Perfluoroalkyl Substances (PFAS) Analysis in Drinking Water, Sediments, and Food Samples by QuEChERS, SPE, and LC-MS/MS

Syljohn Estil[1], Agustin Pierri, PhD[2], Ramkumar Dhandapani, PhD[3]

[1]Sanitation Districts of Los Angeles County-San Jose Creek Water Quality Laboratory, 2965 S. Workman Mill Road, Whittier, CA 90601 USA, [2]Weck Laboratories, 14859 Clark, Ave., Hacienda Heights, CA 91745 USA, [3]Phenomenex, Inc., 411 Madrid Ave., Torrance, CA 90501, USA

Introduction

Perfluoroalkyl substances (PFAS) are a class of highly stable synthetic organic compounds used in a wide variety of industrial and commercial applications including surface treatment for textiles, packaging materials, non-stick cookware, and fire fighting foams. PFAS are characterized by a hydrophobic fully fluorinated alkyl chain and a hydrophilic functional group. They are persistent in the environment due to the exceptional stability of the C-F bond. These have been detected throughout the global environment, food products, and even human plasma. PFAS are associated with various adverse health effects, they are bio-accumulative, ubiquitous, and their analysis level requirements are very low to account for an expected lifetime of exposure. There are several methods available for the extraction and analysis of PFAS in aqueous samples. However, very few procedures are available for extracting these compounds in solid matrices such as sediments and food samples.

Presented here are three methods making use of various sample preparation techniques for the analysis of PFAS. The methods include direct inject technique for dinking water, QuEChERS for sediment samples, and QuEChERS followed by SPE for food samples (milk, eggs, and fish tissue). All are validated procedures and make use of LC-MS/MS.

Water Samples

UHPLC-MS/MS Conditions

Column: Luna™ Omega 1.6 µm PS C18
Dimensions: 50 x 2.1 mm
Part No.: 00B-4752-AN
Mobile Phase: A: 5 mM Ammonium Acetate in Water
B: Acetonitrile

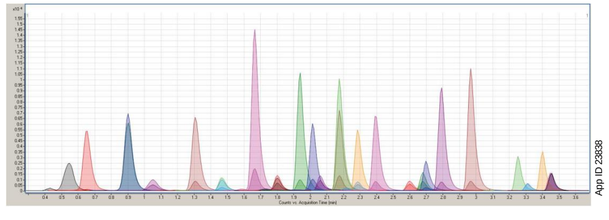
Gradient:

Time (min)	%B
0	40
0.5	40
3	90
3.1	100
4	100

Flow Rate: 0.55 mL/min
Injection: 5 µL
Temperature: 40 °C
System: Agilent® 1290
Detector: Agilent 6460 QQQ
Analytes:

1. 6:2 FTS
2. 8:2 FTS
3. EtFOSA
4. EtFOSE
5. FOSA
6. MeFOSA
7. MeFOSE
8. PFBA
9. PFBS
10. PFDA
11. PFDoA
12. PFDS
13. PFHpA
14. PFHpS
15. PFHxA
16. PFHxS
17. PFNA
18. PFOA
19. PFOS
20. PFPeA
21. PFTeDA
22. PFTrDA
23. PFUdA

Figure 1. Representative Chromatogram of PFAS in Water Samples.



The above application presents a method for the rapid analysis and quantitation of PFAS in water samples by UHPLC-MS/MS using the Luna Omega 1.6 µm PS C18 column. The high resolution and unique mixed-mode selectivity of the Luna Omega 1.6 µm PS C18 column results in excellent chromatography and peak shapes for PFAS in a very short four-minute run with solid retention and peak shape for PFBA and resolution of branched isomers.

Sediment Samples

QuEChERS Extraction Protocol

Step	Description
1	Weigh 2.0 g of dried sediment into a polypropylene container.
2	Add 10 mL deionized water and vortex. Add 10 mL acidified Acetonitrile (1 % Acetic Acid) to the slurry and vortex.
3	Add the extraction salts (1.5 g Sodium Acetate and 2 g Magnesium Sulfate) or add 3.5 g of roQ™ QuEChERS AOAC 2007.01 extraction packet (Part No.: AH0-9043) to the sample and vortex for 1 minute.
4	Centrifuge the samples for 5 minutes at 4000 rpm.
5	Place the samples in a rack and freeze at -20 °C for 30-60 minutes. This freezing step allows for easier extraction of the supernatant.
6	Transfer 8-9 mL of the Acetonitrile supernatant into a roQ QuEChERS PSA/C18 dSPE clean-up tube (Part No.: KS0-8926) and vortex for one minute.
7	Centrifuge the dSPE tubes for 10 minutes at 3000 rpm.
8	Place an aliquot of the extract in an HPLC vial and dilute 1:1 with deionized water. The sample is now ready for analysis.

