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Determination of Perfluoroalkyl Substances (PFAS) in Sediments by QuEChERS Extraction and HPLC-MS/MS

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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, and non-stick cookware. 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. Once released in the aquatic environment, these chemicals will partition between the water phase and the sediment. To better understand the fate and transport of these compounds, it is important to measure both the solid and liquid environmental fractions.

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. Typical methods used are mechanical shaker and ultrasonic-assisted Solid-Liquid Extractions (SLE)[6,7,8]. The extracts are then subjected to additional cleanup steps, usually by solid phase extraction. These are generally solvent-intensive and time-consuming processes. In 2003, an extraction procedure called QuEChERS (Quick-Easy-Cheap-Effective-Rugged-and-Safe) was introduced. It was originally developed to extract pesticide residues in food matrices but has since found applications in the field of environmental analytical chemistry.

Our laboratory (LACSD) previously developed and validated a QuEChERS sediment extraction procedure for emerging contaminants including: pharmaceutical and personal care products, steroids, alkylphenol ethoxylates, and pyrethroid pesticides[2,3,4]. We have successfully applied the same extraction method to determine perfluoroalkyl substances in marine and freshwater sediments.

Materials and Methods

Reagents/Chemicals

- QuEChERS Extraction – In a 50 mL plastic centrifuge tube combine 2.0 g of Anhydrous Magnesium Sulfate, and1.5 g Sodium Acetate or use approximately 3.5 g of AOAC2007.01 roQ™ extraction packet (part no. AH0-9043)
- QuEChERS dSPE Clean-Up — roQ 15 mL dSPE Kit (part no. KS0-8926)

Sample Preparation

QuEChERS Extraction Protocol

1. Weigh 2.0 g of dried sediment into a polypropylene container and spike with isotopically-labeled internal standards. *PPCPs, Steroids, and Pyrethroids can be extracted concurrently with this method by adding the appropriate internal standard and spiking solutions to the samples and QCs [2,3,4].*
2. Add 10 mL deionized water and vortex. Add 10 mL acidified aceto trile (1 % acetic acid) to the slurry and vortex.
3. Add the extraction salts (1.5 g Sodium Acetate and 2 g $MgSO_4$) 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 -20º 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 a 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:	Phenomenex Krudkatcher™ Ultra
Delay Column:	Luna® 5 µm C18 (2) 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
0.0	10
1.5	65
8.0	95
8.1	99
12.0	99
12.5	10

Injection:	90 µl
Flow Rate:	0.6 mL/min
Temperature:	40 °C
Detector:	SCIEX 5500 QTRAP®
Detection:	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

Mass Spectrometer Parameters

Table 1.
MRM Transitions and Compound Dependent Parameters

Compound Name	Q1	Q3	DP	CE
Perfluorobutanoic acid (PFBA)	213	169	-71	-14
Perfluoropentanoic acid (PFPeA)	263	219	-71	-12
Perfluorohexanoic acid (PFHxA)	313	269	-60	-14
Perfluoroheptanoic acid (PFHpA)	363	319	-62	-15
Perfluoroctanoic acid (PFOA)	413	369	-91	-12
Perfluorononanoic acid (PFNA)	463	419	-79	-15
Perfluorodecanoic acid (PFDA)	513	469	-83	-17
Perfluoroundecanoic acid (PFUdA)	563	519	-60	-17
Perfluorododecanoic acid (PFDoA)	613	569	-50	-21
Perfluorotridecanoic acid (PFTrDA)	663	619	-49	-18
Perfluorotetradecanoic acid (PFTeDA)	713	669	-63	-20
Perfluorobutanesulfonate (PFBS)	299	80	-94	-70
Perfluoropentantesulfonate (PFPeS)	349	80	-96	-66
Perfluorohexanesulfonate (PFHxS)	399	80	-92	-75
Perfluoroheptanesulfonate (PFHpS)	449	80	-75	-84
Perfluorooctanesulfonate (PFOS)	499	80	-78	-96
Perflluorooctanesulfonamide (PFOSA)	498	78	-60	-84
Perfluorononanesulfonate (PFNS)	549	80	-87	-100
Perfluorodecanesulfonate (PFDS)	599	80	-55	-100
Perfluoro-n-^{13}C4-butanoic acid (M4PFBA)	217	171.9	-71	-13
Perfluoro-n-^{13}C5-pentanoic acid (M5PFPeA)	268	222.7	-71	-12
Perfluoro-n-^{13}C5-hexanoic acid (M5PFHxA)	318	272.9	-60	-13
Perfluoro-n-^{13}C4-heptanoic acid (M4PFHpA)	367	321.8	-62	-14
Perfluoro-n-^{13}C8-octanoic acid (M8PFOA)	421	376	-91	-12
Perfluoro-n-^{13}C9-nonanoic acid (M9PFNA)	472	427	-79	-17
Perfluoro-n-^{13}C6-decanoic acid (M6PFDA)	519	474	-83	-21
Perfluoro-n-^{13}C7-undecanoic acid (M7PFUdA)	570	525	-60	-17
Perfluoro-n-^{13}C2-dodecanoic acid (M2PFDoA)	615	570	-50	-24
Perfluor-n-^{13}C2-tetradecanoic acid (M2PFTeDA)	715	670	-63	-25
Perfluro-^{13}C3-butanesulfonate (M3PFBS)	302	80	-94	-55
Perfluoro-^{13}C3-hexanesulfonate (M3PFHxS)	402	80	-92	-85
Perfluoro-^{13}C8-octanesulfonate (M8PFOS)	507	80	-78	-100

