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Streamlined Measurement of Ultra-Short Chain PFAS in Landfill Groundwater via Altura Column Chemistry and LC-MS/MS

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Introduction

The increasing detection of ultra-short chain PFAS in environmental waters has created a need for highly sensitive, reliable methods capable of separating and quantifying these poorly retained analytes on conventional reversed phase LC columns. Compounds such as TFA and DFA show minimal retention on typical C18 columns, requiring specialized column chemistry, optimized mobile phases, and contamination control. This work evaluates a direct-injection LC–MS/MS workflow using the Altura Poroshell 120 PFAS Column paired with an Agilent 1290 Infinity III LC and 6495D triple quadrupole LC/MS (LC/TQ) for analyzing 9 ultra-short chain PFAS in high ionic strength synthetic water and landfill groundwater. The study examines detection limits, retention-time stability under varying ionic strengths, matrix-spike recovery and precision, and results from seven landfill sites, including PFBA comparison to collaborator data generated using EPA 1633A.

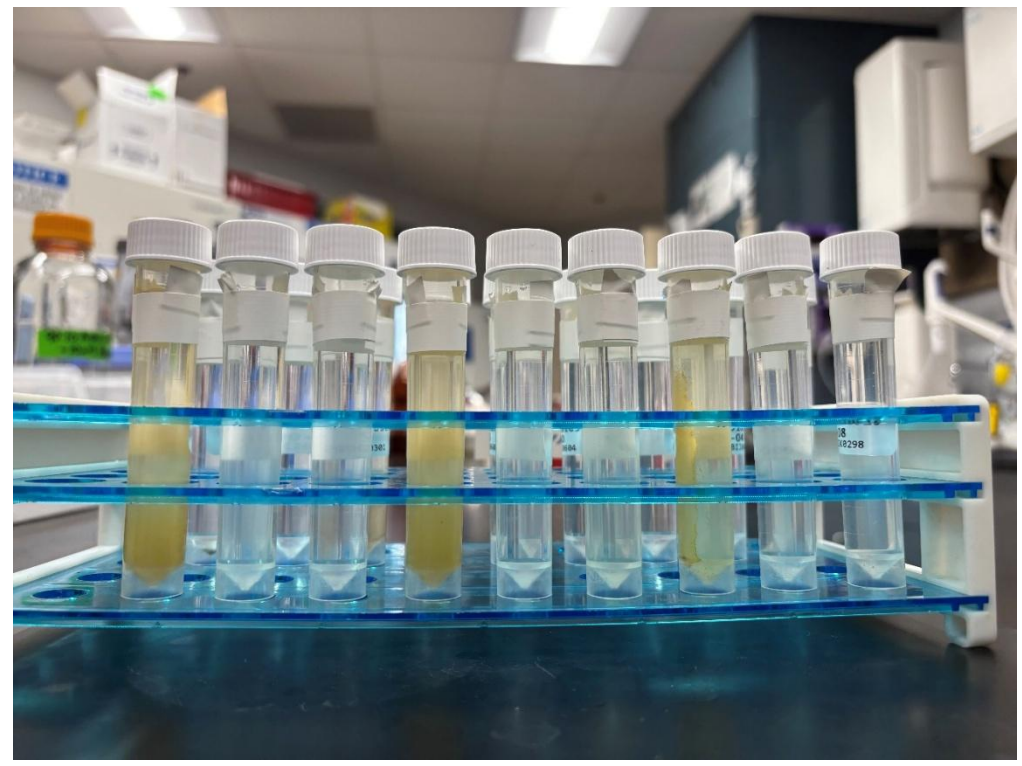

Figure 1. Groundwater monitoring well samples.

Experimental

Table 1. Target Analytes.

Compound name	Compound formula
13C2-TFA	[13C]2HF3O2
13C3-PFPrA	[13C]3HF5O2
PFEtS	C2F5SO3H
PFMeS	CF3SO3H
PFOMAA	C3F5O3H
PFPrA	C3F5O2H
PFPrS	C3F7SO3H
TFA	C2F3O2H
DFA	C2H2F2O2
PFBA	C4HF7O2
TFSI	C2F6NO4S2

Sample Preparation

Waters samples were prepared by aliquoting 600 µL into an Eppendorf tube and centrifuging for 10 min. Supernatant was aliquoted into LC-MS/MS vial and labeled internal standard was added.

