

Direct Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Ground, Surface and Wastewater by LC-MS/MS

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ABSTRACT

Purpose: Demonstrate method performance for the PFAS analysis at low level (ng/L) in a wide variety of non-drinking water matrices by direct analysis.

Methods: Simple water sample preparation based on dilution, filtration, and acidification followed with LC-MS/MS analysis.

Results: Thermo Scientific™ TSQ Altis™ mass spectrometer provides excellent quantitative performance for PFAS direct analysis in the low ng/L range in non-drinking water matrices.

INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) have been manufactured and used in a variety of industries around the globe, including in the United States since the 1940s. PFOA and PFOS have been the most extensively produced and studied of these chemicals. Both chemicals are very persistent in the environment and in the human body and accumulate over time. There is evidence that exposure to PFAS can lead to adverse human health effects. 1-3 As a result, analytical testing has expanded beyond the simple analysis of drinking water and is now being performed on several matrices such as ground, surface and wastewater. In this work, we report a direct analysis method for the determination of a list of 24 PFAS and their labelled surrogates in a wide variety of non-drinking water matrices.

MATERIALS AND METHODS

Sample Preparation

Field water samples were provided by the U.S. EPA Region 5 and included reagent water, surface water, ground water and wastewater through a participating EPA study. Each water sample was spiked with a low (60 ng/L) and high level (200 ng/L) of 24 PFAS compounds (N=5) prior to shipment to the lab. Five blank samples of each water matrix were also provided.