Note: DP = Declustering Potential
CE = Collision Energy

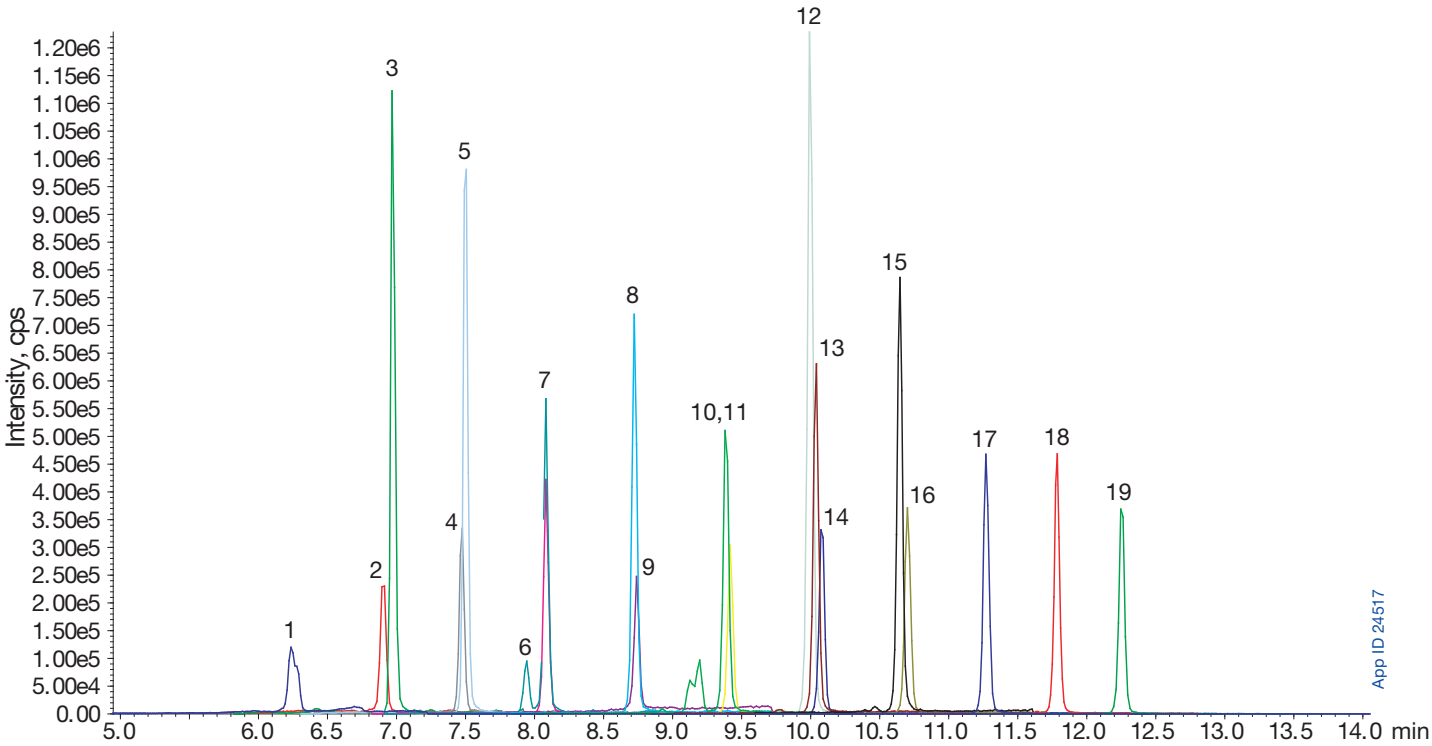
Table 2.
MS Source Parameters

Source Parameters	Settings
Temperature	400 °C
Gas 1	50
Gas 2	50
Curtain Gas	35
Ionization Energies	-4500 V
Collision Gas	High

Table 3.
Method Performance Data for Sediments Spiked at 1 ng/g of the Target Analytes (n=4)

Compound	Average % Recovery	% RSD
PFBA	91.7	0.76
PFPeA	86.3	6
PFHxA	89.4	1.2
PFHpA	93.1	2.9
PFOA	98.3	1.5
PFNA	93	1.6
PFDA	87.7	4.5
PFUdA	92.3	2.1
PFDoA	92.5	4.1
PFTrDA	88.2	2.1
PFTeDA	87.6	2.1
PFBS	86.3	2.1
PFPeS	96.2	3.2
PFHxS	81.3	5
PFHpS	92.3	2.6
PFOS	92.1	2.6
PFOSA	104.5	6.3
PFNS	89.8	6.8
PFDS	87.3	6.7

Figure 1
Extracted ion chromatogram of sediments spiked with 1.0 ng/g of the target analytes



Results and Discussion

QuEChERS is a vortex-assisted solid-liquid extraction procedure that uses acetonitrile, salts, and buffering agents for extraction, phase-separation, and pH adjustment respectively. Extracts are subsequently transferred to a dispersive solid phase extraction (dSPE) tube containing a drying agent ($MgSO_4$) and SPE sorbents such as C18 or PSA for sample cleanup.

The modified QuEChERS method presented here is a simple, efficient, and cost-effective method for determining PFAS levels in sediments. Accuracy and precision were assessed using four replicates of sediments spiked with the target analytes. Average % recoveries are all within the 80-120 % range and % RSDs for all analytes are below 10 % (**Table 3**). Reporting limits were set at 0.05 ng/g dry weight based on a 2.0 g initial sample weight.

