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Ultimate Sensitivity for the Detection of Per- and Polyfluorinated Alkyl Substances in Environmental Water Samples

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EPA Announces New Drinking Water Health Advisories for PFAS Chemicals, $1 Billion in Bipartisan Infrastructure Law Funding to Strengthen Health Protections

Compound	US EPA Health Advisory Level (ng/L)	UCMR 5 Minimum Reporting Level (ng/L)
PFOA	0.004 (interim)	4
PFOS	0.02 (interim)	4
PFBS	2000	3
GenX	10	5

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How do we get there?

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Waters New Tandem Quadrupole Family

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Xevo™
TQ-S cronos

Xevo™
TQ-S micro

Xevo™
TQ-XS

Xevo™
TQ ABSOLUTE

waters_connect™ + MassLynx™

Performance

Routine Tier – Accessible, reliable performance	Mid-Tier – Sensitive, flexible and Compact	High-Tier – Ultimate sensitivity and flexibility

Negative ion performance

Back to back comparison of New Detector and Original Detector Technology

Solvent standards – 1 ng/mL

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PFOS

498.9 > 80.1

PFOA

412.9 > 169

GenX

285 > 169

PFBS

298.9 > 80.1

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Solvent standards – 0.01 ng/mL

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PFOS

498.9 > 80.1

PFOA

412.9 > 169

GenX

285 > 169

PFBS

298.9 > 80.1

Peak Area Comparison Across 30 compounds

Quan Ion Only

		New Detector		Original Detector		
Name	Trace	peak area avg	%RSD (n=3)	peak area avg	%RSD (n=3)	Area Fold Increase
PFBA	212.9 > 169	1059686	2.0	297284	1.1	3.56
PFPeA	262.9 > 219	342863	1.9	146817	0.7	2.34
PFHxA	312.9 > 269	1025210	2.5	333190	0.7	3.08
PFHpA	362.9 > 319	1150837	1.8	464807	0.6	2.48
PFOA	412.9 > 369	1087382	1.7	264112	2.8	4.12
PFNA	462.9 > 418.9	937797	0.8	246796	2.2	3.80
PFDA	512.9 > 468.9	680782	3.1	274876	2.0	2.48
PFUnDA	562.9 > 518.9	622403	2.6	272736	2.0	2.28
PFDoDA	612.9 > 568.9	522179	0.1	216799	3.1	2.41
PFTriDA	662.9 > 618.9	353340	0.9	142210	2.4	2.48
PFTreDA	712.9 > 668.9	356300	4.8	147132	3.0	2.42
PFBS	298.9 > 80.1	583380	1.6	51904	0.2	11.24
PFPeS	348.9 > 80.1	480329	2.9	40086	1.1	11.98
PFHxS	398.9 > 80.1	405195	1.1	23908	0.4	16.95
PFHpS	448.9 > 80.2	335243	1.1	28368	0.6	11.82

		New Detector		Original Detector		
Name	Trace	peak area avg	%RSD (n=3)	peak area avg	%RSD (n=3)	Area Fold Increase
PFOS	498.9 > 80.2	247831	0.8	27653	1.8	8.96
PFNS	548.9 > 80.2	256320	1.1	30196	1.6	8.49
PFDS	598.9 > 80.2	188799	1.0	23161	2.1	8.15
GenX	285 > 169	251985	6.5	212717	0.8	1.18
ADONA	376.9 > 251	1715363	1.6	513845	1.7	3.34
9ClPF3ONS	530.9 > 350.9	774327	2.3	319860	2.4	2.42
11ClPF3OUdS	630.9 > 450.8	414468	1.7	193034	1.3	2.15
4_2 FTS	326.9 > 307	47940	3.8	18065	0.2	2.65
6_2 FTS	426.9 > 407	63514	1.3	19173	5.2	3.31
8_2 FTS	526.9 > 506.8	56244	1.8	24324	2.6	2.31
FBSA	297.9 > 78	1664620	2.8	140859	0.9	11.82
FHxSA	398 > 78.1	1559212	1.9	106869	1.1	14.59
FOSA	497.9 > 78.2	1051289	1.4	108621	0.3	9.68
NMeFOSAA	569.9 > 418.9	94332	5.8	54571	1.3	1.73
NEtFOSAA	584 > 418.8	68510	4.1	40380	1.8	8.96

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How do we use this to benefit PFAS analysis?

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ASTM D7979-20 ⓘ

Standard Test Method for Determination of Per- and Polyfluoroalkyl Substances in Water, Sludge, Influent, Effluent, and Wastewater by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)

Previous approach

TQ Absolute

30 µL (or >)
injection volume

Can we reduce
injection volume?

