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EPA 533 and 537.1 with the Novel LCMS-8050RX: Demonstration of Instrument and Method Performance to meet PFAS regulatory levels

TP 270

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1. Introduction

The harmful impacts of per- and polyfluorinated alkyl substances (PFAS) continue to afflict the environment. Water utilities require sensitive and robust analytical methods to assess the current and ongoing burden of PFAS from source waters to meet regulatory demands in treated water and to protect public health. Improvements in sensitivity and/or runtime without sacrificing robustness can aid laboratories by increasing sample throughput to better meet the significant demand for PFAS sample analysis. The novel RX probe was developed to yield better heat distribution and more consistent nebulization to improve sensitivity and reproducibility. Chromatographic improvements compared to existing EPA methods were also performed to decrease runtime while maintaining the integrity of sample analysis.

2. Methods

PFAS were separated by a Nexera LC and quantified by a Shimadzu LCMS-8050RX for EPA methods 533 and 537.1 (EPAM533 and EPAM537.1). Neat standards were analyzed in the required composition (i.e., 80% methanol for EPAM533 and 96% methanol for EPAM537.1). Standards were analyzed twenty times to determine the instrument detection limits.

Table 1. LC parameters for EPAM533 and 537.1.

Parameter	Value
Analytical Column (533)	Shim-pack GIST C18, 3.0 µm, 2.1 x 50mm
Analytical Column (537.1)	Shim-pack Velox SP-C18, 2.7, µm, 2.1 x 50mm
Delay Column	Nexcol PFAS Delay Column
Mobile Phase	A: 2 mM Ammonium Acetate in LCMS Grade Water
	B: LCMS Grade Acetonitrile
Flow Rate	0.4 mL/min
Elution Scheme	Gradient elution: 5-95% B
Run Time (533)	15 minutes
Run Time (537.1)	18 minutes

3. Results and Conclusion

- ◆ All PFAS were sufficiently analyzed by the respective methods and passed regulatory criteria at a reduced runtime (19 minutes shorter).
- ◆ Superb precision and reproducibility were demonstrated with the RX probe, which resulted in an analytical blueprint that greatly exceeds the Final PFAS National Primary Drinking Water Regulation promulgated in 2024.

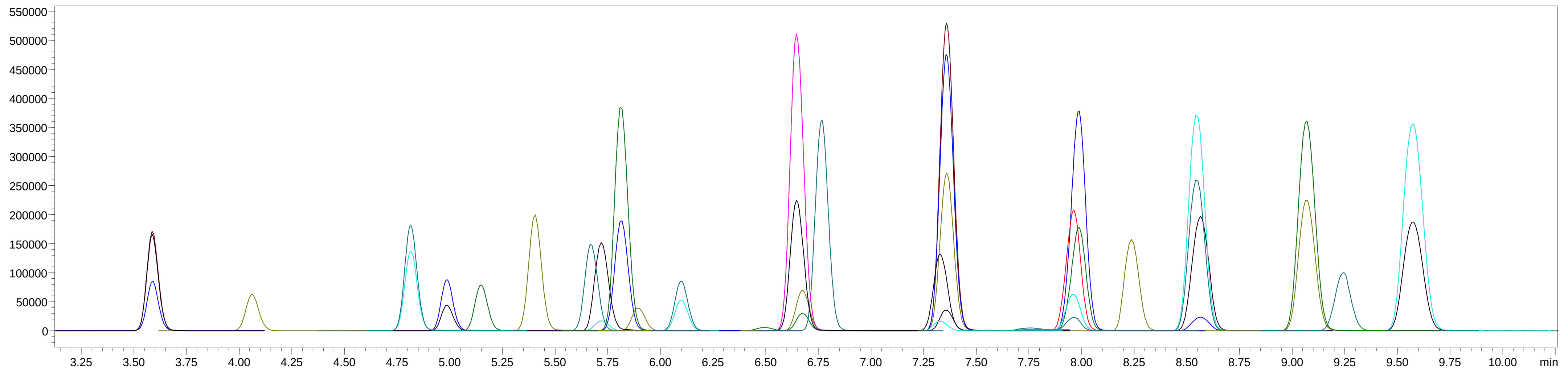

Figure 1. Chromatogram of PFAS standards analyzed by EPAM533 at 5 ppb.

