

# Improved Analysis of Polyfluorinated Alkyl Substances (PFAS) in Environmental Samples Using Optimized ASTM Method 7968/7979

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## Introduction

There has been an increasing awareness of the presence of polyfluorinated alkyl substances (PFAS) in water. A simple and robust method with quick turn-around time to determine these compounds is essential to providing accurate responses in a timely manner. In the method presented here, direct injection without solid-phase extraction (SPE) allows us to maximize throughput and to minimize background caused by the sample preparation step. We used liquid chromatography with triple-quadrupole mass spectrometry (LC-MS/MS) to

analyze the fluorotelomer and unsaturated fluorotelomer acids included in ASTM International method 7968/7979. Fluorotelomer acids are observed as [M-H]<sup>-</sup> and [M-HF-H]<sup>-</sup>. Since the loss of HF in the fluorotelomer acids results in an ion with the same formula as the unsaturated fluorotelomer acids, and these two classes of compounds showed very similar retention times, we reduced the electrospray ionization (ESI) heater temperature to reduce HF loss and minimize false identifications.

## Experimental

The method was developed to study 30 PFAS compounds and 19 surrogates, for a total of 49 compounds. The target list includes new PFAS of concern, including

- Perfluoroalkane sulfonic acids (PFASs),
- Perfluoroalkyl carboxylic acids (PFCAs),
- Perfluorooctanesulfonic acids (PFOSs),
- Perfluorooctane sulfonamide acetic acids (FOSAAs),
- Fluorotelomer alcohols (FTOHs),
- Fluorotelomer acids (FTAs),
- Unsaturated Fluorotelomer acids (FTUAs)
- Fluorotelomer sulfonic acids (FTSs)

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Table 1: Instrument conditions

Parameter	Value																
LCMS	: Shimadzu LCMS-8060																
Analytical Column	: Shim-pack GIST Phenyl-Hexyl (2.1 mm ID. x 100 mm L., 3 µm)																
Solvent Delay Column	: Shim-pack XR-ODS (3 mm ID. x 50 mm L., 2,2 µm)																
Column Oven Temperature	: 40 °C																
Injection Volume	: 10 µL																
Mobile Phase	: Reagent A = 20 mmol Ammonium Acetate in LCMS grade water Reagent B = Acetonitrile																
Gradient Flow rate	: 0.4 mL/ minute																
Gradient	: <table border="1" data-bbox="634 689 1013 993"> <thead> <tr> <th>Time (minutes)</th> <th>% Reagent B</th> </tr> </thead> <tbody> <tr> <td>0</td> <td>10</td> </tr> <tr> <td>1</td> <td>10</td> </tr> <tr> <td>3</td> <td>30</td> </tr> <tr> <td>14</td> <td>65</td> </tr> <tr> <td>14.1</td> <td>98</td> </tr> <tr> <td>17.1</td> <td>10</td> </tr> <tr> <td>20</td> <td>10</td> </tr> </tbody> </table>	Time (minutes)	% Reagent B	0	10	1	10	3	30	14	65	14.1	98	17.1	10	20	10
Time (minutes)	% Reagent B																
0	10																
1	10																
3	30																
14	65																
14.1	98																
17.1	10																
20	10																
Run time	: 20 minutes																
Nebulizing gas flow	: 3 L / minute																
Heating gas flow	: 15 L/minute																
Interface temperature	: 300 °C																
Desolvation Line temperature	: 100 °C																
Heat Block temperature	: 200 °C																
Drying gas flow	: 5 L / minute																
Acquisition cycle time	: 20 minutes																
Total MRMs	: 74																

## Instrument Operating Conditions

The analysis of PFAS was performed using a Shimadzu Nexera X2 SIL-30AC autosampler and a LCMS-8060 triple quadrupole mass spectrometer. Table II lists the compounds tested, the MRM transitions, and retention times.

Chromatography was adjusted to obtain maximum resolution between peaks in the shortest time possible. This approach minimizes the coelution of isomers. The total run time of 20 minutes includes a final wash out with concentrated acetonitrile to remove contamination. Fluorotelomer acids, observed as [M-H]<sup>-</sup> and [M-HF-H]<sup>-</sup>, can result in an ion with the same formula as the unsaturated fluorotelomer acid. Even under optimized

chromatography, these compounds have near identical retention times. The lower desolvation line temperature reduces HF loss and minimizes false identification.

The modified mobile phase reagents compared to the ASTM method do not use reagent C containing 400 mM ammonium acetate in 95:5 acetonitrile–water. The new reagents are easier to prepare, and obtain equivalent, if not better, peak shape and sensitivity. Reagents commonly contain PFAS contamination. Mobile phase passes through the delay column positioned between the pump and the injection valve shifting the retention time of contamination peaks and ensuring that they are not coeluted with the analyte.

