

Automated Low Background Solid Phase Extraction System for Perfluorinated Compounds from Water

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Fluid Management Systems



Perfluorinated Compounds

Name	Chemical formula	Acronym	CAS no. ^a
<i>Sulfonates</i>			
Perfluorobutane sulfonate	$\text{F}(\text{CF}_2)_4\text{SO}_3^-$	PFBS	375-73-5
Perfluorooctane sulfonate	$\text{F}(\text{CF}_2)_8\text{SO}_3^-$	PFOS	1763-23-1
<i>Carboxylates</i>			
Perfluorobutanoate	$\text{F}(\text{CF}_2)_3\text{CO}_2^-$	PFB	375-22-4
Perfluorooctanoate	$\text{F}(\text{CF}_2)_7\text{CO}_2^-$	PFO	335-67-1
Perfluorononanoate	$\text{F}(\text{CF}_2)_8\text{CO}_2^-$	PFN	375-95-1
Perfluoroundecanoate	$\text{F}(\text{CF}_2)_{10}\text{CO}_2^-$	PFUn	2058-94-8
<i>Alcohols</i>			
Perfluorohexyl ethanol	$\text{F}(\text{CF}_2)_6\text{CH}_2\text{CH}_2\text{OH}$	8-2 FTOH	678-39-7
Perfluorooctyl ethanol	$\text{F}(\text{CF}_2)_8\text{CH}_2\text{CH}_2\text{OH}$	6-2 FTOH	647-42-7
<i>Other</i>			
1H,1H,2H,2H-Perfluorooctane sulfonate	$\text{F}(\text{CF}_2)_6\text{CH}_2\text{CH}_2\text{SO}_3^-$	6-2 FTS	27619-97-2
Perfluorooctyl sulfonamide	$\text{F}(\text{CF}_2)_8\text{SO}_3\text{NH}_2$	PFOSA	754-91-6

^aFor acids, the CAS number is for the protonated form, e.g., $\text{F}(\text{CF}_2)_3\text{COOH}$ (=PFBA).

- $\text{F}(\text{CF}_2)_n\text{-R}$ $\text{F}(\text{CF}_2)_n\text{-(C}_2\text{H}_4\text{)-X}$
- $\text{R} = \text{SO}_3^-$ CO_2^- SO_3NH_2
- $\text{X} = \text{OH}$ SO_3^-



- Stain resistant coatings
- Leather and carpets
- Grease-proof coatings for food contact
- Firefighting foams
- Mining and oil well surfactants
- Floor polishes
- Insecticide formulations



Environmental concerns

- Perfluorooctane sulphonate (PFOS) and Perfluorooctanoic acid (PFOA) represent the final environmental degradation products.
- Increasing regulation in a number of countries.
- Adverse affects on organs, developing fetus.
- Extremely persistent and bioaccumulative.



Extraction Procedure

- 200 ml -500ml sample volume.
- Samples spiked with ^{13}C labeled surrogates
- Samples in polypropylene container, no Teflon liner



Lowering PFC Background



Extraction procedure

- Waters Oasis HLB plus 225 mg, 60 μm
- Condition 5 ml methanol, 10 ml DI
- Load 500 ml sample under -12 psi vacuum.
- N_2 dry cartridge for 20 min.
- Elute 2 ml methanol, soak 2 min, elute 2ml methanol into PP centrifuge tube.
- Purge fraction line with N_2

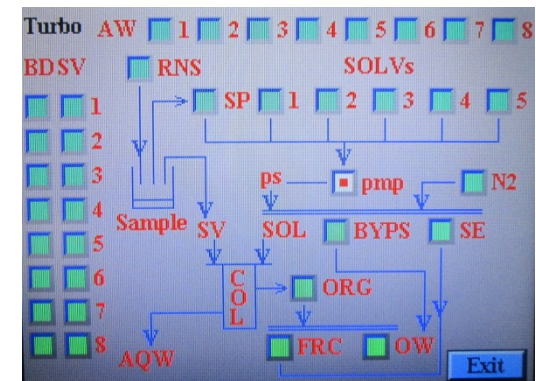


SuperVap Evaporation

- System pre-heated to 40 °C
- Samples evaporated at 40 °C under 10 PSI N₂.
- Evaporator tube walls rinsed with methanol as volume is reduced to ~1 ml.
- ~300 µl extract transferred to PP vial with Teflon-free septa.
- Volume to appropriate measure with IS solution.



