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Direct analysis of selected per- and polyfluorinated alkyl substances (PFAS) in ground, surface, and waste water by LC-MS/MS

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ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) have unique properties in consumer products that lead to a wide variety of uses. Unfortunately, their toxicity, bioaccumulation, prevalence and persistence in waters and soils make them a hot topic and global concern. The traditional compounds studied to investigate environmental impacts have focused on two compounds, perfluorooctanoic acid (PFOA) and perfluorooctanoic acid sulfonate (PFOS). However, it is now well established that there are possibly 3-4000 forms that can vary in length, linear or branched and ether telomer forms. The term used for this variety is now designated as per- and polyfluorinated acids (PFAS). PFAS chain lengths vary from C2-C14 and are a combination of linear and branched structures. The chemical properties for PFAS compounds, background concentrations and presence in sampling equipment, instrumentation and lack of standards make analysis and accurate quantitation a real challenge. Though EPA 537 and 537.1 have been developed by the EPA, these are only validated in drinking water matrices and have a limited set of linear compounds. Several branches of the US EPA are in the process of validating methods for PFAS in water and soils using direct injection and SPE followed by LC-MS/MS.

INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are a group of man-made chemicals that includes perfluorooctanoic (PFOA), perfluorooctyl sulfonic acid (PFOS), and hexafluoropropylene oxide dimer acid (HFPO-DA, which is part of GenX process). PFAS compounds have been manufactured since the 1940s. The most well-known PFAS compounds, PFOA and PFOS, have been the most extensively produced and studied for chemical properties and toxicological effects. Both chemicals are very persistent in the environment and accumulate in the human body over time. It is well documented that exposure to PFAS can lead to adverse human health effects[1-3] and are found in food packaging material as well as food processing equipment. Plants can accumulate PFAS when grown in PFAS-containing soil and/or water. These compounds are also found in a wide variety of consumer products.
Of particular note, drinking water can contain PFAS and can be associated with domestic and specific workplace facilities. Living organisms, including fish, animals and humans, have been shown to have accumulations of PFAS compounds and thus can build up and persist over time.[1-4] For these reasons, most people have been exposed to PFAS.

PFAS compounds can be per- and polyfluorinated along a carbon backbone, typically ending with a carboxylic or sulfonic acid. PFOA and PFOS are made up of a C_8F_{17} subunit with either a carboxylic group (PFOA) or sulfonate group (PFOS). Replacement chemicals, like GenX, tend to have fewer carbon atoms in the chain, but have many similar physical and chemical properties as their predecessors (e.g., they both repel oil and water). Industries in the United States have phased out production of PFOA and PFOS because of health risks to humans and have been using replacement PFAS, such as GenX. There is a substantial body of knowledge for managing risk from PFOS and PFOA, but much less knowledge about the replacement PFAS. The US EPA office of Ground Water and Drinking Water has developed a method specifically for the analysis of PFAS in drinking water, EPA 537, which is based on solid-phase extraction (SPE) followed by LC-MS/MS detection.[5] This methodology was developed for use during the EPA's Unregulated Contaminant Rule 3 (UCMR3) monitoring program.[6] Recently, an updated version of this method EPA 537.1 has been validated to include additional PFAS compounds such as GenX.[8] An alternative method developed for additional water matrices such as surface, ground, and waste waters is ASTM D7979,7 and is based on simple sample extraction and filtration followed by LC-MS/MS analysis. This application note describes a direct analysis method for the determination of a list of 24 PFAS in a wide variety of non-drinking water matrices. The data was used for the validation of a new method, EPA 8327, for a wide variety of water matrices as part of an interlaboratory study sponsored by the EPA Office of Water.

MATERIALS AND METHODS

This poster presentation describes the quantitation of selected PFAS in reagent, ground, surface, and waste water based on the recent EPA 8327 method. The list of PFAS included in this study is shown in Table 1.

Table 1. List of PFAS compounds included in this method.