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Table 2: MRM transitions, retention times, calibration range, MDL, and accuracy and precision (n=8).

Component	Transition (m/z)	Retention Time (minutes)	MDL (ng/L)	Calibration Range (ng/L)	% Recovery (20 ng/L)	% RSD (20 ng/L)
PFBA	212.90 > 169.00	3.092	4.1	5 - 200	112	6.6
MPFBA	217.00 > 172.10	3.095	5.0	5 - 200	86	10.2
PFPeA	263.00 > 219.00	4.753	0.9	5 - 200	101	2.9
M5PFPeA	268.00 > 223.00	4.754	0.6	5 - 200	100	1.4
4-2 FTS	327.00 > 307.00	5.347	1.7	5 - 200	102	3.2
M4-2 FTS	329.00 > 309.00	5.347	1.2	5 - 200	92	3.0
PFHxA	312.90 > 269.00	5.652	1.3	5 - 200	101	3.9
M4PFHxA	317.90 > 273.00	5.653	1.1	5 - 200	101	2.3
PFBS	298.90 > 80.10	5.824	1.5	5 - 200	101	10.4
M3PFBS	301.90 > 80.10	5.825	1.1	5 - 200	98	4.1
FHUEA	357.00 > 293.00	6.210	2.6	5 - 200	108	5.6
FHEA	376.90 > 293.00	6.225	32.5	100 - 4000	99*	5.3*
PFHpA	362.90 > 319.00	6.642	1.4	5 - 200	103	4.2
M4PFHpA	366.90 > 322.00	6.643	0.7	5 - 200	99	2.2
PFPeS	348.90 > 79.90	6.992	1.1	5 - 200	100	4.7
6-2 FTS	427.00 > 406.90	7.194	2.5	5 - 200	113	7.3
M6-2 FTS	429.00 > 408.90	7.195	1.8	5 - 200	101	3.8
PFOA	412.90 > 369.00	7.635	5.1	5 - 200	96	5.7
M8PFOA	420.90 > 376.00	7.636	0.7	5 - 200	99	2.0
FhpPA	440.90 > 337.00	7.965	9.4	5 - 200	84	28
FOEA	476.90 > 393.00	8.066	48.3	100 - 4000	103*	5.5*
FOUEA	456.90 > 392.90	8.076	1.6	5 - 200	104	3.6
PFHxS	398.90 > 80.10	8.094	1.5	5 - 200	96	9.8
M3PFHxS	401.90 > 80.10	8.102	1.7	5 - 200	100	3.4
PFNA	462.90 > 418.90	8.588	1.7	5 - 200	104	6.3
M9PFNA	471.90 > 426.90	8.589	1.6	5 - 200	103	4.2
8-2 FTS	526.90 > 506.90	9.011	3.2	5 - 200	90	25.2
M8-2 FTS	528.90 > 508.90	9.012	1.8	5 - 200	89	12.3
PFHpS	448.90 > 79.90	9.131	1.6	5 - 200	99	8.2
N-MeFOSAA	569.90 > 419.00	9.410	3.6	5 - 200	101	15.0
d3M N-MeFOSAA	572.90 > 419.00	9.420	5.4	5 - 200	102	9.6
PFDA	512.90 > 468.90	9.486	2.3	5 - 200	108	5.7
M6PFDA	518.90 > 473.90	9.487	1.1	5 - 200	98	4.7
FDEA	576.90 > 493.00	9.762	35.5	100 - 4000	89*	7.0*
N-EtFOSAA	583.90 > 419.00	9.767	5.3	5 - 200	118	16.3
M N-EtFOSAA	588.90 > 419.00	9.768	4.2	5 - 200	130	13.0
PFOS	498.90 > 80.10	10.076	3.0	5 - 200	105	7.8
M8PHOS	506.90 > 80.10	10.077	1.5	5 - 200	107	5.0
PFUdA	562.90 > 519.00	10.330	2.9	5 - 200	100	11.6
M7PFUdA	569.90 > 525.00	10.331	1.5	5 - 200	103	4.6
PFNS	548.90 > 79.90	10.946	1.3	5 - 200	112	7.3
PFDoA	612.90 > 568.90	11.122	2.2	5 - 200	98	6.5
MPFDoA	614.90 > 569.90	11.123	0.8	5 - 200	100	4.1
FOSA	497.90 > 77.90	11.586	0.6	5 - 200	88	6.8
M8FOSA	505.90 > 77.90	11.588	1.6	5 - 200	94	5.4
PFDS	598.90 > 79.90	11.760	2.1	5 - 200	108	5.4
PFTTrDA	662.90 > 618.90	11.877	1.1	5 - 200	99	4.6
PFTeDA	712.90 > 668.90	12.586	1.1	5 - 200	92	3.5
M2PFTeDA	714.90 > 669.90	12.587	0.7	5 - 200	92	4.3

\* FHEA, FOEA, FDEA (spike :mdl at100 ng/L; p&amp;a at 400 ng/L)

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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.

