.12	16.54	0.01
PFHxS	8.78	0.2	62.5	103.13	9.56	103.13	0.18	31.19	0.008
PFHpS	9.29	0.2	62.5	100.94	10.68	100.94	0.07	10.80	0.01
PFOS	9.71	0.2	62.5	104.09	11.42	104.09	0.21	50.62	0.015
PFNS	10.20	0.2	62.5	113.14	10.88	113.14	0.12	16.77	0.009
PFDs	10.96	0.2	62.5	94.83	11.37	94.83	0.18	34.16	0.005
PFDoS	12.52	0.2	62.5	109.76	6.70	109.76	0.17	19.79	0.006
4:2FTS	4.40	0.8	250	83.92	15.20	83.92	0.24	9.70	0.027
6:2FTS	8.40	0.8	250	80.44	15.82	80.44	0.50	26.45	0.013
8:2FTS	9.32	0.8	250	108.43	10.40	108.43	0.32	12.78	0.036
PFOSA	11.44	0.2	62.5	113.56	11.92	113.56	0.22	35.66	0.004
NMeFOSA	13.18	0.2	62.5	110.25	10.66	110.25	0.14	19.22	0.032
NETFOSA	13.48	0.2	62.5	107.01	9.04	107.01	0.12	15.94	0.05
NMeFOSAA	9.49	0.2	62.5	102.36	5.69	102.36	0.09	15.71	0.019
NETFOSAA	9.65	0.2	62.5	112.22	10.59	112.22	0.18	34.30	0.05
NMeFOSE	13.02	2	625	92.74	6.52	92.74	0.85	11.82	0.01
NETFOSE	13.31	2	625	101.23	6.01	101.23	0.38	5.63	0.006
HFPO-DA	5.69	0.8	250	100.05	4.20	100.05	0.22	9.04	0.007
ADONA	8.21	0.8	250	101.71	3.84	101.71	0.13	5.14	0.002
9Cl-PF3ONS	10.03	0.8	250	94.21	4.70	94.21	0.16	6.11	0.002
11Cl-PF3OUdS	11.73	0.8	250	111.72	9.08	111.72	0.35	14.03	0.004
3:3 FTCA	2.94	1	312.5	104.45	8.49	104.45	0.31	12.02	0.053
5:3 FTCA	6.08	5	1562.5	112.09	6.11	112.09	0.84	5.14	0.055
7:3 FTCA	8.95	5	1562.5	111.16	5.90	111.16	1.89	11.20	0.066
PFEESA	5.94	0.4	125	105.06	3.19	105.06	0.11	7.91	0.001
PFMPA	2.68	0.4	125	104.14	2.67	104.14	0.09	6.87	0.053
PFMBA	3.92	0.4	125	113.02	7.73	113.02	0.14	10.19	0.003
NFDHA	4.72	0.4	125	85.56	8.37	85.56	0.24	17.57	0.005