Analytes	Abbreviation	CAS number	Surrogates
PFAS Sulfonic Acids			
Perfluorobutyl sulfonic acid	PFBS	29420-49-3	$^{13}C_3$-PFBS
Perfluorohexyl sulfonic acid	PFHxS	3871-99-6	$^{13}C_3$-PFxS
Perfluorooctyl sulfonic acid	PFOS	1763-23-1	$^{13}C_8$-PFOS
1H, 1H, 2H, 2H-perfluorohexane sulfonic acid	4:2 FTS	757124-72-4	$^{13}C_2$-4:2 FTS
1H, 1H, 2H, 2H-perfluorooctane sulfonic acid	6:2 FTS	27619-97-2	$^{13}C_2$-6:2 FTS
1H, 1H, 2H, 2H-perfluorodecane sulfonic acid	8:2 FTS	39108-34-4	$^{13}C_2$-8:2 FTS
Perfluoro-1-pentanesulfonic acid	PFPeS	706-91-4	-
Perfluoro-1-heptanesulfonic acid	PFHpS	375-92-8	-
Perfluoro-1-nonanesulfonic acid	PFNS	68259-12-1	-
Perfluoro-1-decanesulfonic acid	PFDS	2806-15-7	-
PFAS Carboxylic Acids			
Perfluorobutanoic acid	PFBA	375-22-4	$^{13}C_4$-PFBA
Perfluoropentanoic acid	PFPeA	2706-90-3	$^{13}C_5$-PFPeA
Perfluorohexanoic acid	PFHxA	307-24-4	$^{13}C_5$-PFHxA
Perfluoroheptanoic acid	PFHpA	375-85-9	$^{13}C_4$-PFHpA
Perfluorooctanoic acid	PFOA	335-67-1	$^{13}C_8$-PFOA
Perfluorononanoic acid	PFNA	375-95-1	$^{13}C_9$-PFNA
Perfluorodecanoic acid	PFDA	335-76-2	$^{13}C_6$-PFDA
Perfluoroundecanoic acid	PFUnA	2058-94-8	$^{13}C_7$-PFUnA
Perfluorododecanoic acid	PFDoA	307-55-1	$^{13}C_2$-PFDoA
Perfluorotridecanoic acid	PFTriA	72629-94-8	-
Perfluorotetradecanoic acid	PFTreA	376-06-7	$^{13}C_2$-PFTreA
PFAS sulfonamides and sulfonamidoacetic acids			
N-ethylperfluoro-1-octanesulfonamidoacetic acid	N-EtFOSAA	2991-50-6	D_5-N-EtFOSAA
N-methylperfluoro-1-octanesulfonamidoacetic acid	N-MeFOSAA	2355-31-9	D_3-N-MeFOSAA
Perfluoro-1-octanesulfonamide	PFOSA	754-91-6	$^{13}C_8$-PFOSA

LC-MS/MS analysis

Since the required limits of detection are in the low ng/L range, careful selection of reagents and consumables is necessary to ensure they are PFAS-free. The LC-MS/MS system comprised a Thermo Scientific™ Vanquish™ Flex Binary UHPLC system fitted with a Thermo Scientific™ PFC-free kit and interfaced with a Thermo Scientific™ TSQ Altis™ triple quadrupole mass spectrometer equipped with a HESI ionization probe. An isolator column was also installed after the LC pump and prior to the injection valve to offset background contaminants from the LC pump, autosampler, degasser, and mobile phases.

Data processing

Thermo Scientific™ Chromeleon™ Chromatography Data System software, version 7.2.9.

Test Method(s)

European method EN:1948 standard solutions; EN-1948CVS, WM48-CVS (calibration and quantitation), EN-1948ES, EN-1948IS, P48-W-ES, P48-M-ES, and P48-RS (extraction) were utilized for the extraction, calibration, and quantitation of PCDD/Fs, dioxin-like PCBs, and indicator PCBs. All standards were obtained from Wellington Laboratories Inc., Canada.

Data Analysis

Data were acquired using timed-SRM mode, processed and reported using Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, version 7.2, which allows instrument control, quantitative/qualitative analysis, and customizable.

Sample preparation

PFAS standard solutions

Target and surrogate PFAS standard mixtures in methanol at 2000 and 1000 µg/L, respectively, were purchased from Wellington Laboratories and kept away from PFAS packaging and material during storage. A stock solution of 24 target PFAS compounds was prepared in methanol at a concentration of 2 µg/L. Calibration solutions, with concentrations of 5–200 ng/L (ppt), were prepared by serial dilutions of the stock solution in 50:50 (v/v) methanol/water containing 0.1% acetic acid.