The plots shown in Figure 1 demonstrate that the 50% methanol in water solution used in the ASTM methods sufficiently dissolves the PFAS and keeps them in solution. Standard were purchased from Wellington Laboratories.

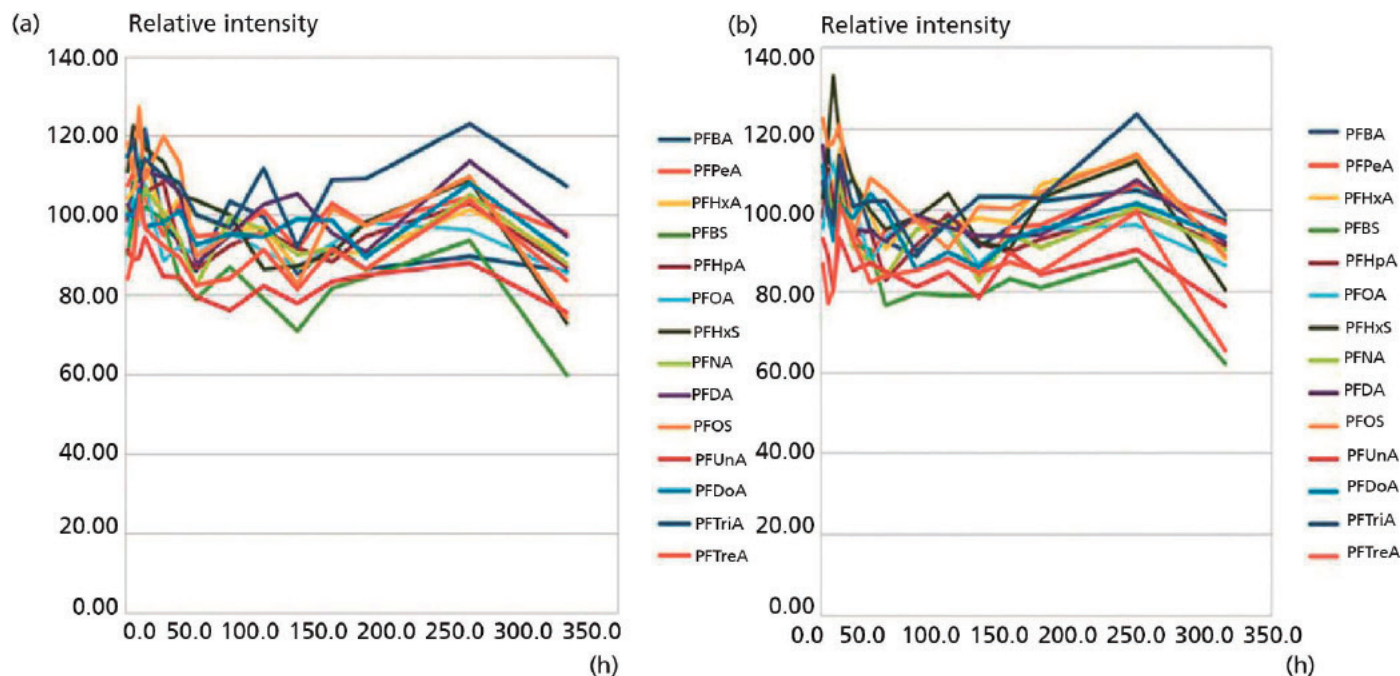


Figure 1: Shelf life study showing recovery for the 50% methanol solution in (a) glass vials and (b) polypropylene vials.

## Calibration and Standardization

Nine calibration standards containing the PFAS compounds were prepared from purchased stock standard solutions. Target analytes and surrogate spike solutions were combined to ensure consistency. Each standard was diluted with a 50:50 methanol–water mixture containing 0.1% acetic acid.

Next, 5 mL aliquots of each calibration standard were diluted with 50:50 methanol–water containing 0.1% acetic acid. Solutions were transferred to 2-mL amber glass LC vials. Calibration standards may be used multiple times since glass vials with removable caps are being used.

Calibration standards are not filtered.