HPLC-MS/MS Conditions

Column: Gemini™ 3 µm C18
Dimensions: 100 x 3 mm
Part No.: 00D-4439-Y0
Inline Filter: KrudKatcher™ Ultra
Delay Column: Luna™ 5 µm C18(2)
Dimensions: 30 x 2.0 mm
Part No.: 00A-4252-B0
Mobile Phase: A: 20 mM Ammonium Acetate in Water
B: Methanol

Gradient:

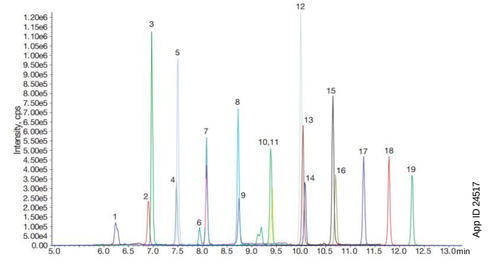
Time (min)	%B
0.00	10
1.50	65
8.00	95
8.10	99
12.0	99
12.5	10

Flow Rate: 0.6 mL/min
Injection: 90 µL
Temperature: 40 °C
Detector: SCIEX® 5500 QTRAP®
Detector: MS/MS ESI Negative (sMRM)

Analytes:

1. PFBA
2. PFPeA
3. PFBS
4. PFHxA
5. PFPS
6. PFHxS
7. PFHpA
8. PFHpS
9. PFOA
10. PFOS
11. PFNA
12. PFOSA
13. PFNS
14. PFDA
15. PFDS
16. PFUdA
17. PFDoA
18. PFTrDA
19. PFTeDA

Figure 2. Extracted Ion Chromatogram of Sediments Spiked with 1.0 ng/g of the Target Analytes.



The above sediment extraction makes use of a modified QuEChERS method and is a fast, effective, and efficient way of extracting 19 PFAS from marine and river sediment matrices. The procedure significantly minimizes sample preparation time, solvent consumption, and overall cost of analysis. Executing a QuEChERS-like extraction and exploiting available kitted QuEChERS salts and dSPE products, effective, and accurate extraction of PFAS from solid and oily sediments enabled analysis down to low ng/g range.

Food Samples (Dairy and Fish)

Sample Preparation

Step	Description
roQ Extraction Kit (Part No.: KS0-8910)	
1	Take 1 g homogenized sample and add into 50 mL centrifuge tube.
2	Add 10 mL acetonitrile and 10 mL Water.
3	Add salts in salt packets (4 g Magnesium Sulfate and 1 g Sodium Chloride). ***CAUTION:*** Exothermic Reaction. ***NOTE:*** Salt pack will clump (vortexing is not violent enough to break up clumps), specifically shake the sample violently until homogenous and then vortex for 30 sec.
4	Centrifuge until there is distinct separation between Acetonitrile, Water and solids layers.
5	Transfer 200 µL to autosampler vial for LC-MS/MS analysis, or remove 1 mL clean Acetonitrile and proceed to dSPE Protocol.
roQ QuEChERS dSPE Kit (part No.: KS0-8920)	
7	Transfer 1 mL of Acetonitrile and add to dSPE kit tube (150 mg Magnesium Sulfate and 50 mg Primary/Secondary Amine).
8	Vortex for 30 seconds and centrifuge.
9	Remove 1 mL clean Acetonitrile and analyze or proceed to SPE Protocol.
SPE using Strata™-X-AW 200 mg / 3 mL (Part No.: 8B-S038-FBJ)	
10	**Condition:** 3 washes of 2 mL 0.3 % Ammonium Hydroxide / Acetonitrile.
11	**Equilibrate:** 3 mL Water.
12	**Load:** About 15 mL of diluted QuEChERS extract.
13	**Wash:** 5 mL Water.
14	**Elute:** 4 mL 0.3 % Ammonium Hydroxide / Acetonitrile.
15	**Dry:** Evaporate to near dryness and reconstitute to 500 µL.
16	Transfer to autosampler vial and LC-MS/MS analysis.

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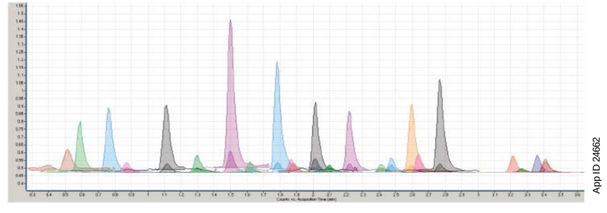
15. MeFOSA
16. PFDA
17. EtFOSE
18. EtFOSA
19. PFDS
20. PFUdA
21. PFDoA
22. PFTrDA
23. PFTeDA

Figure 3. Representative Chromatogram of a 0.05 ppb LLOQ.



The demand for PFAS analysis is not limited only to environmental samples, but also at low levels in food matrices for human consumption. Developed here is a fast and sensitive LC-MS/MS method to meet PFAS analysis needs in diverse food samples, including dairy and fish, down to low ppb levels. The use of the traditional QuEChERS technique enabled 1 ng/g sensitivities, and an additional (optional) solid phase extraction can help bring this down to 0.1 ng/g and ensure the optimum effectiveness of LC-MS/MS analysis.

Conclusion

Even with decreased use of PFAS on commercial products, PFAS contamination will persist throughout the environment doe to their bio-accumulative properties. This, demand for PFAS analysis is increasing and is not limited only to environmental samples such as water and soil. They are also in demand for low level testing in food matrices for human consumption and supply chain characterization. Presented here are three fast and sensitive LC-MS/MS methods developed to meet PFAS analysis needs in diverse sample matrices including water, sediments, and dairy and fish down to low ppb levels. The use of the QuEChERS technique along with further clean-up using SPE is an effective extraction and clean-up procedure to ensure the optimum effectiveness of LC-MS/MS analysis that may be adapted for most laboratory and workflow needs.

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