Non-drinking water matrices

Field water samples (5 mL) were provided by the US EPA Region 5 and included reagent water, surface water, ground water, and waste water through a participating EPA study. Each water sample was spiked with a low (60 ng/L) and high level (200 ng/L) of a selected target PFAS compounds (five replicates of each) prior to shipment to the lab. Five blank samples of each water matrix were also provided.

The 5 mL water samples were then spiked with 40 µL of a 20 µg/L isotopically labeled PFAS surrogates solution (Table 1). 5 mL of methanol were added and the mixture vortexed for 1 minute. The mixture was then filtered through a washed Acrodisc® GxF/0.2 µm GHP membrane syringe-driven filter with methanol and acetonitrile (Pall Corporation). The 10 mL filtrates were acidified by addition of 10 µL of acetic acid, and an aliquot of each sample was transferred to a polypropylene autosampler vial sealed with a polyethylene cap with integrated polyethylene membrane.

Control samples

The EPA 8237 method requires control samples (method blank, laboratory control, and reporting limit checking samples) to be run with field non-drinking water samples. Therefore, two method blanks were prepared by measuring 5 mL of water UHPLC-MS grade into 15 mL polypropylene Falcon™ tubes (BD Falcon) and spiking with 40 µL of a 20 µg/L PFAS surrogate solution in methanol. Two laboratory control samples were prepared by spiking 5 mL of water UHPLC-MS grade at 160 ng/L of 24 selected PFAS, and a reporting limit of quantitation checking sample was prepared by spiking 5 mL of water UHPLC-MS grade at 10 ng/L. Control samples were then taken through the sample preparation as field water samples.

RESULTS

Excellent chromatographic separation was achieved on an Accucore RP-MS analytical column using different mobile phases compositions. Figure 1 shows an overlaid chromatogram of all PFAS compounds analyzed in this method.

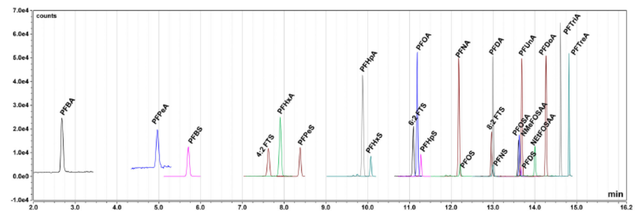

Figure 1. Overlaid chromatograms of all PFAS compounds included in this method.

Excellent linearity and quantitative accuracy were achieved over the range of 5 to 200 ng/L, with correlation coefficients greater than 0.99 for all transitions and the respective residuals within 20% of the nominal values. Representative calibration curves for PFOS and PFTriA are shown in Figure 2, with correlation coefficients of 0.9955 and 0.9950, respectively. Figure 2 also shows chromatograms of overlaid quantitation and confirming ions injected at 1 ng/L, which is five times lower than the LLOQ reported by ASTM D7979-17 for these two compounds. Additionally, Table 3 shows the LLOQs for all 24 PFAS analyzed in this method, based on accuracy and RSD ≤20%, demonstrating the high sensitivity achieved with the TSQ Altis mass spectrometer for the quantitation of PFAS at very low levels (ppt range).

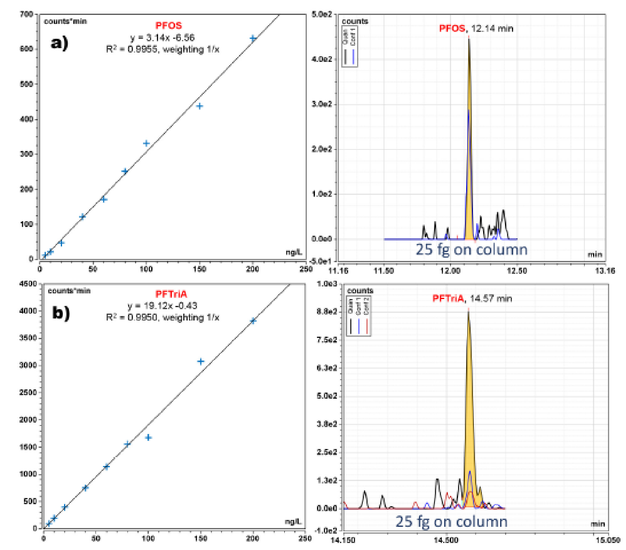

Figure 2. Representative calibration curves for a) PFOS and b) PFTriA, and chromatograms of an injection of 1 ng/L, which is five times lower than the reporting limit of quantitation.