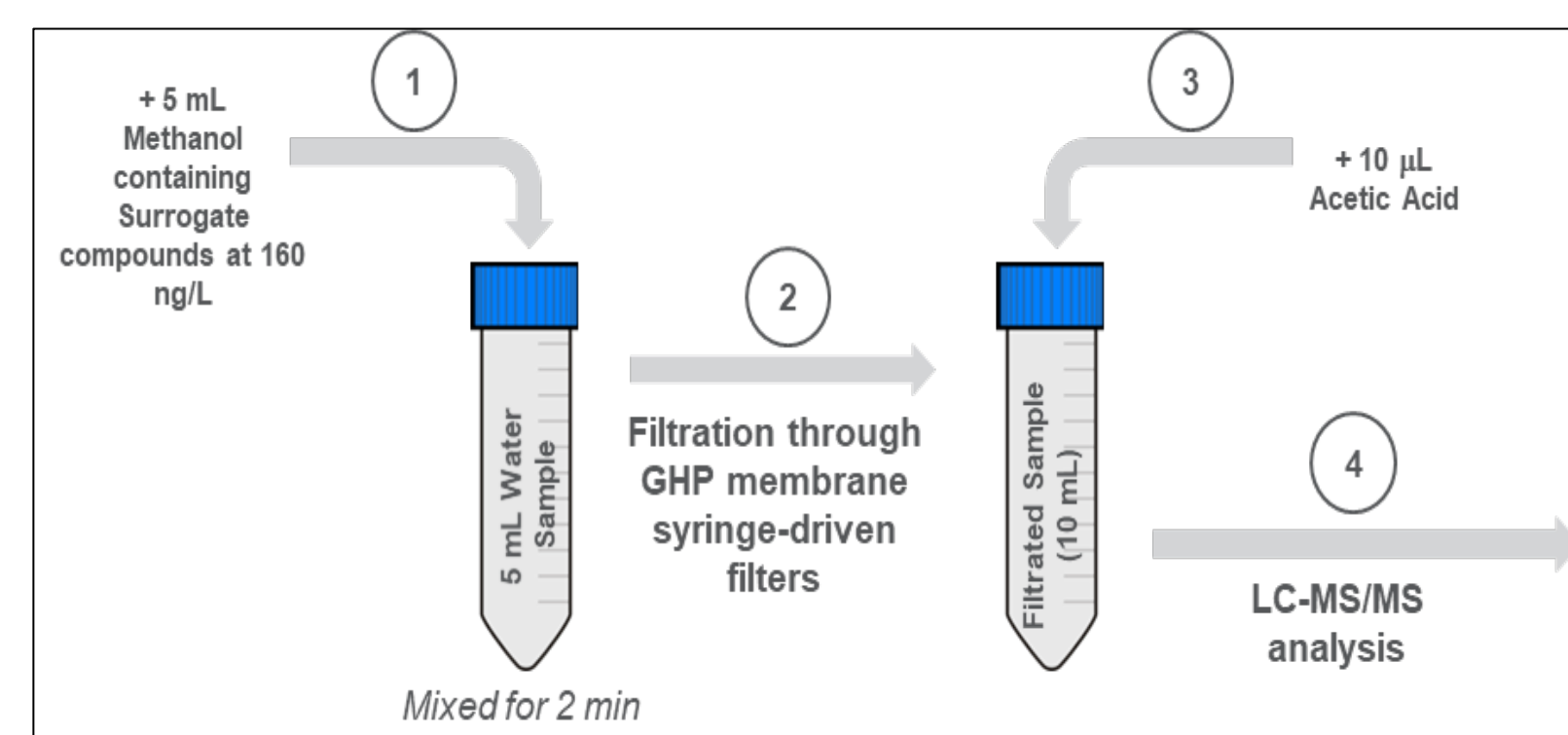


Figure 1. Water sample preparation scheme.

LC-MS/MS Analysis

Thermo Scientific™ Vanquish™ Flex Binary system fitted with Thermo Fisher PFC free kit and interfaced with a TSQ Altis triple quadrupole mass spectrometer.

LC Conditions

Analytical Column	Thermo Scientific™ Accucore™ RP-MS, 2.1 x 100 mm, 2.6 µm	Gradient:	Time (min)	% Solvent B
Isolator column	Thermo Scientific™ Hypersil™ BDS C18, 5 µm, 2.1 x 50 mm		0	0
Flow rate	500 mL/min		1	30
Column temperature	45 °C		6	45
Solvent A	Water containing 2mM ammonium acetate, 2% methanol and 0.1% AA		13	80
Solvent B	Methanol containing 2mM ammonium acetate, 2% water and 0.1%AA		14	95
Injection volume	25 µL*		17	95
			18	0
			21	0

MS Parameters

HESI Source: negative ionization mode	Vaporizer temperature : 300 °C
Spray Voltage: 2.5 kV	Cycle time :0.3 s
Sheath Gas (Arb): 50	Q1 Resolution (FWHM): 0.7 Da
Auxiliary Gas (Arb): 10	Q3 Resolution (FWHM): 1.2 Da
Sweep Gas (Arb): 0	CID gas: 2 mTorr
Ion transfer tube temp.: 325 °C	Monitored SRM transitions listed in application note # 65397

Data Analysis

The acquired data was processed using Thermo Scientific™ Dionex™ Chromleon™ 7 Chromatography Data System software, version 7.2.9.

RESULTS

The LC-MS/MS method described herein differs from the reported ASTM 9797-17 method, where excellent chromatographic separation was achieved on a Accucore RP-MS analytical column using different mobile phases compositions (Fig. 2).