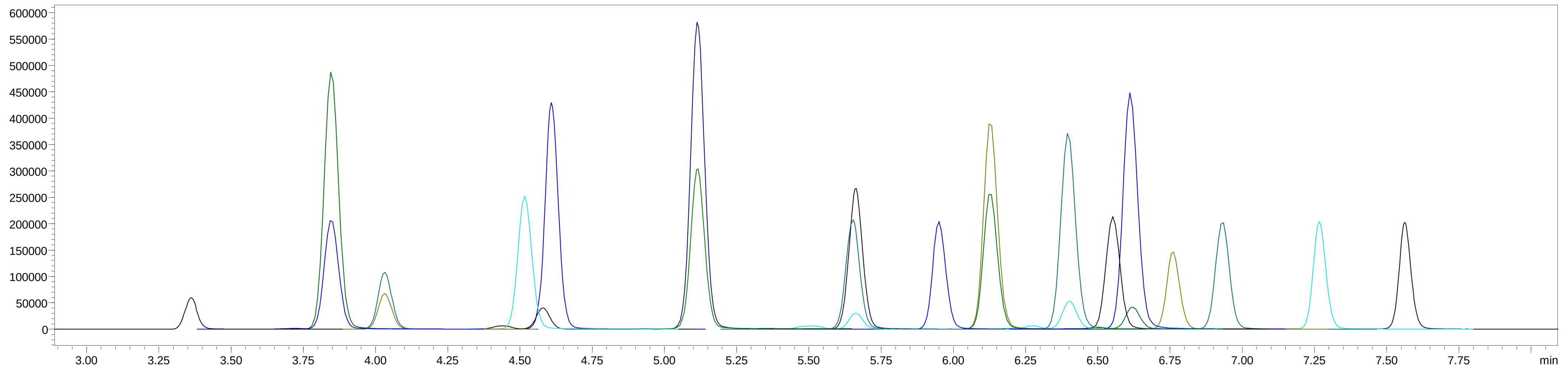

Figure 2. Chromatogram of PFAS standards analyzed by EPAM537.1 at 5 ppb.

