Poly- and Perfluoroalkyl Substances (PFAS) in Water Samples by Liquid Chromatography/Tandem Mass Spectrometry

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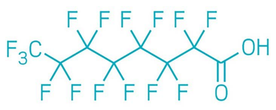
Introduction

Poly- and perfluoroalkyl substances, also known as PFAS compounds, are found in numerous components, but are most commonly found in non-stick and waterproof items that are used in everyday life, including Teflon. Even items like the inside of microwave popcorn bags, fast food wrappers, and aqueous fire-fighting foams (AFFF) contain PFAS compounds.

While these compounds are not acutely toxic, PFAS are known to be bioaccumulative, i.e. they collect in organ tissue over time and are potentially carcinogenic and contribute to other health issues. Because of the pervasiveness and stability of PFAS, these compounds are being detected in many areas of the environment, including water, sediment/soil, and in the tissues and organs of marine and terrestrial wildlife.

To test for the ubiquity of PFAS compounds in the environment, various types of water samples were collected from the Bryan/College Station area, including tap water, filtered tap water, collected rain water, and pond water and were analyzed by liquid chromatography/tandem mass spectrometry.



Perfluorooctanoic acid

The PFAS Challenge

PFAS' prevalence and stable nature are the very reasons these compounds are challenging for analytical chemists in all areas, from extraction to detection.

The most common way to detect PFAS is by liquid chromatography/triple quadrupole mass spectrometry (LC/MS/MS). In nearly all instances, LC solvent delivery systems contain Teflon components due to its inability to react with the solvents. This concern is addressed by installing a smaller LC column between the pump and the LC autosampler, delaying the elution of interfering compounds.

Chemically, PFAS are hydrophobic and contain a strong carbon-fluorine chain. They also maintain charged functional groups in the form of sulfonates, carboxylic acids, telomer sulfonates, and sulfonamides, with ever-growing variations to add to the PFAS family. Because of the strong nature of the carbon-fluorine bond, these compounds are nearly impossible to fragment using LC/MS/MS. Furthermore, the inability of these compounds to break down has contributed to their pervasiveness in the environment and status as carcinogens.

The unique nature of PFAS makes them difficult to extract from complex matrices such as soil and tissue. In some cases, because of their charged functional group, an ion-pairing agent is used to form an ion pair that will more easily partition into an organic phase.

The analytical chemist performing these tasks must understand that these compounds can be associated with laboratory implements, such as aluminum foil, traditional homogenizers and blenders, and solvent bottles. For best results, a method that intentionally uses polypropylene implements that have not been washed with detergent should be developed.

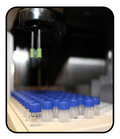
Materials and Extraction

Sample Preparation-100 mL

- Sample salination
- Sodium thiosulfate ($Na_2S_2O_3$)(to remove free chlorine)

Solid Phase Extraction (SPE)

- HLB SPE Cartridges
- Collect 2 Elution Fractions, Methanol (1), Methanol/*tert*-Butyl methyl ether (2)
- Dry to a residue using N_2 and a heated water bath



Resuspension for Analysis

- Blend of water, methanol, and external standard M9PFNA
- Stored in a polypropylene vial

Solid Phase Extraction

Solid Phase Extraction (SPE) uses a solid sorbent to separate matrix components from the target analytes. The benefits of SPE include:

- Cleaner extracts
- Lower detection limits with less sample
- Less solvent waste
- Use of analyte and matrix chemistries to maximize recoveries

PFAS in water are extracted using an HLB (hydrophilic-lipophilic balance) sorbent, a water-wettable, hydrophilic, reversed-phase copolymer ideal for the variety of chemistries found in the PFAS family.

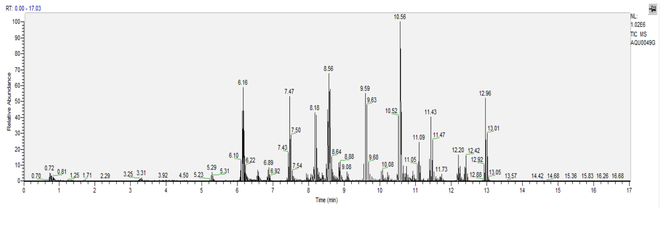
Analysis by LC/MS/MS

The calibration curves for each analyte have a range of 5 ng/L to 250 ng/L and calibration curve samples are prepared and extracted in the same manner as the samples and alongside quality control samples that include spikes, second source standards, and standard reference materials. All calibration curves are linear.

The method detection limits (MDLs) for this analysis range from 0.18-1.9 ng/L and were calculated using multiple spiked and extracted negative control matrix samples. A brief outline of instrument method parameters can be found in Table 1.

Table 1. Parameters for the PFAS instrument method, for LC and MS/MS features.

LC	MS/MS
Mobile Phases: ~5 mM Ammonium Acetate in water (A) and methanol (B)	Ionization Mode: HESI-
Flow Rate: 0.7 mL/min	Collision energy (CE): compound-specific
Injection volume: 15 µL	Segmented SRM
Gradient Start: 85%A/15%B	Peak Resolution: 0.7 FWHM



Target Analytes

- There are 27 PFAS compounds, 12 isotopically-labeled internal standards, and 1 external standard included in this analysis.

Quantitative Analysis

- Analytes were quantitated using analyte/internal standard peak area ratios to correct for extraction deficiencies and matrix interferences.

Qualitative Analysis

- Analytes are identified based on their retention time and transition ions, where applicable (some do not fragment).

Results

The results from this study are summarized in Figures 1 and 2 for natural and potable water sources, respectively.

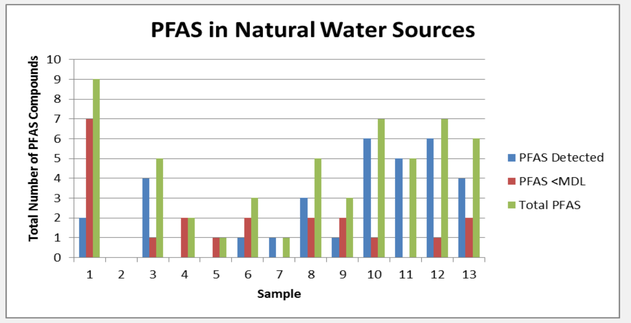


Figure 1. Total PFAS compounds for natural water sources, which include ponds, rain water, storm drain runoff, and pooled water.

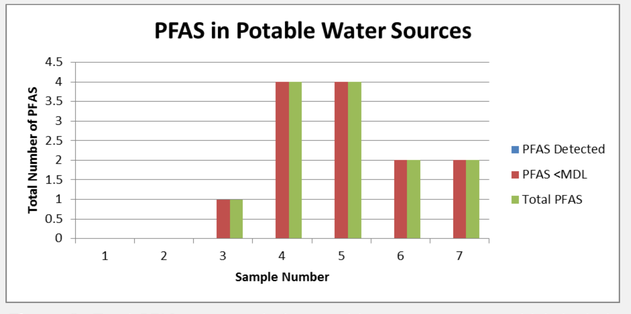


Figure 2. Total PFAS compounds for potable water sources, which include tap water and filtered tap water.

Conclusion

PFAS were detected in 85% of samples, showing the pervasiveness of these chemicals in our environment. Solid phase extraction provided cleaner extracts for trace-level PFAS analysis in all types of water samples.

References

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