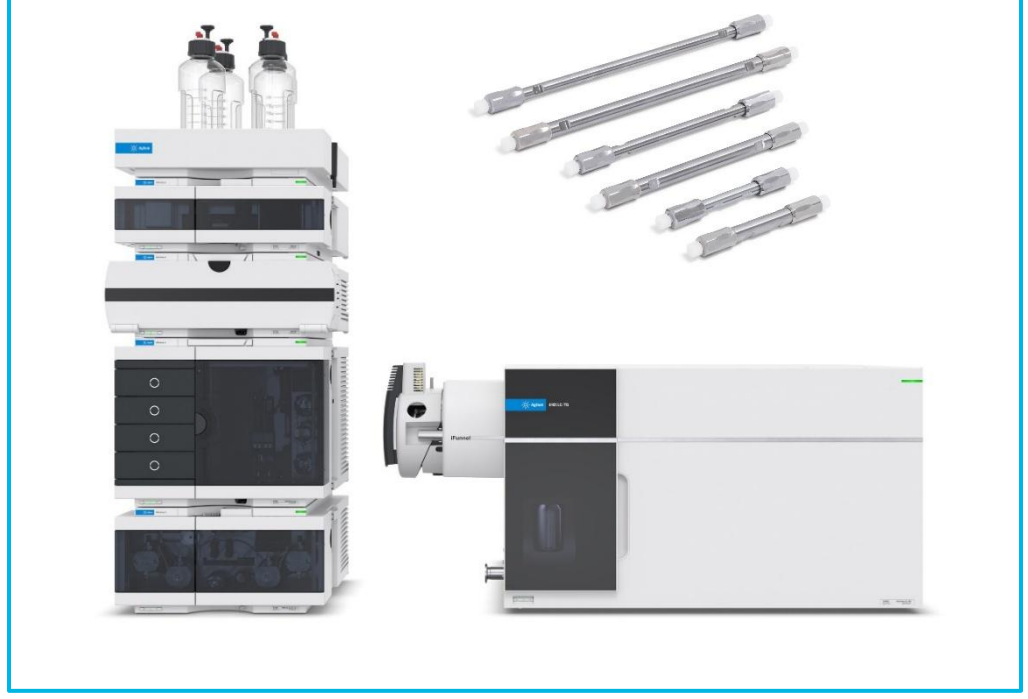

Figure 2. Agilent 1290 Infinity III LC, 6495D LC/TQ and Altura Poroshell PFAS Columns.

Test Samples

Reverse osmosis (RO) water was used for preparation of calibration standards, method blanks, and spikes. The calibration range was 0.005–2 ng/mL. Laboratory synthetic water (SW) containing 20 mg/L nitrate, 150 mg/L bicarbonate, 250 mg/L chloride, and 250 mg/L sulfate was formulated for column testing. Unknown test samples from groundwater monitoring of landfill wells (Figure 1.) were provided by a collaborator and had been previously analyzed using EPA Method 1633A.