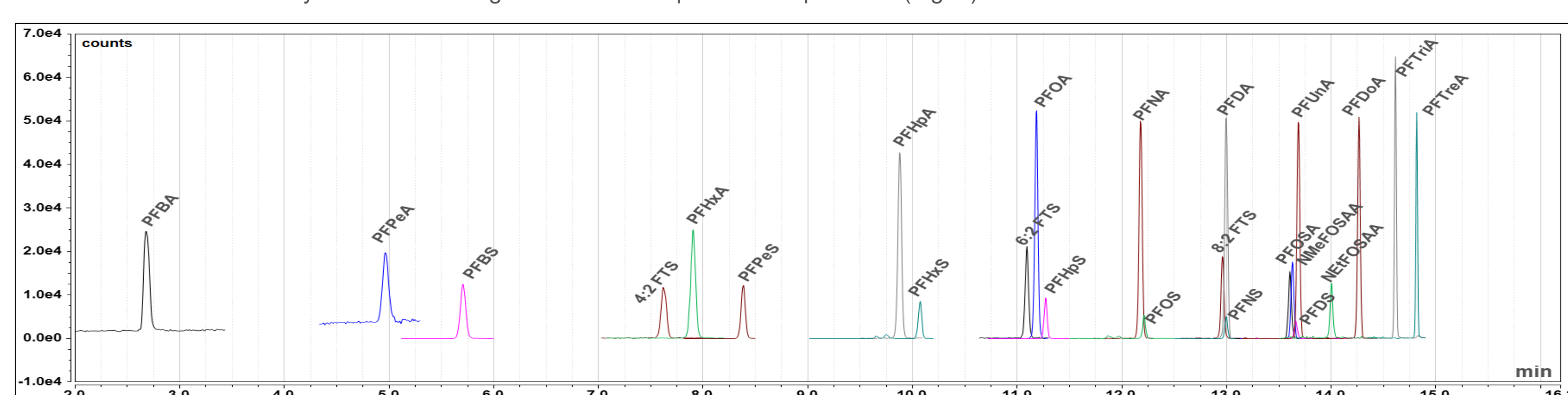


Figure 2. Overlay chromatograms of all PFAS compounds included in this method.

Linearity and Sensitivity

Excellent linearity and quantitative accuracy were achieved over the range of 10 – 400 ng/L with correlation coefficients greater than 0.99 for all transitions and the respective residuals were within 20% of the nominal values. The concentrations were calculated taking into consideration the 50% dilution with methanol.

TSQ Altis mass spectrometer can quantitate the majority of PFAS compounds 5 times lower than the LLOQ reported by ASTM D7979-17 as demonstrated by the results shown in Table 1.

Compounds	LLOQ (N=3) ng/L	ASTM D7979-17 LLOQ (ng/L)
PFBA	10	50
PFPeA	10	50
PFBS	2	10
4:2 FTS	10	-
PFHxA	2	10
PFPeS	2	-
PFHpA	5	10
PFHxS	5	10
6:2 FTS	5	-
PFOA	2	10
PFHpS	2	-
PFNA	2	10
PFOS	2	10
8:2 FTS	5	-
PFDA	2	10
PFNS	10	-
N-MeFOSAA	5	-
PFOSA	10	-
PFDS	10	-
PFUnA	2	10
N-EtFOSAA	5	-
PFDoA	2	10
PFTriA	2	10
PFTreA	2	10

Table 1. Reporting lower limit of quantitation obtained by this method and ASTM D7979-17 Reporting ranges.