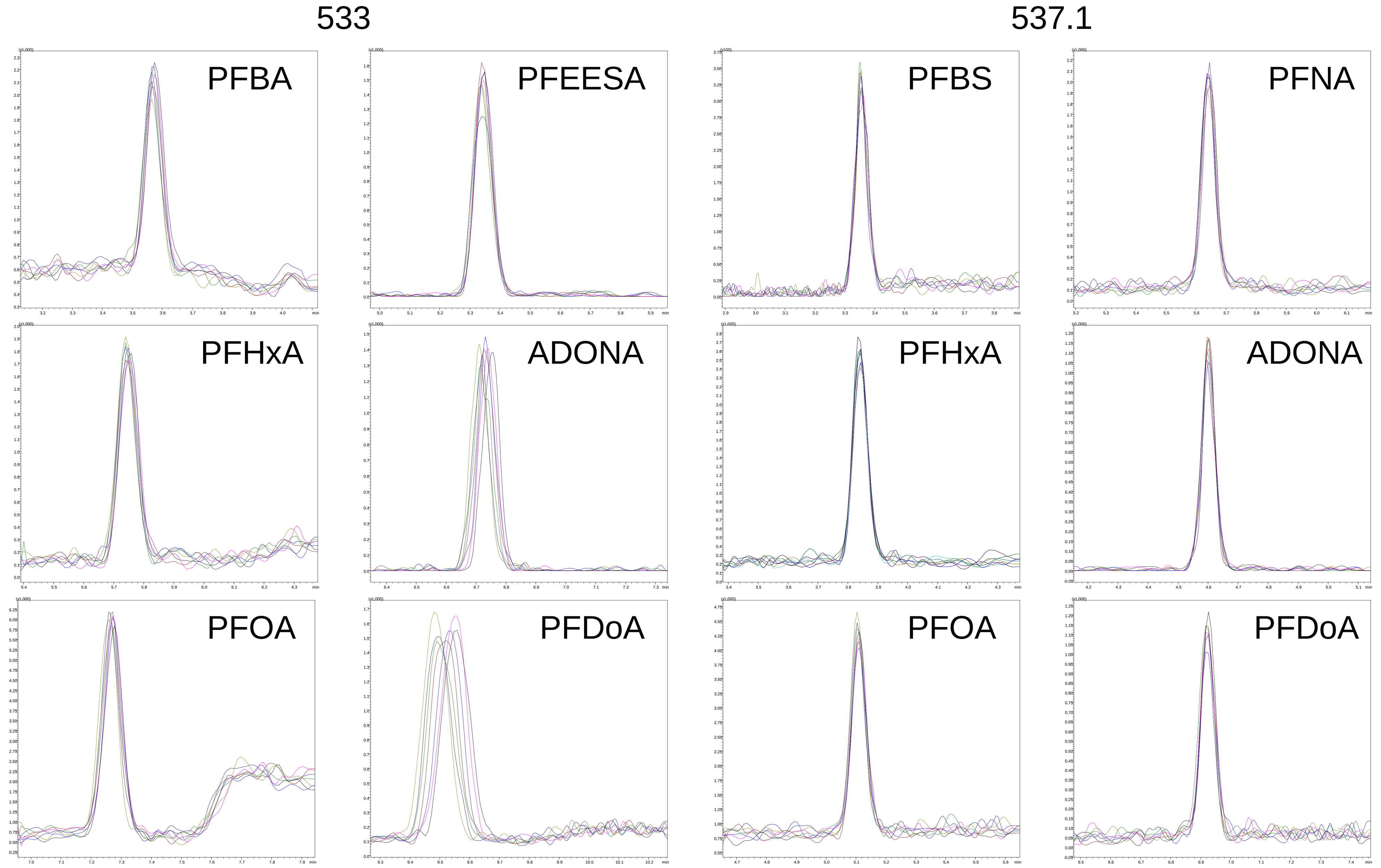

Figure 3. Seven replicate injections of PFAS standards at the LOQ.

Table 2. PFAS calibration curve and IDL sample information.