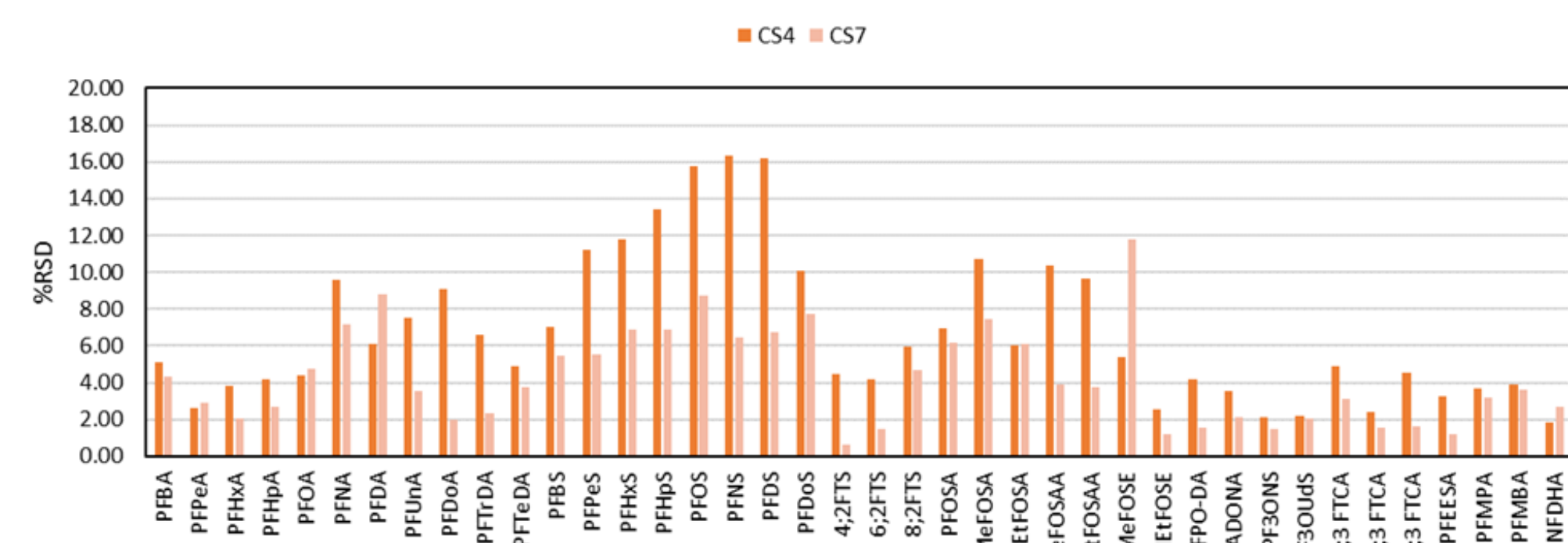


Figure 2. %RSD of target compounds in CS4 (n=6) and CS7 (n=6)

Table 3. %Recovery of EIS spiked at CS1 concentration (lowest calibration standard) in ultra pure water (UPW) and wastewater effluent (WW)

EIS	% Recovery CS1 Spike in UPW (n=5)	% Recovery CS1 Spike in WW (n=7)
13C4-PFBA EIS	94.09	32.78
13C5-PFPeA EIS	96.48	85.57
13C5-PFHxA EIS	99.69	93.64
13C4-PFHpA EIS	100.51	91.56
13C8-PFOA EIS	104.16	93.28
13C9-PFNA EIS	107.61	98.75
13C6-PFDA EIS	104.58	89.06
13C7-PFUnA EIS	97.69	72.58
13C2-PFDaA EIS	82.12	58.55
13C2-PFTeDA EIS	65.92	42.09
13C3-PFBS EIS	96.04	92.31
13C3-PFHxS EIS	105.44	100.97
13C8-PFOS EIS	109.04	99.40
13C2-4:2FTS EIS	86.72	82.76
13C2-6:2FTS EIS	93.63	83.95
13C2-8:2FTS EIS	93.09	84.67
13C8-PFOSA EIS	72.53	85.68
D3-NMeFOSA EIS	52.33	54.40
D5-NETFOSE EIS	47.86	44.46
D3-NMeFOSAA EIS	102.61	79.32
D5-NETFOSAA EIS	91.70	61.64
D7-NMeFOSE EIS	56.78	49.43
D9-NETFOSE EIS	53.77	45.35