Results: Method Performance

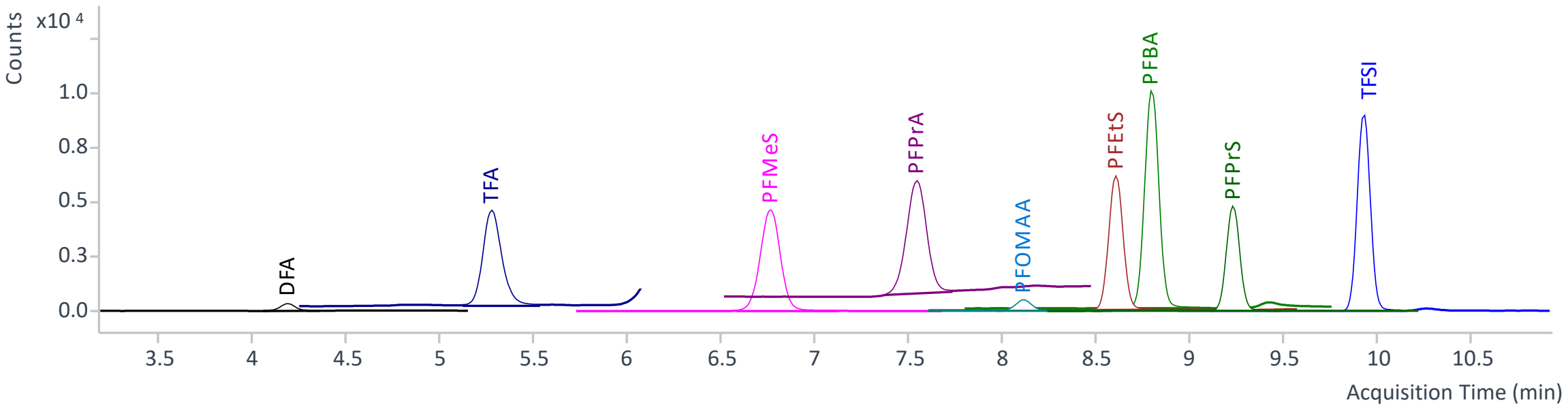

Figure 3. Chromatogram of Ultra Short PFAS. 0.1 ng\mL standard..

Analytical Method

Chromatography is described in Table 2. The 6495D was operated in dynamic MRM mode with a gas temperature of 240 ºC, drying gas flow 18 L/min, sheath gas temperature 350 ºC, sheath gas flow 11 L/min, nebulizer 20 psig and Vcap of 2000V.

Table 2. LC Conditions

LC Conditions		
Column	Altura PFAS 2.1 x 100 mm, 2.7 um	
Delay Column	Poroshell PFAS Delay column, 4.6 x 30 mm	
Column Temperature	40 ºC	
Injection Volume	25 µL	
Autosampler Temp	20 ºC	
Standard Wash	1:1 Methanol : water, 5 sec flush	
Mobile Phase	A: 0.1% Acetic Acid in Water	B: 90:10 ACN: Water + 10 mM Ammonium Acetate
Flow Rate	0.5 mL/min	
Gradient program	Time (min)	B (%)
	0.0	10
	0.5	10
	2.0	40
	6.0	40
	10.0	98
	12.0	98
	12.1	10
Stop Time	12.50 min	
Post Time	4.00 min	

Method Detection Levels

Initial tests indicated the presence of background TFA in all samples. Although instrument blanks were clean, TFA was consistently detected in method blanks. Because the laboratory is a mixed-use space, complete elimination of ambient TFA was not feasible. Accordingly, the method detection limit (MDL) evaluation was adjusted by elevating the TFA spike concentration to clearly distinguish it from persistent background levels. MDLs were determined in accordance with EPA procedures (2).

Table 3. Method Detection Levels. * indicates MDL was determined by blank levels

	MDL (ng/mL)
DFA	0.008
TFA *	0.054
PFMeS *	0.007
PFPrA	0.005
PFOMAA	0.004
PFEtS	0.004
PFBA	0.004
PFPrS	0.004
HQ-115	0.005

Retention Time Stability

Retention stability was evaluated by comparing the retention time (RT) of TFA in RO water with that in synthetic water (SW) and groundwater samples. The greatest fluctuation was observed in synthetic water, where RTs were shifted slightly earlier for all peaks. Groundwater samples showed RTs consistent with those observed in RO water.