533								
Compound	Transition	RT (min)	Linear Range in vial (ppt)	R^2	Accuracy Range (%) at LOQ	%RSD Concentration at LOQ (%)	IDL in vial (ppt)	Equivalent MDL after 250X concentration (ppq)
PFBA	213.00>169.00	3.63	78.1 - 20000	0.999	94.3 - 126.2	6.54	16.3	65.3
PFMPA	228.95>85.00	4.11	156.3 - 20000	0.999	80.6 - 113.4	8.52	9.2	36.7
PFPeA	263.00>219.00	4.87	78.1 - 20000	0.999	93.9 - 120.9	5.62	13.8	55.0
PFBS	298.95>79.95	5.04	78.1 - 20000	0.999	82.8 - 106.9	7.09	14.7	59.0
PFMBA	278.95>85.00	5.21	156.3 - 20000	0.999	77.2 - 108.0	9.05	9.3	37.4
PFEESA	314.95>135.00	5.47	156.3 - 20000	0.999	86.0 - 109.7	5.43	5.7	23.0
NFDHA	294.95>201.00	5.74	78.1 - 20000	0.997	91.2 - 123.9	3.26	8.4	33.5
4:2 FTS	326.95>306.95	5.79	78.1 - 20000	0.998	70.7 - 129.6	14.7	33.1	132.3
PFHxA	312.95>269.00	5.88	156.3 - 20000	0.999	91.5 - 126.1	6.36	8.0	31.9
PFPeS	348.95>79.95	5.97	78.1 - 20000	0.999	73.3 - 108.1	9.50	18.6	74.2
HFPO-DA	285.00>169.00	6.18	78.1 - 20000	0.999	74.3 - 107.8	10.3	20.8	83.4
PFHpA	362.95>319.00	6.73	78.1 - 20000	0.999	92.4 - 118.3	4.75	11.3	45.1
PFHxS	398.95>79.95	6.75	78.1 - 20000	0.999	76.4 - 105.8	7.51	15.9	63.7
ADONA	376.95>251.00	6.85	312.5 - 20000	0.999	74.9 - 106.4	5.89	2.8	11.0
6:2 FTS	426.95>406.95	7.42	78.1 - 20000	0.999	70.1 - 120.1	16.6	34.8	139.1
PFOA	412.95>369.00	7.45	78.1 - 20000	0.999	93.1 - 121.3	3.11	8.0	32.2
PFHpS	448.95>79.95	7.44	78.1 - 20000	0.998	75.6 - 112.0	10.9	21.5	86.2
PFNA	462.95>418.95	8.09	156.3 - 20000	0.999	85.9 - 116.2	7.61	8.6	34.2
PFOS	498.95>79.95	8.06	78.1 - 20000	0.999	88.9 - 135.9	10.7	27.6	110.5
9Cl-PF3ONS	530.90>350.95	8.35	156.3 - 20000	0.998	70.2 - 111.5	8.60	8.8	35.0
8:2 FTS	526.95>506.95	8.70	78.1 - 20000	0.996	73.9 - 120.7	9.19	20.2	80.7
PFDA	512.95>468.95	8.67	156.3 - 20000	0.999	80.2 - 106.6	6.53	6.9	27.7
PFUnA	562.95>518.95	9.22	312.5 - 20000	0.999	70.8 - 107.7	9.72	4.9	19.6
11Cl-PF3OUdS	630.90>450.95	9.39	156.3 - 20000	0.999	81.8 - 104.6	5.94	6.0	24.0
PFDoA	612.95>568.95	9.77	156.3 - 20000	0.999	90.2 - 113.0	4.12	4.5	18.0
13C4-PFBA	217.00>172.00	3.63	NA	NA	89.1 - 108.3	0.68	NA	NA
13C5-PFPeA	268.00>223.00	4.87	NA	NA	89.3 - 110.7	1.29	NA	NA
13C3-PFBS	301.95>79.95	5.04	NA	NA	88.1 - 108.1	3.65	NA	NA
13C2-4:2FTS	329.00>308.95	5.79	NA	NA	87.2 - 109.0	3.16	NA	NA
13C5-PFHxA	318.00>273.00	5.89	NA	NA	87.6 - 110.7	1.54	NA	NA
13C3-HFPO-DA	287.00>169.00	6.18	NA	NA	86.6 - 117.9	4.05	NA	NA
13C4-PFHpA	367.00>322.00	6.73	NA	NA	88.6 - 112.0	1.79	NA	NA
13C3-PFHxS	401.95>79.95	6.75	NA	NA	88.0 - 108.8	2.76	NA	NA
13C2-6:2FTS	428.95>408.95	7.42	NA	NA	86.4 - 109.5	3.84	NA	NA