Conclusion

The sediment extraction using the modified QuEChERS method is a fast, effective, and efficient way of extracting 19 perfluoroalkyl substances from marine and river sediment matrices. The procedure significantly minimizes sample preparation time, solvent consumption, and overall cost of analysis. Only minor modifications were made to the well-established QuEChERS method to accommodate the target analytes. Excellent extraction recoveries and precision were achieved and method reporting limits are in the low ng/g range.

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Ordering Information

Gemini® HPLC Columns Ordering Information

3 µm Microbore, Minibore and MidBore™ Columns (mm)										SecurityGuard™ Cartridges (mm)
Phases	50 x 1.0	20 x 2.0	30 x 2.0	50 x 2.0	100 x 2.0	150 x 2.0	50 x 3.0	100 x 3.0	150 x 3.0	4 x 2.0*
Gemini® C18	00B-4439-A0	00M-4439-B0	00A-4439-B0	00B-4439-B0	00D-4439-B0	00F-4439-B0	00B-4439-Y0	00D-4439-Y0	00F-4439-Y0	AJ0-7596

for ID: 2.0-3.0 mm

Luna® HPLC Columns Ordering Information

5 µm Microbore and Minibore Columns (mm)								SecurityGuard™ Cartridges (mm)
Phases	50 x 1.0	150 x 1.0	250 x 1.0	30 x 2.0	50 x 2.0	150 x 2.0	250 x 2.0	4 x 2.0*
Luna® C18(2)	00B-4252-A0	00F-4252-A0	00G-4252-A0	00A-4252-B0	00B-4252-B0	00F-4252-B0	00G-4252-B0	AJ0-4286

for ID: 2.0-3.0 mm

PFAS CRM Native Standards

All analytes at the same concentration in acid form for easy calculation and dilution.