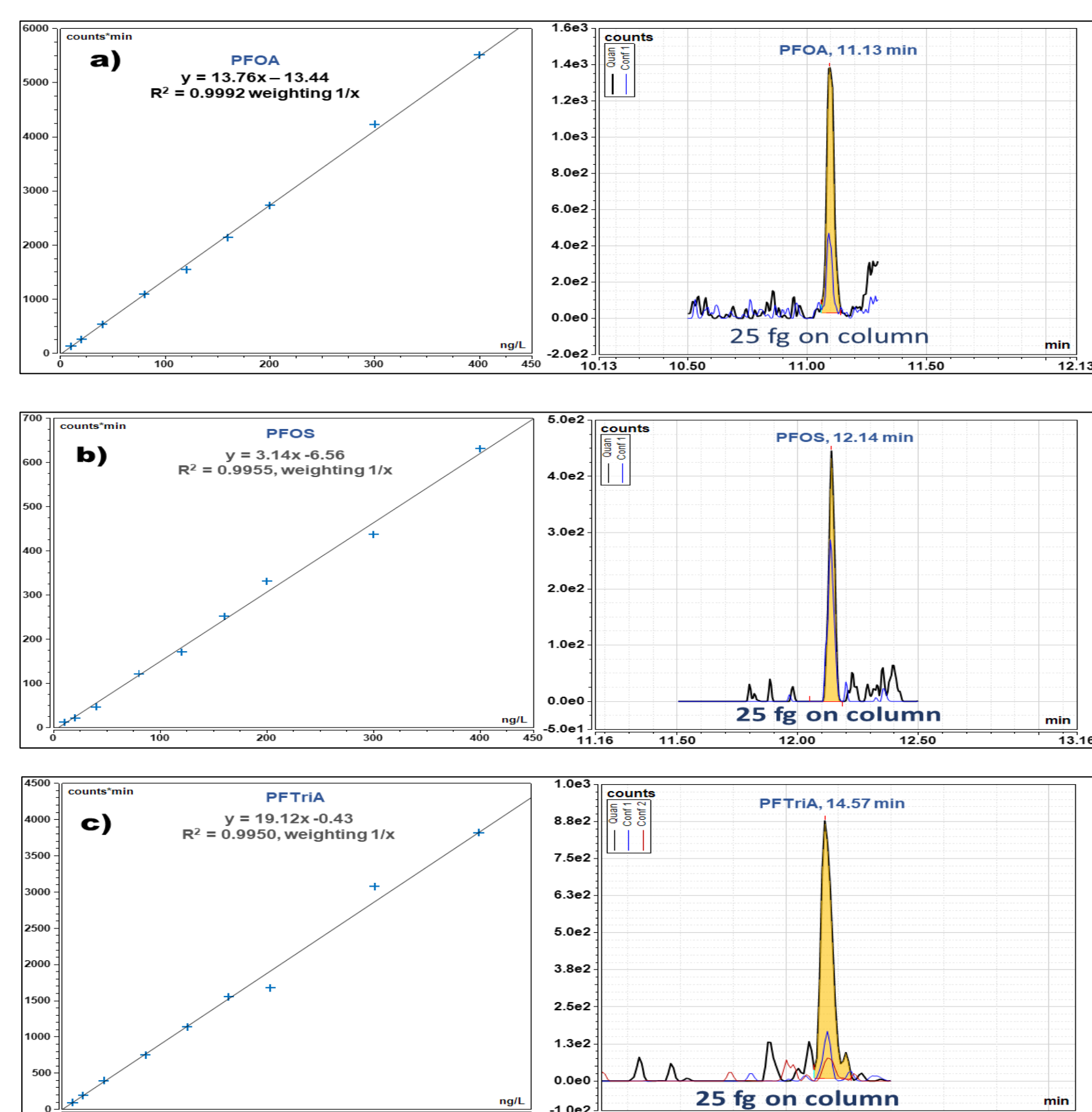


Figure 3. Representative calibration curves for a) PFOA; b) PFOS and c) PFTriA, and chromatograms of an injection of 1 ng/L which is 5 times lower than the reporting limit of quantitation.

RESULTS (cont.)

Control Samples

Table 2 summarizes the ASTM D9797-17 control criteria, and the results demonstrate all compounds passed in this method. Figure 3 shows the overlaid chromatogram of all PFAS of a method blank and a reagent water spiked at 10 ng/L (LLOQ check sample) and taken through sample preparation. PFBA and PFPeA are quantifiable at an injected concentration of 10 ng/L, which is much lower than the reported limit of quantitation in the ASTM D7979-17 method.