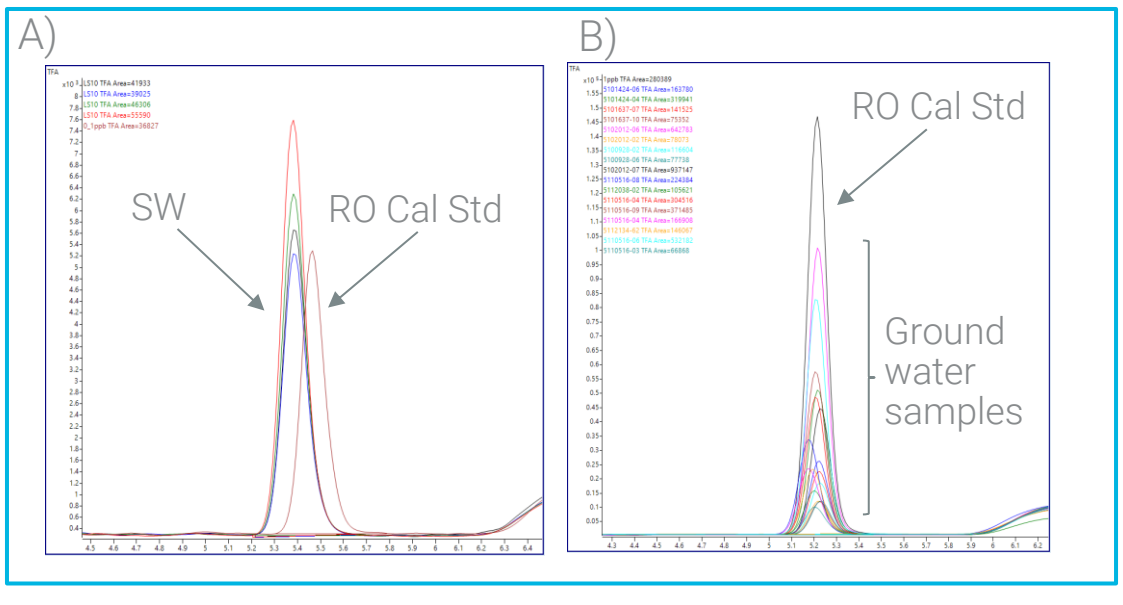

Figure 4. A) overlay of TFA in SW and RO standards. B) Overlay of TFA in RO standards and groundwater samples

Results: Field Samples

Quantitation in Laboratory Synthetic Water

SW was spiked at three levels to evaluate method reproducibility and recovery. The lowest spiking level was 0.01 ng/mL (0.1 ng/mL for TFA), followed by 1.5× and 2× the lowest level. With the exception of DFA and TFA, relative standard deviations were excellent (< 15%), and recoveries fell within the 70–130% range. Results are shown in Figure 5.

The first two eluting compounds presented specific challenges. DFA exhibited poor recovery, likely due to matrix suppression caused by the high salt content of the synthetic water. Because no isotopically labeled analogue for DFA was available, quantitation was corrected using $13C_2$-TFA, which negatively affected both accuracy and reproducibility. To clarify results the experiment would need to be repeated with a higher DFA spiking level.

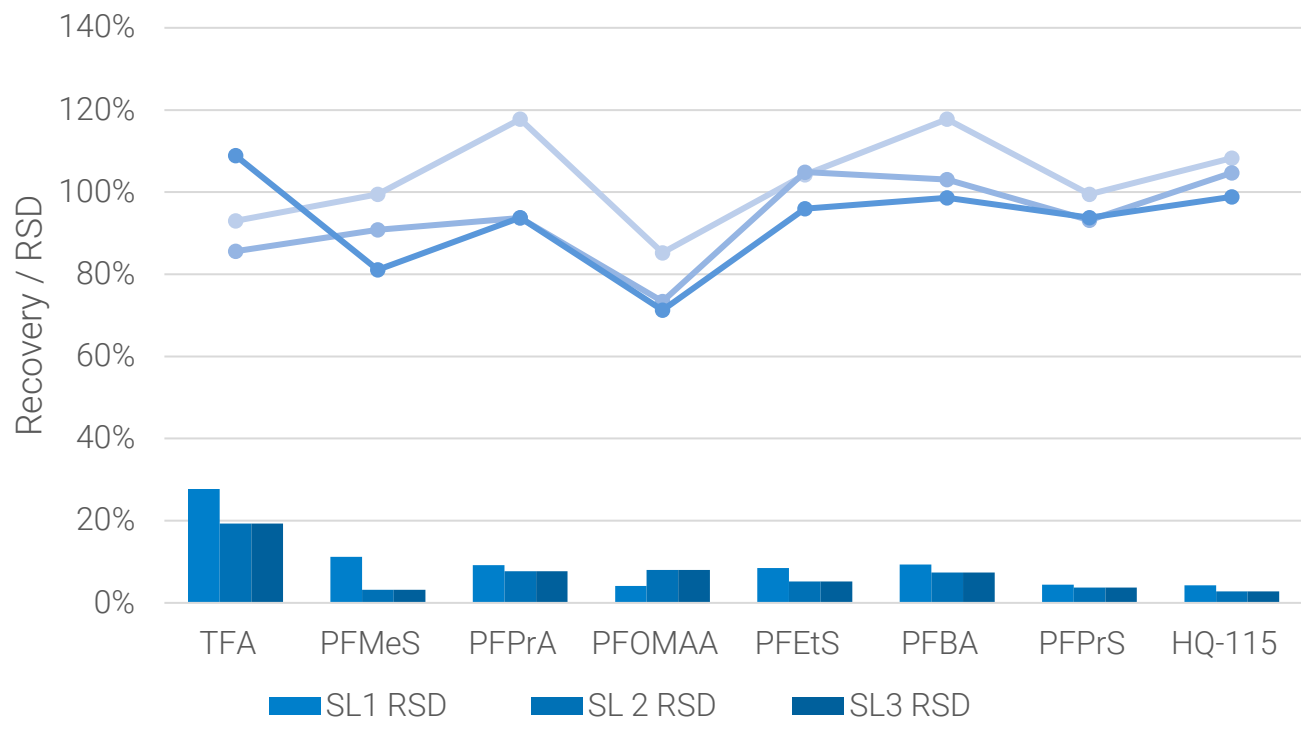

Figure 5. Spike recovery and reproducibility in synthetic water samples.