Product	PN	Qty.	Conc.
EPA 533 mix	AL0-101838	1 mL	2 µg / mL in methanol
EPA 537.1 mix	AL0-101839	1 mL	2 µg / mL in methanol
EPA 533 + 537.1 mix	AL0-101840	1 mL	2 µg / mL in methanol

More PFAS Products for Your PFAS Methods

Description	Part No.
Luna™ Omega Column 3 µm PS C18 50 x 3 mm	00B-4758-Y0
Kinetex™ EVO Column 5 µm C18 100 x 2.1 mm	00D-4633- AN
Strata™ PFAS (WAX/GCB) SPE 200 mg, /50 mg, /6 mL tubes, 30/pk	CS0-9207
Strata SDB-L SPE 500 mg/6 mL tubes, 30/pk	8B-S014-HCH
Verex™ Vial, 9 mm Screw, PP, 1.7 mL, 1000/pk	AR0-39P0-13
Verex Vial, 9 mm Screw, PP, 300 µL, 1000/pk	AR0-39P2-13
Verex Vial, 9 mm Screw, PP, 700 µL, 1000/pk	AR0-39P1-13
Vial Cap Verex™ Cert+ Cap (one-piece), 9 mm, PE w/ Starburst pre-Slit, 2 mL, 1000/pk	AR0-89P6-13-C

roQ dSPE Kits

dSPE Kits contain pre-weighed sorbents/salts inside 2 mL or 15 mL centrifuge tubes

Description	Unit	Part No.
2 mL dSPE Kits		
150 mg $MgSO_4$, 25 mg PSA, 25 mg C18-E	100/pk	KS0-8913
150 mg $MgSO_4$, 25 mg PSA, 2.5 mg GCB	100/pk	KS0-8914
150 mg, $MgSO_4$, 25 mg PSA, 7.5 mg GCB	100/pk	KS0-8915
150 mg $MgSO_4$, 25 mg PSA	100/pk	KS0-8916
150 mg $MgSO_4$, 50 mg PSA, 50 mg C18-E, 50 mg GCB	100/pk	KS0-8917
150 mg $MgSO_4$, 50 mg PSA, 50 mg C18-E	100/pk	KS0-8918
150 mg $MgSO_4$, 50 mg PSA, 50 mg GCB	100/pk	KS0-8919
150 mg $MgSO_4$, 50 mg PSA	100/pk	KS0-8920
15 mL dSPE Kits		
900 mg $MgSO_4$, 150 mg PSA, 150 mg C18-E	50/pk	KS0-8921
900 mg $MgSO_4$, 150 mg PSA, 15 mg GCB	50/pk	KS0-8922
900 mg $MgSO_4$, 150 mg PSA, 45 mg GCB	50/pk	KS0-8923
900 mg $MgSO_4$, 150 mg PSA	50/pk	KS0-8924
1200 mg $MgSO_4$, 400 mg PSA, 400 mg C18-E, 400 mg GCB	50/pk	KS0-8925
1200 mg $MgSO_4$, 400 mg PSA, 400 mg C18-E	50/pk	KS0-8926
1200 mg $MgSO_4$, 400 mg PSA, 400 mg GCB	50/pk	KS0-8927
1200 mg $MgSO_4$, 400 mg PSA	50/pk	KS0-8928

roQ™ Extraction Kits

Extraction Kits contain fifty easy-pour salt packets and fifty 50 mL stand-alone centrifuge tubes

Description	Unit	Part No.
EN 15662 Method Extraction Kits		
4.0 g $MgSO_4$, 1.0 g NaCl, 1.0 g SCTD, 0.5 g SCDS	50/pk	KS0-8909*
AOAC 2007.01 Method Extraction Kits		
6.0 g $MgSO_4$, 1.5 g NaOAc	50/pk	KS0-8911*
Original Non-Buffered Method Extraction Kits		
4.0 g $MgSO_4$, 1.0 g NaCl	50/pk	KS0-8910
6.0 g $MgSO_4$, 1.5 g NaCl	50/pk	KS0-8912

*AOAC and EN Extraction Kits also available in traditional non-collared 50 mL centrifuge tubes, Part No.: KS0-8911-NC and KS0-8909-NC

Bulk roQ QuEChERS Sorbents

Phases	10 g	100 g
C18-E	–	04G-4348
GCB (Graphitized Carbon Black)	04D-4615	04G-4615
PSA	–	04G-4610

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