Inject each standard and obtain its chromatogram. Figure 2 shows a chromatogram of 49 PFAS, which includes PFOA, PFOS, and related compounds. The concentration of each compound was determined using the external calibration technique with the nine point calibration curves developed earlier. Concentrations were calculated using LabSolutions software to generate a linear regression. The point of origin is excluded and a fit weighting of 1/x is used to give more emphasis to the lower concentrations.

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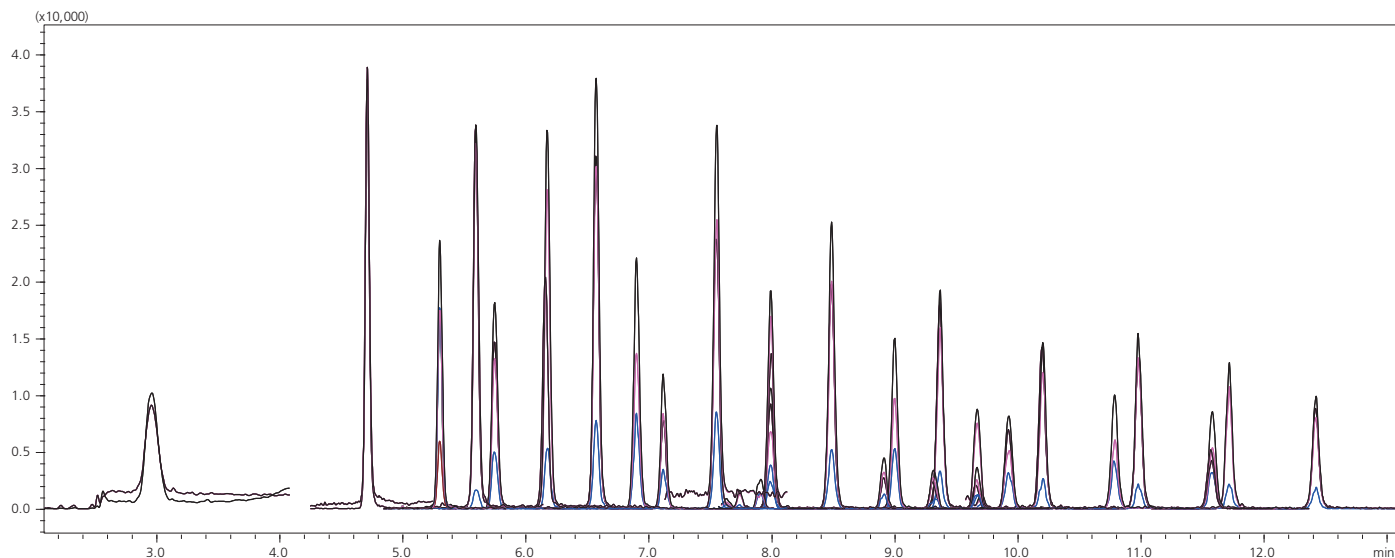


Figure 2: Direct Inject Method ASTM D7968/D7979 - Standard Test Method for Determination of PFAS Compounds by LCMS-8060 : Chromatogram at 100 ng/L Using Optimized Conditions

## Sample Extraction and Analysis

A surrogate spiking solution containing each isotopically labeled PFAS was added to all samples, including method blanks, duplicates, laboratory control samples, matrix spikes, and reporting limit checks. The results obtained for the surrogate recoveries fell within the 70–130 % method criteria.

Next, 5 mL of sample was collected in a 15-mL centrifuge vial. Also, 5 mL of reagent water for a blank was prepared

as well as an LCS containing known amounts of PFAS and a reporting limit check containing each PFAS at the lowest calibration concentration. Then 40  $\mu$ L of the surrogate spiking solution and 5 mL of methanol were added to each sample, blank, and control sample. Next, the sample was shaken and mixed on a vortex mixer for 2 minutes. 10  $\mu$ L of acetic acid was added, and it was transferred to an autosampler vial for analysis.

## Instrument and Method Performance

Experiments were made to verify linearity, accuracy, precision, and method detection limits (MDL). A series of nine initial calibration standards ranging from 5 to 200 ng/L (100ng/L – 4000ng/L for FTA mix) were prepared. The

linearity of the curves were evaluated using 1/x weighting and ignoring the origin. Figure 3 shows the calibration curves for the calibration range. MDLs and accuracy & precision data are shown in Table 2.