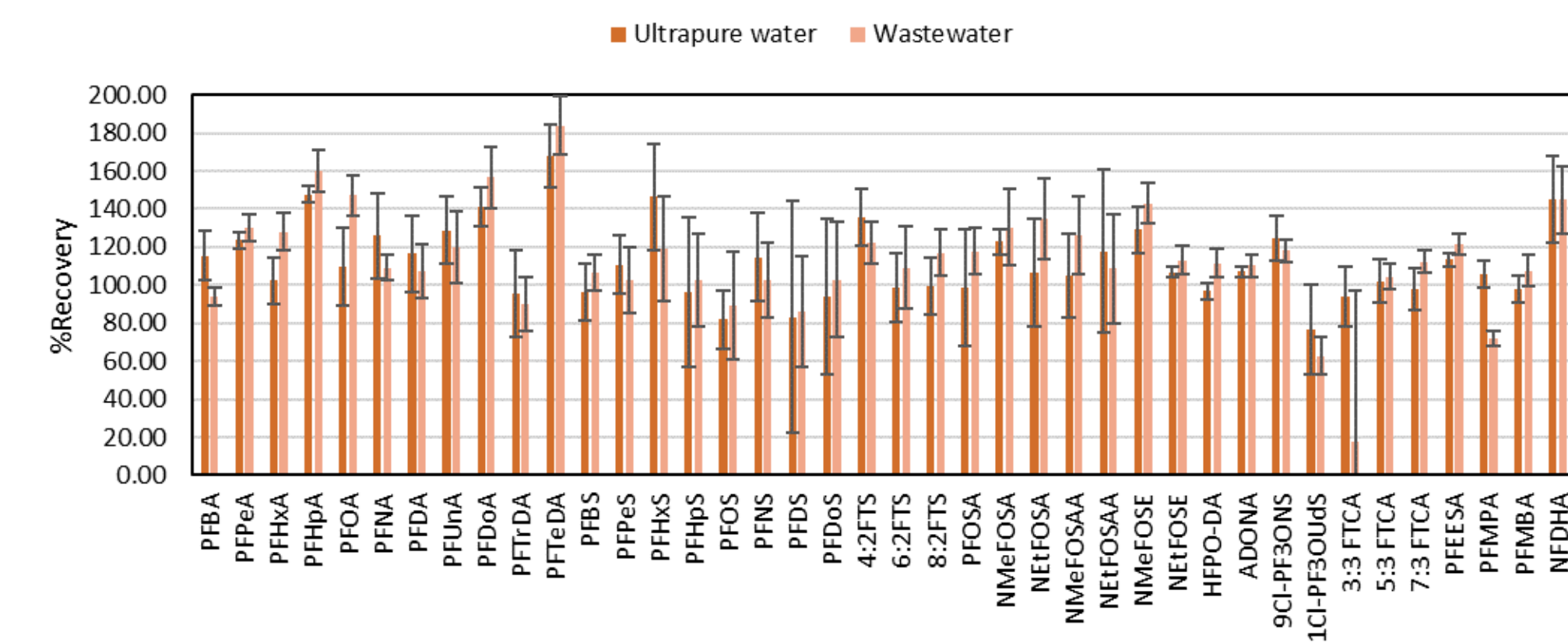


Figure 3. %Recovery of target compounds spiked at CS1 concentration (lowest calibration standard) in ultra pure water (UPW) and wastewater effluent (WW).

CONCLUSIONS

This study demonstrates the analysis of PFAS in accordance with EPA Draft Method 1633 in wastewater samples using the Shimadzu LCMS-8050. The results show excellent performance of the LCMS-8050 for key quality control parameters defined in the method. Lower instrument detection limits can be achieved by using a higher sensitivity LCMS.

Two types of aqueous samples were analyzed following the extraction procedure outlined in EPA Draft 1633: ultrapure reagent water (UPW, n=5) and wastewater effluent (WW, n=7), both spiked at concentrations equal to CS1. Table 3 shows the %recovery of the EIS in UPW and WW. In UPW, the recoveries from all EISs were within 50% and 150%, except D5-NETFOSE (48%). The recoveries of the EIS in WW were slightly lower for all compounds than in UPW, but still exceeding the reported ranges in EPA Draft 1633. Figure 3 shows the recovery of the target compounds spiked in UPW and WW (error bars displaying %RSD).