Sample type	Definition	Criteria	Results
Reagent Blank	Methanol: Water (50:50, v/v) + 0.1% Acetic acid	Concentration must be one half the LLOQ	Target compounds NOT DETECTED OR BELOW <LLOQ
Method Blank	Reagent Water + surrogates at 160 ng/L. Taken through sample preparation	Concentration must be one half the LLOQ	Target compounds NOT DETECTED OR BELOW LLOQ
LLOQ checking	Reagent water + targets at 10 ng/L. Taken through sample preparation	S/N ratio ≥ 3 for all quantitative ions & Target Recoveries < 50% deviation	LLOQ at 10 ppt Recoveries <30% deviation for most of the compounds
Laboratory controls	Reagent water + targets at 160 ng/L. Taken through sample preparation.	Target Recoveries < 30% deviation	Target Recoveries <30% deviation for most of the compounds

Table 2. Summary of method control criteria according ASTM D 9797-17 method.

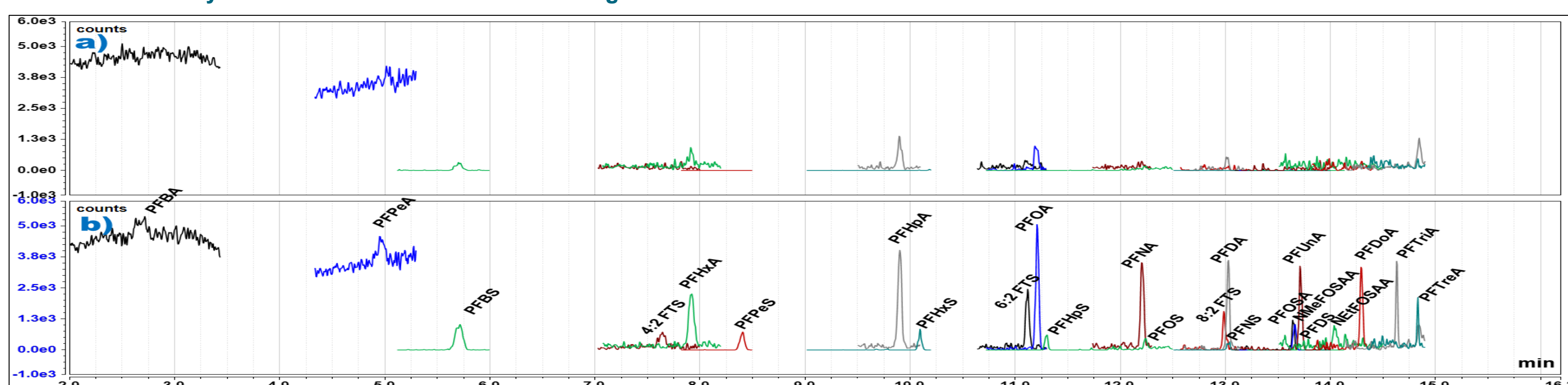


Figure 3. PFAS overlay chromatograms: a) method blank sample and b) reporting limit checking sample spiked at 10 ng/L.

Sample Analysis

Each spiked water matrix (N=5) at low and high concentrations were prepared using the method described in ASTM D7979-17 and analyzed using the LC-MS/MS method described herein. The 60 samples received were divided into 3 batches of 20 samples and analyzed on 3 different days. All 24 PFAS compounds were detected and quantifiable at both low (60 ng/L) and high spike (200 ng/L) concentrations. Figure 4 shows an example of overlay chromatograms of all PFAS spiked at 60 ng/L in reagent, ground, surface and waste samples.