13C8-PFOA	421.00>376.00	7.45	NA	NA	88.3 - 108.3	0.66	NA	NA
13C9-PFNA	472.00>427.00	8.09	NA	NA	86.8 - 120.6	5.18	NA	NA
13C8-PFOS	506.95>79.95	8.06	NA	NA	87.7 - 109.2	1.24	NA	NA
13C2-8:2FTS	528.95>508.95	8.69	NA	NA	89.2 - 112.9	2.24	NA	NA
13C6-PFDA	519.00>474.00	8.67	NA	NA	87.9 - 117.9	2.28	NA	NA
13C7-PFUnA	570.00>525.00	9.21	NA	NA	86.4 - 113.4	2.12	NA	NA
13C2-PFDoA	614.95>569.95	9.76	NA	NA	87.2 - 112.8	1.91	NA	NA
537.1								
Compound	Transition	RT (min)	Linear Range in vial (ppt)	R^2	Accuracy Range (%)	%RSD Concentration at LOQ (%)	IDL in vial (ppt)	Equivalent MDL after 250X concentration (ppq)
PFBS	298.95>79.95	3.39	312.5 - 20000	0.997	98.3 - 118.6	4.20	4.48	17.9
PFHxA	312.95>269.00	3.88	156.3 - 20000	0.998	119.1 - 136.6	3.95	7.19	28.8
HFPO-DA	285.00>169.00	4.06	312.5 - 20000	0.996	101.9 - 128.1	6.11	3.91	15.6
PFHpA	362.95>319.00	4.56	312.5 - 20000	0.998	92.2 - 123.7	7.39	4.70	18.8
PFHxS	398.95>79.95	4.62	156.3 - 20000	0.996	89.3 - 118.5	6.83	8.14	32.6
ADONA	376.95>251.00	4.65	625.0 - 20000	0.995	102.5 - 118.9	5.42	1.54	6.17
PFOA	412.95>369.00	5.15	156.3 - 20000	0.994	112.8 - 133.2	4.31	6.20	24.8
PFOS	498.95>79.95	5.70	78.1 - 20000	0.998	109.1 - 131.2	4.46	13.1	52.3
PFNA	462.95>418.95	5.69	156.3 - 20000	0.996	95.4 - 119.6	5.72	6.57	26.3
9Cl-PF3ONS	530.90>350.95	5.99	625.0 - 20000	0.996	78.6 - 124.9	9.80	2.98	11.9
PFDA	512.95>468.95	6.17	312.5 - 20000	0.997	98.4 - 139.6	7.17	4.46	17.8
NMeFOSAA	569.95>418.95	6.44	78.1 - 20000	0.998	89.8 - 132.8	9.23	23.2	92.9
PFUnA	562.95>518.95	6.60	156.3 - 20000	0.998	98.0 - 125.4	8.32	10.5	42.1
NEtFOSAA	584.00>418.95	6.66	78.1 - 20000	0.998	89.7 - 126.6	9.38	23.9	95.6
11Cl-PF3OUdS	630.90>450.95	6.80	625.0 - 20000	0.996	89.9 - 132.5	11.0	5.06	20.2
PFDoA	612.95>568.95	6.97	312.5 - 20000	0.995	101.0 - 131.7	5.75	3.70	14.8
PFTrDA	662.95>618.95	7.31	312.5 - 20000	0.997	98.0 - 129.0	7.52	4.70	18.8
PFTA	712.95>668.95	7.60	625.0 - 20000	0.995	101.0 - 137.6	7.36	2.60	10.4
13C2-PFHxA	315.00>270.00	3.88	NA	NA	96.9 - 102.8	1.03	NA	NA
13C3-HFPO-DA	287.00>169.00	4.07	NA	NA	91.3 - 109.3	4.56	NA	NA
13C2-PFDA	514.95>469.95	6.17	NA	NA	96.0 - 103.3	1.19	NA	NA
d5-NEtFOSAA	589.00>418.95	6.65	NA	NA	96.9 - 103.6	1.36	NA	NA

References:

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2. Shoemaker, J. & Dan Tettenhorst. Method 537.1 Determination of Selected Per- and Polyflourinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS). U.S. Environmental Protection Agency, Washington, DC, 2020.

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