Control samples

Table 4 summarizes the method 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 checking sample) and taken through sample preparation. PFBA and PFPeA are quantifiable at an injected concentration of 5 ng/L, which is much lower than the reported limit of quantitation in EPA 8327 and ASTM D7979 (25 ng/L without considering 2-fold dilution in methanol).

Sample analysis

Each water matrix was spiked at low and high concentrations as described, (N=5 ea.) The 60 samples received were divided into three batches of 20 samples and analyzed on three different days. All 24 PFAS compounds were detected and quantifiable at both low and high spike concentrations. Figure 4 shows an example of overlaid chromatograms of all PFAS spiked at 60 ng/L in reagent, ground, surface, and waste samples. In Figure 4 fronting was observed with the first eluting chromatographic peaks in ground, surface, and waste water samples due to the overload of the analytical column by large injection volumes (25 µL). Reduced injection volumes (15 µL) improved peak shape and will also improve robustness (due to less matrix on column) while still maintaining good sensitivity as shown in Figure 5.

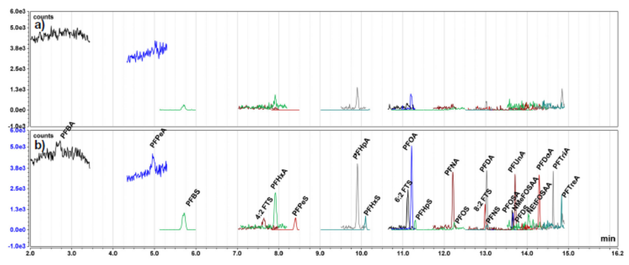

Figure 3. PFAS overlaid chromatograms: a) method blank sample and b) reporting limit checking sample spiked at 10 ng/L.

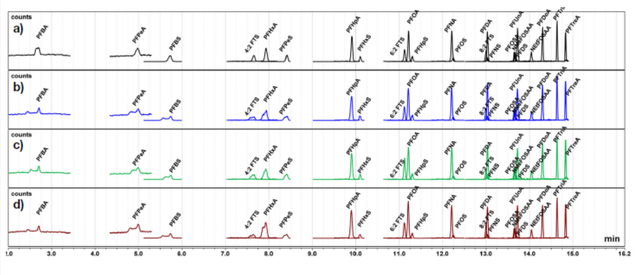

Figure 4. Overlaid chromatograms of 24 PFAS spiked at 60 ng/L in field samples: a) Reagent water; b) ground water; c) surface water; and d) waste water.

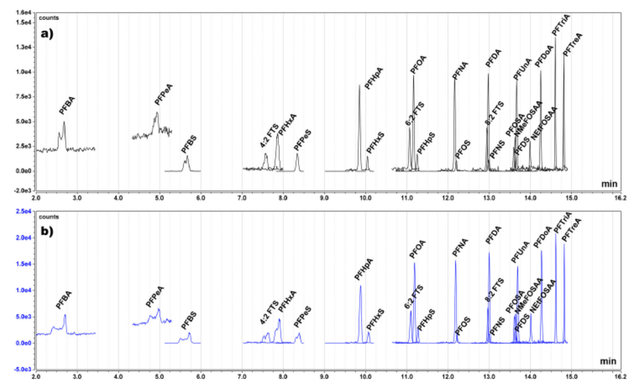

Figure 5. Overlaid chromatograms of a ground water sample spiked at 60 ng/L: a) 15 µL injection volume; b) 25µL injection volume.

CONCLUSIONS

The method referenced in this application note shows excellent quantitative performance of the TSQ Altis mass spectrometer for PFAS direct analysis in the low ng/L range in non-drinking water matrices.

- 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 five times 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 within the range required.
- All spiked water samples, in a variety of matrices, showed RSDs below 20% for most of the PFAS compounds, demonstrating the high robustness and reproducibility of the method.

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