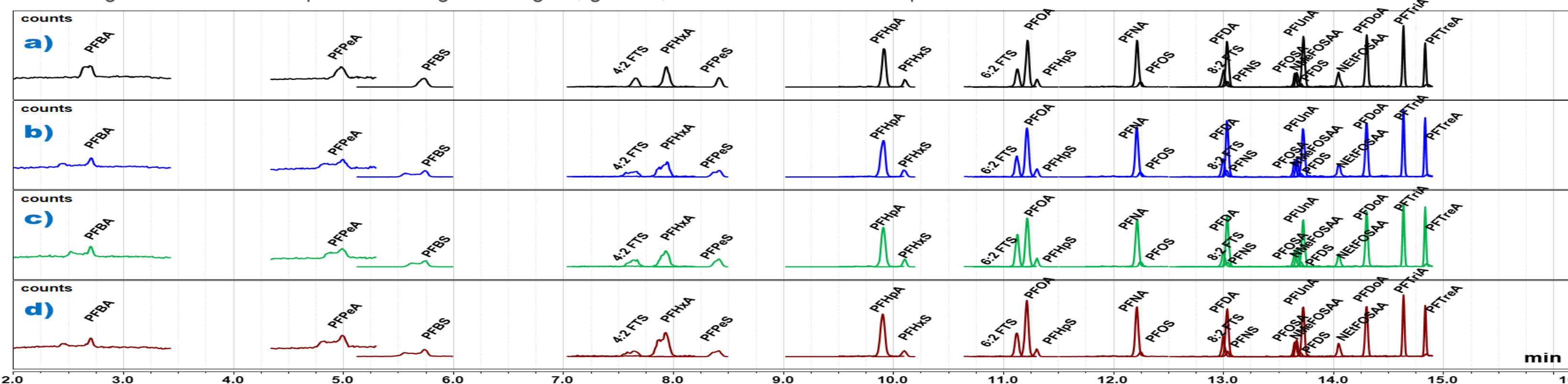


Figure 4. Overlay chromatograms of 24 PFAS spiked at 60 ng/L in field samples. a) Reagent water; b) ground water; c) surface water and d) wastewater.

Recovery of the 24 PFAS compounds spiked into the different water matrices is summarized in table 3. All compounds analyzed in this method were within the range of 70% to 130% as required by ASTM D7979-17, except for PFBA spiked at low level in wastewater (58% with an imprecision of 34%). The lower recovery observed might be related to co-eluting wastewater matrix components which might be suppressing the signal. The LC-MS/MS method has proven to be very reproducible and robust as demonstrated by the precision values of all PFAS compounds spiked in non-drinking water matrices (N=5) summarized in table 4.

Compounds	REAGENT WATER		GROUND WATER		SURFACE WATER		WASTE WATER	
	60 ng/L	200 ng/L	60 ng/L	200 ng/L	60 ng/L	200 ng/L	60 ng/L	200 ng/L
PFBA	77%	78%	71%	75%	74%	74%	58%	75%
PFPeA	84%	80%	104%	80%	115%	81%	88%	78%
PFBS	87%	81%	95%	81%	95%	79%	72%	77%
4:2 FTS	82%	81%	83%	79%	86%	80%	77%	74%
PFHxA	81%	82%	90%	78%	87%	79%	76%	91%
PFPeS	80%	80%	82%	79%	85%	78%	80%	83%
PFHpA	84%	81%	88%	80%	89%	80%	74%	81%
PFHxS	81%	81%	87%	78%	94%	81%	85%	85%
6:2 FTS	84%	82%	85%	80%	87%	94%	78%	79%
PFOA	83%	80%	88%	82%	123%	83%	83%	86%
PFHpS	81%	81%	84%	76%	83%	78%	79%	86%
PFNA	79%	81%	84%	80%	86%	80%	79%	82%
PFOS	91%	82%	91%	78%	93%	81%	79%	90%
8:2 FTS	85%	80%	81%	75%	76%	79%	78%	83%
PFDA	85%	75%	89%	79%	81%	76%	72%	78%
PFNS	80%	81%	86%	78%	85%	79%	74%	83%
N-MeFOSAA	77%	81%	80%	77%	86%	81%	82%	84%
PFOSA	76%	76%	87%	75%	91%	75%	79%	81%
PFDS	82%	78%	89%	77%	85%	79%	72%	81%
PFUnA	76%	76%	80%	81%	75%	78%	75%	83%
N-EtFOSAA	82%	79%	89%	77%	89%	81%	80%	85%
PFDoA	79%	82%	83%	78%	85%	82%	79%	85%
PFTriA	87%	86%	89%	79%	92%	91%	87%	89%
PFTreA	109%	103%	112%	91%	113%	119%	100%	110%

Table 3. PFAS recoveries in different water matrices.

