ULTRA LOW-LEVEL DETECTION OF PERFLUOROALKYL SUBSTANCES USING LC MS/MS

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INTRODUCTION

Perfluoroalkyl substances (PFASs) encompass a range of fully fluorinated alkyl compounds, typically with an anionic end group. As a result of their widespread use and subsequent leaching from materials, they have been found in various environmental and biological samples. Analytical approaches require increasingly lower levels of detection for risk assessment and legislative purposes. Additionally, PFASs are ubiquitous in the laboratory environment, namely in Teflon components used in analytical equipment, thus requiring special considerations in the LC system configuration. Here we present detection results for various chain length carboxylic and sulfonic perfluorinated acids, using enhanced MS/MS configuration with the Xevo TQ-S for ultimate sensitivity and a ACQUITY I-Class UPLC modified with the Waters PFC Analysis Kit to remove laboratory contamination sources.

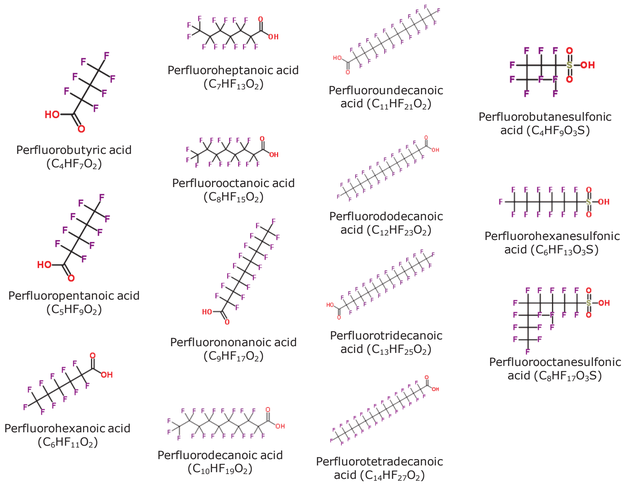

Figure 1: Commonly monitored PFASs featured in this study.

METHODS

The LC analysis was performed using a modified system comprised of PEEK tubing to replace Teflon tubing for solvent lines. Also, a BEH C18 isolator column and pre-cut stainless steel tubings were placed following solvent mixing and ensured that PFAS contamination was retained prior to injection of the sample. These modifications are captured in Figure 1A and B, and described elsewhere[1,2]. MRMs were established and collision energies optimized for 17 native and isotopically labeled PFASs (Table 1) typically analyzed in biological and environmental samples. Standards were prepared over three orders of magnitude, and used as calibration curves. Tap and river water samples were filtered and extracted according to a previously described method[1].

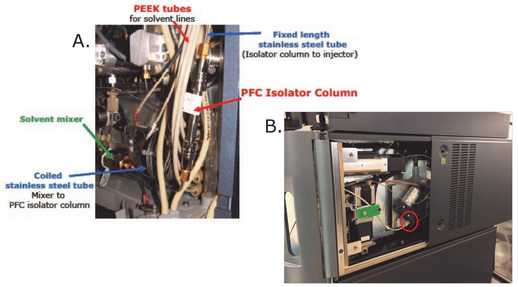

Figure 1: Waters PFC Analysis Kit components. (A) Configuration of isolator column in flow path of LC. (B) Connection of PEEK tubing (which acts as a replacement for Teflon tubing typically employed on LC sytems) for sample manager flow path for ACQUITY H– and I-Class FTN models.

LC Conditions
LC System: Waters ACQUITY UPLC I-Class equipped with Waters PFC Kit
Column: BEH C18 1.7µm 2.1x50 mm
Column Temperature (°C): 55
Mobile Phase A: 98:2 Water:MeOH 2 mM ammonium acetate
Mobile Phase B: MeOH 2 mM ammonium acetate
Gradient:

Min.	*Flow Rate*	*%A*	*%B*
Initial	0.65	90.0	10.0
0.5	0.65	90.0	10.0
5.10	0.65	0.0	100.0
6.60	0.65	0.0	100.0
6.70	0.65	90.0	10.0
8.50	0.65	90.0	10.0

MS Conditions
MS System: Waters Xevo TQ-S
Acquisition Polarity: ESI-
Capillary voltage (kV): 0.4
Source temperature (°C): 150
Desolvation temp. (°C): 500
Cone gas flow (L/hr): 150
Desolvation gas flow (L/hr): 1000

Table 1: RTs and optimized MRMs, collision energies (CE) and cone voltages.