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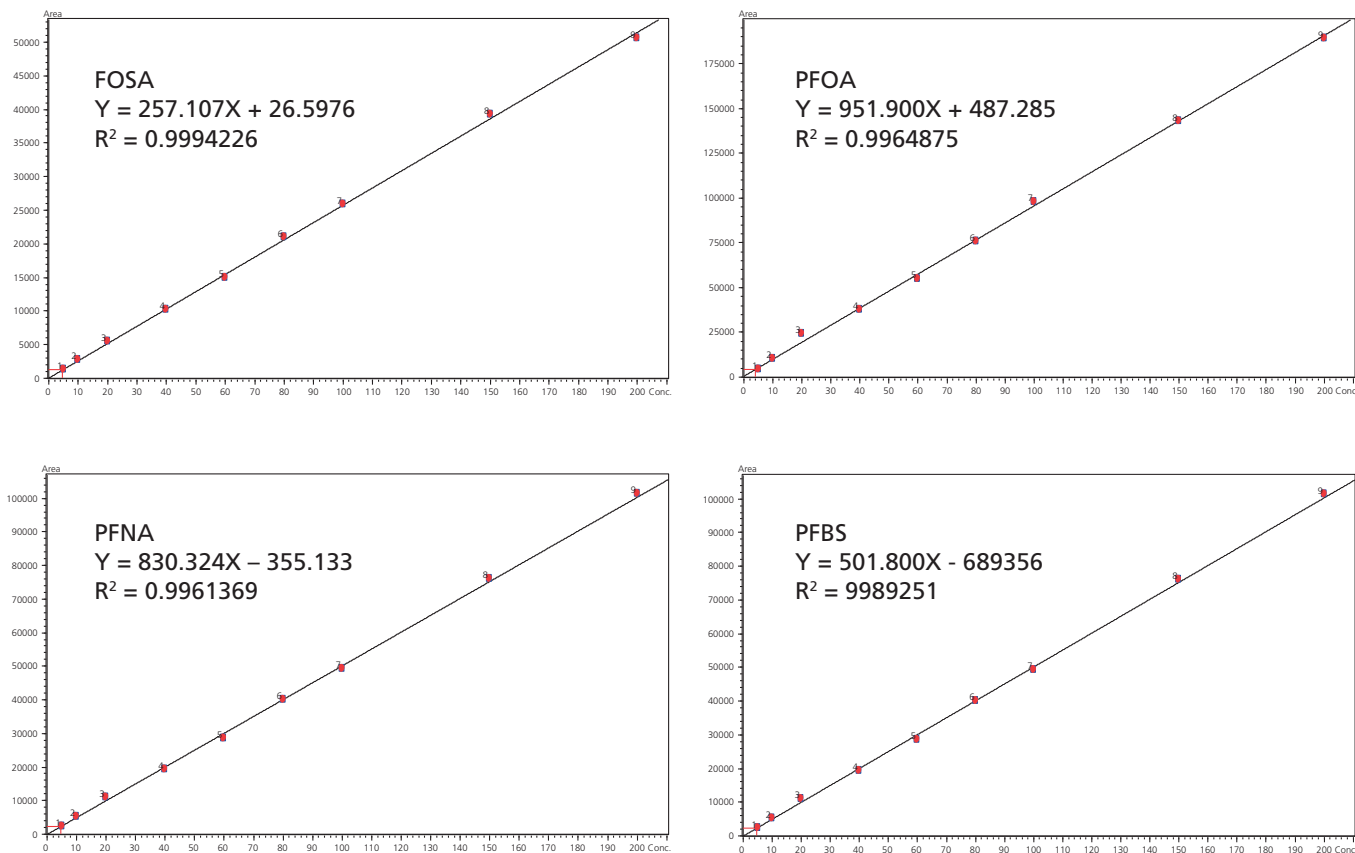


Figure 3: Calibration Curves of select PFAS compounds obtained by direct injection 10  $\mu$ L of PFAS standard mixtures using LCMS-8060

## Conclusion

This poster evaluated ASTM D7968/D7979 for the “direct” analysis of 30 PFAS and 19 mass-labeled surrogates. Instead of solid-phase extraction, as is used by the EPA drinking water Method 537, the ASTM methods specify solubilizing the PFAS in a methanol–water mix, filtering if necessary, and injecting the sample into an LC–MS/MS system. 19 isotopically labeled surrogates were used in this study. The results obtained for the surrogate recoveries were well within the QC limits. The results obtained for labeled surrogates were not used for recovery corrections

for the native compounds. The method simplifies extraction and analysis, eliminating sources of contamination and potential loss of analyte. With the exception of a few method-allowed modifications, we ran the method exactly as written. The method appears to be rugged and of sufficient accuracy and precision to analyze the matrices listed in the scope. The new methods takes the advantage of new technology that minimizes labor while still obtaining data suitable for its intended purpose.



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### References

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