Compounds	REAGENT WATER		GROUND WATER		SURFACE WATER		WASTE WATER	
	60 ng/L	200 ng/L	60 ng/L	200 ng/L	60 ng/L	200 ng/L	60 ng/L	200 ng/L
PFBA	6%	3%	23%	6%	17%	6%	34%	6%
PFPeA	9%	6%	9%	6%	25%	9%	9%	3%
PFBS	7%	4%	7%	4%	15%	3%	13%	3%
4:2 FTS	4%	4%	5%	3%	11%	4%	3%	10%
PFHxA	6%	1%	2%	4%	15%	7%	10%	18%
PFPeS	2%	4%	6%	4%	16%	3%	8%	4%
PFHpA	6%	3%	6%	5%	11%	3%	5%	3%
PFHxS	4%	5%	10%	6%	17%	4%	16%	5%
6:2 FTS	12%	4%	9%	4%	16%	14%	26%	7%
PFOA	4%	5%	8%	8%	32%	11%	12%	10%
PFHpS	12%	2%	6%	5%	14%	6%	10%	10%
PFNA	6%	4%	5%	3%	14%	3%	7%	3%
PFOS	13%	5%	5%	4%	13%	4%	5%	4%
8:2 FTS	6%	6%	11%	5%	16%	5%	8%	4%
PFDA	10%	6%	11%	4%	10%	3%	13%	5%
PFNS	4%	3%	6%	4%	19%	5%	5%	4%
N-MeFOSAA	11%	7%	11%	5%	18%	4%	11%	3%
PFOSA	11%	10%	13%	5%	17%	8%	8%	5%
PFDS	10%	8%	3%	5%	13%	2%	4%	8%
PFUnA	9%	5%	3%	5%	25%	4%	8%	4%
N-EtFOSAA	16%	4%	7%	5%	21%	8%	13%	5%
PFDoA	6%	5%	4%	6%	15%	8%	9%	4%
PFTriA	8%	5%	10%	6%	15%	11%	6%	5%
PFTreA	22%	14%	19%	12%	20%	23%	14%	14%

Table 4. Reproducibility represented by CV% of 24 PFAS Compounds analyzed in this method.

CONCLUSIONS

- Method blank samples confirmed that reagents and LC-MS/MS system fitted with PFC-free kit were PFC-free from contaminants and interferences
- The Accucore RP-MS column provides excellent chromatographic separation and maintains robustness in challenging water matrices.
- The TSQ Altis mass spectrometer can quantitate the majority of PFAS compounds lower than the LLOQ reporting requirements in ASTM D7979-17 and EPA 8327.
- PFAS compounds were detected in the different water matrices at both low and high spike concentrations with recoveries in the required range.
- All spiked water samples, in a variety of matrices, showed RSDs below 20% for most of PFAS compounds, demonstrating the high robustness and reproducibility of the method.

REFERENCES

- National Institute of Environmental Health Sciences. Perfluorinated Chemicals (PFCs), https://www.niehs.nih.gov/health/materials/perfluorinated_chemicals_508.pdf
- U.S. Environmental Protection Agency (EPA). Per- and Polyfluoroalkyl Substances (PFAS), <https://www.epa.gov/pfas>
- Agency for Toxic Substances and Disease Registry (ATSDR). An Overview of Perfluoroalkyl and Polyfluoroalkyl Substances and Interim Guidance for Clinicians Responding to Patient Exposure Concerns. https://www.atsdr.cdc.gov/pfc/docs/pfas_clinician_fact_sheet_508.pdf

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TRADEMARKS/LICENSING

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