Benefits of Reducing Injection Volume

- Chromatography improvements
- Increased column lifetime
- Reduction of downtime from instrument cleaning and maintenance

Sample Preparation

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Water

Drinking	Influent
Surface	Snow
Ground	

5 mL sample
Spike surrogate
Dilute with 5 mL methanol

Syringe filter entire sample

Acidify and transfer to polypropylene vial

PFAS targeted in method (35)

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Carboxylates

C4 – C14

Sulfonates

C4 – C13

Emerging/Ethers

GenX

ADONA

11Cl-PF3OUdS

9Cl-PF3ONS

Precursors

4:2 /6:2 / 8:2 FTS

Sulfonamides (C4, C6, C8)

NMeFOSAA / NEtFOSAA

NMeFOSE / NEtFOSE

Method Detection Limits in Reagent Water (10 µL injection)

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- 10 replicates of reagent water spiked with 5 ng/L and taken through sample prep
- MDL = St Dev * t_{n-1}

Compound	Method Detection Limit (ng/L)
PFBA	21.90
PFPeA	7.74
PFHxA	1.62
PFHpA	0.76
PFOA	1.24
PFNA	1.18
PFDA	1.53
PFUnDA	2.01
PFDoDA	1.52
PFTriDA	1.36
PFTreDA	1.23

Compound	Method Detection Limit (ng/L)
PFBS	0.76
PFPeS	0.90
PFHxS	0.78
PFHpS	0.97
PFOS	0.97
PFNS	1.32
PFDS	1.12
PFUnDS	1.66
PFDoDS	1.00
PFTrDS	1.48

Compound	Method Detection Limit (ng/L)
GenX	1.08
ADONA	0.90
9Cl-PF3ONS	1.04
11Cl-PF3OUdS	1.47
4:2 FTS	1.38
6:2 FTS	7.51
FBSA	1.09
FHxSA	1.06
FOSA	1.05
N-Me-FOSAA	1.23
N-Et-FOSAA	1.60

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MDL samples – 2.5 ng/L on column PFBS
Average S:N 160

MDL samples – 2.5 ng/L on column PFOS
Average S:N 82

MDL samples – 2.5 ng/L on column PFOA
Average S:N 84

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MDL samples – 2.5 ng/L on column GenX
Average S:N 55

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Calibration Curves

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Water Samples

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PFAS Detected in Water Samples

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Compound	Wastewater (ng/L)	Drinking Water (ng/L)	Ground Water	Surface Water
PFHxA	17.43	4.55	3.8	3.8
PFHpA	4.07	2.03	2.0	2.2
PFOA	16.16	4.44	2.8	4.3
PFNA	2.55	< LLOQ	-	-
PFDA	1.61	-	-	-
PFBS	2.55	1.94	1.5	< LLOQ
PFHxS	1.17	< LLOQ	-	< LLOQ
PFOS	1.78	-	-	1.0
FBSA	< LLOQ	< LLOQ	-	< LLOQ
FOSA	< LLOQ	-	-	-
NMeFOSAA	2.72	-		

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Wastewater Sample Overview

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Common contaminants (6:2 FTS and PFBA)

One sample missing internal standard (blank)

RT deviation 10%

Response 30%

GenX Internal Standard

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One sample missing internal standard (blank)

Response Deviation

Retention Time Deviation

Wastewater Sample Unknowns - PFOS

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Post spiked samples

Pre spiked samples

Unknown sample

Solvent Blanks

Wastewater Sample Unknowns - PFNA

Waters
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Post spiked samples

Pre spiked samples

Unknown sample

Solvent Blanks

Perfluorooctanesulfonate (C8F17O3S)
Wastewater Sample diluted 2x with 10 µl injection

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Perfluorotridecanesulfonate (C13F27O3S)
Drinking Water Sample diluted 2x with 10 µl injection

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Repeatability of spiked samples

Repeatability of spiked samples

SPE + Xevo TQ Absolute for EPA HALs?

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- Enrichment will push the possible detection limits even lower
- Reduce the volume of sample needed?
- Blanks will be challenging!

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Solvent Blanks on TQ Absolute

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500x enrichment (250 mL → 0.5 mL) - Standards

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0.5 ng/L = 0.001 ng/L in sample

2.5 ng/L = 0.005 ng/L in sample

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Acknowledgements

- University of Massachusetts Amherst
  - Aarthi Mohan

- Waters
  - Henry Foddy
  - Stuart Adams
  - Olga Alvarez-Aviles
  - Edgar Falfan
  - Don Kwet