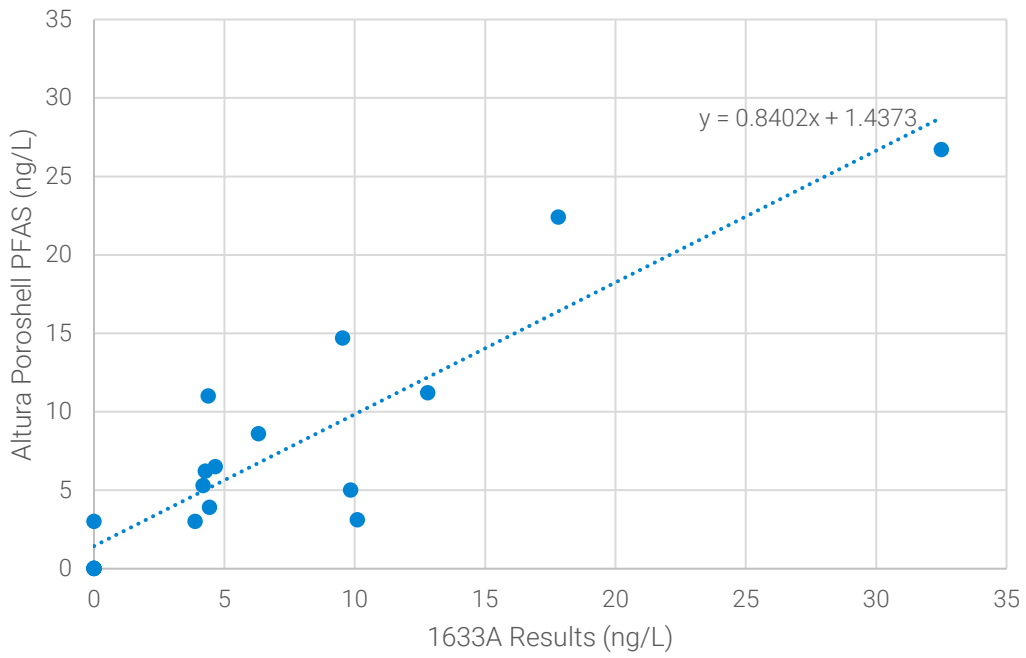

Figure 6. A method comparison scatter plot of direct-injection PFBA results vs. EPA 1633A results.

Groundwaters samples comparison between 1633A and presented method.

Direct-injection results for PFBA obtained using the method presented here were compared with collaborator data in which PFBA was quantified using solid-phase extraction as prescribed in EPA Method 1633A. Figure 6 shows PFBA results plotted with direct injection (presented method) on the y-axis and EPA 1633A results on the x-axis. Perfect agreement between the two methods would yield a slope of 1. The results were significantly correlated ($p < 0.001$), confirming the direct-injection method performs comparably to EPA 1633A.

Conclusions

- Ultra-short chain PFAS (C2–C3) were successfully retained and resolved using the Altura Poroshell PFAS column.
- Consistent retention times across matrices of different conductivities
- Altura workflow performs comparably to EPA 1633A for PFBA
- Application Note: Reliable Ultra Short Chain PFAS Analysis in Water and Landfill Groundwater Using the Agilent Altura Poroshell PFAS column and LC/MS/MS (5994-9019EN)

References

1) U.S. Environmental Protection Agency. (2024). *Method 1633A: Analysis of per- and polyfluoroalkyl substances (PFAS) in aqueous, solid, biosolids, and tissue samples by LC-MS/MS* (EPA 820-R-24-007). https://www.epa.gov/system/files/documents/2024-12/method-1633a-december-5-2024-508-compliant.pdf

2) U.S. Environmental Protection Agency. (2016). *Definition and procedure for the determination of the method detection limit (MDL), Revision 2* (EPA 821-R-16-006). https://www.epa.gov/sites/default/files/2016-12/documents/mdl-procedure_rev2_12-13-2016.pdf

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