Compound	Formula	MRM (Quant. in Bold)	RT (min.)	CE (V)	Cone Voltage (V)
PFBuA	$C_4HF_7O_2$	**212.9 > 168.9**	0.76	15	30
		212.9 > 212.9		2	30
PFPA	$C_5HF_9O_2$	**262.9 > 262.9**	1.94	2	30
		262.9 > 218.9		10	30
PFBuS	$C_4HF_9O_3S$	**298.9 > 79.9**	2.25	35	20
		298.9 > 98.9		25	20
PFHxA	$C_6HF_{11}O_2$	**312.9 > 268.9**	2.84	5	30
		312.9 > 118.9		20	30
PFHpA	$C_7HF_{13}O_2$	**362.9 > 318.9**	3.42	10	30
		362.9 > 168.9		15	30
PFHxS	$C_6HF_{13}O_3S$	**398.9 > 79.9**	3.49	40	30
		398.9 > 98.9		40	30
		398.9 > 118.9		30	30
PFOA	$C_8HF_{15}O_2$	**412.9 > 368.9**	3.84	10	30
		412.9 > 168.9		20	30
		412.9 > 218.9		15	30
PFNA	$C_9HF_{17}O_2$	**462.9 > 418.9**	4.18	10	30
		462.9 > 218.9		10	30
PFOS	$C_8HF_{17}O_3S$	**498.9 > 79.9**	4.20	45	30
		498.9 > 98.9		45	30
		498.9 > 229.9		35	30
PFDA	$C_{10}HF_{19}O_2$	**512.9 > 218.9**	4.46	20	30
		512.9 > 268.9		15	30
		512.9 > 468.9		10	30
PFUnDA	$C_{11}HF_{21}O_2$	**562.9 > 518.9**	4.69	15	30
		562.9 > 268.9		20	30
		562.9 > 318.9		20	30
PFDoDA	$C_{12}HF_{23}O_2$	**612.9 > 568.9**	4.90	15	35
		612.9 > 168.9		30	35
PFTiA	$C_{13}HF_{25}O_2$	**662.9 > 618.9**	5.07	15	35
		662.9 > 318.9		20	35
		662.9 > 368.9		20	35
PFTeTA	$C_{14}HF_{27}O_2$	**712.9 > 668.9**	5.22	15	35
		712.9 > 218.9		25	35
^{13}C PFOS		***502.9 > 79.9***	*4.20*	45	30
		502.9 > 98.9		35	30
^{13}C PFOA		***416.9 > 168.9***	*3.84*	18	30
		416.9 > 171.9		16	30
^{13}C PFDA		***514.9 > 269.9***	*4.46*	15	30
		514.9 > 219.9		20	30

RESULTS AND DISCUSSION

The Xevo TQ-S MRM method showed exceptional sensitivity for the analytes. Measured limits-of-detection (based on peak-to-peak signal to noise measurements of 1:3) for the analytes were below 0.07 ng/mL in solvent standards. In the case of the most commonly monitored PFAS analyte, perfluorooctanesulfonate (PFOS), the limit-of-detection was 0.0125 ng/mL (Table 2 and Figure 3). These low limits of detection highlight the notable sensitivity of this platform for PFASs analysis. Analysis of water samples was performed and PFOS was found in both samples (Figure 4A and B).

Table 2: LOD/Qs, Linearity (R^2) and linear dynamic range for selected PFASs monitored. Results for PFOS are highlighted in bold.

Compound	LOD (ng/mL)	LOQ (ng/mL)	R^2	Range (ng/mL)
PFBuS	<0.0125	<0.0125	0.9999	0.0125 to 6.25
PFHxA	<0.0125	<0.0125	0.999	0.0125 to 12.5
PFHpA	<0.0125	<0.0125	0.999	0.0125 to 12.5
PFHxS	<0.0125	<0.0125	0.999	0.0125 to 12.5
PFNA	<0.0125	<0.0125	0.997	0.0125 to 12.5
PFOS	**0.0125**	**0.0625**	**0.999**	**0.0625 to 12.5**
PFDA	<0.0125	<0.0125	0.996	0.0125 tp 12.5
PFUnDA	0.0125	0.0625	0.992	0.0625 to 12.5
PFDoDA	<0.0125	<0.0125	0.998	0.0125 to 12.5
PFTiA	0.0625	0.0625	0.997	0.0625 to 12.5
PFTeTA	0.0625	0.125	0.991	0.125 to 12.5

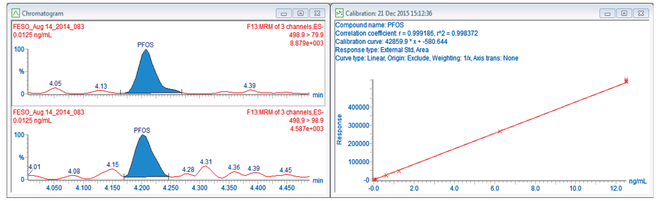

Figure 3: LOD for PFOS in solvent standard, and calibration curve covering 2.5 orders of magnitude.

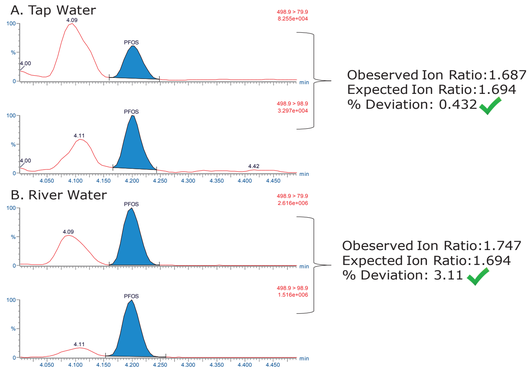

Figure 4: PFOS detected at an on-column concentration 0.1 ng/mL in tap water (A), and on-column 2.1 ng/mL in river water. Samples were subjected to a 500x preconcentration factor. Ion ratio deviations were calculated for the from the mean of the analytical standards

CONCLUSIONS

- **Accurate PFAS analysis free of laboratory background contaminants can be achieved using the Waters PFC Analysis Kit, adaptable to any ACQUITY UPLC system**
- **Sub-ng/µL levels of detection for solvent standards are easily attained with the developed MRMs on the highly sensitive Waters Xevo TQ-S**

REFERENCES

1. Lee P. et al. Waters APNT10090111
2. Mullin L. et al. Waters APNT134893168

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