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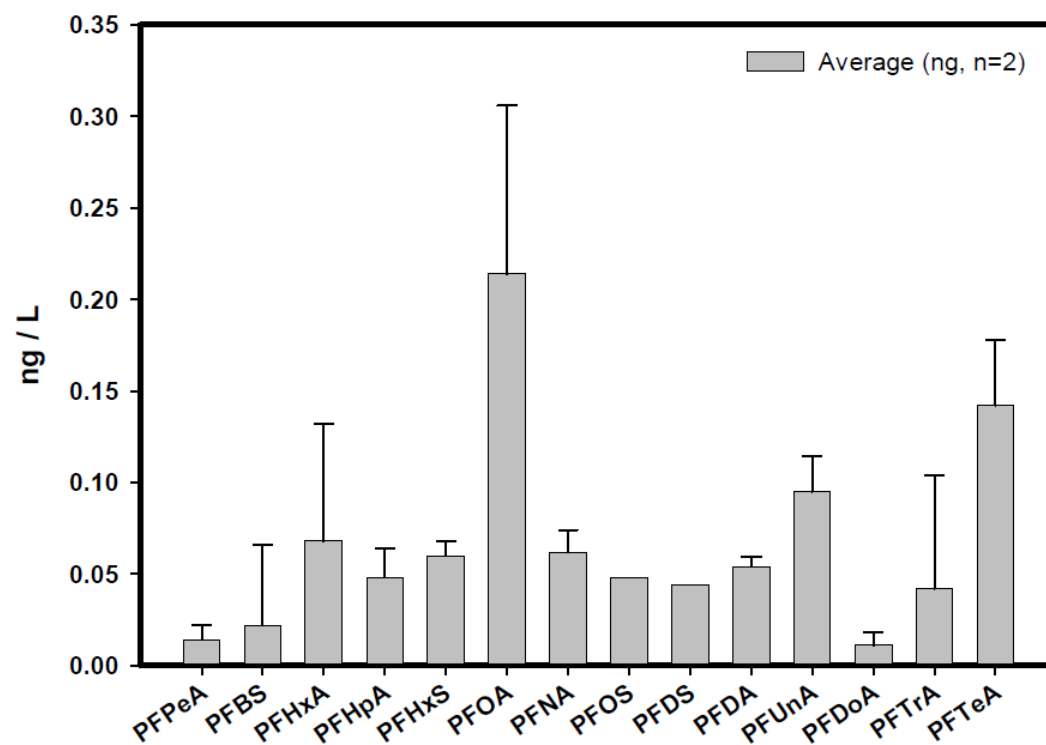


- Waters Acquity H-Class UPLC
- Waters Xevo TQD mass spectrometer
 - MRM



Blank study

Blank concentration 1 liter LCMS grade water



Transition Events

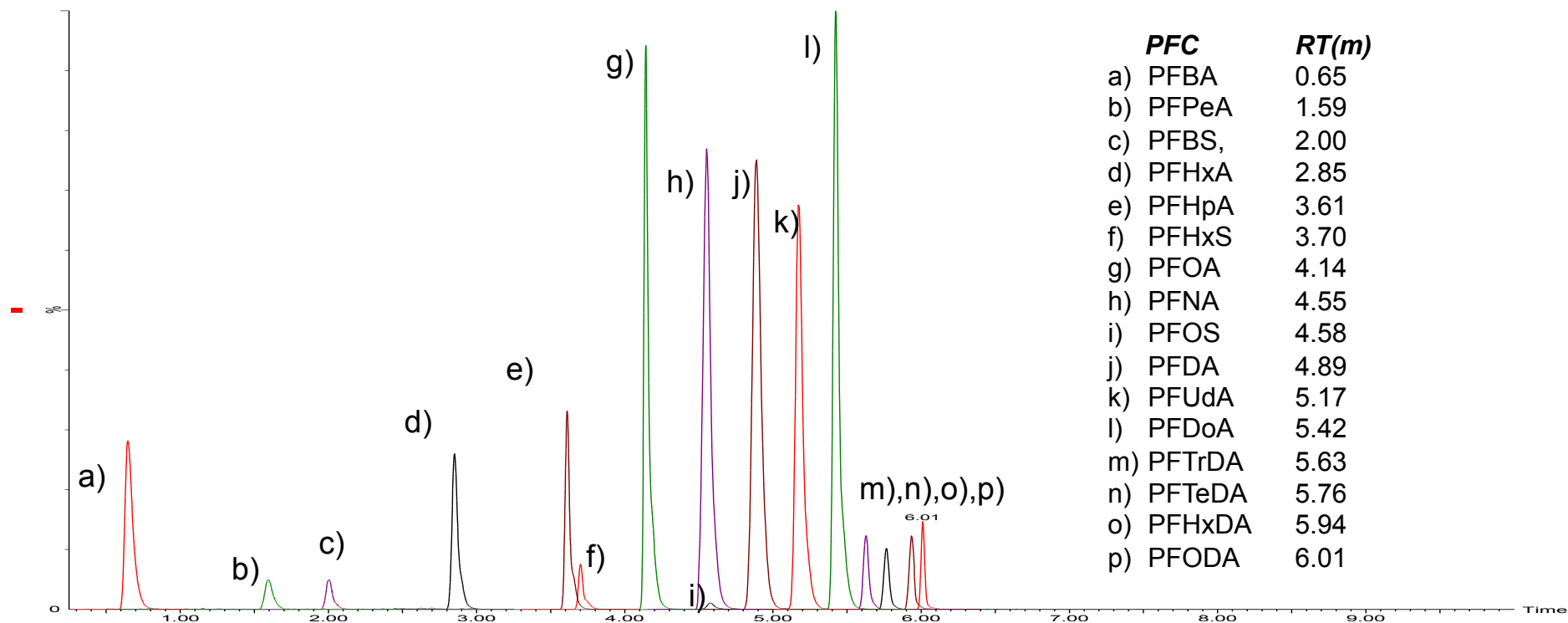
Compound	RT window	MRM	Cone (V)	Coll (eV)	Compound	RT window	MRM	Cone (V)	Coll (eV)
PFBA	0.25-1.05	212.93>168.91	17	8	PFOS	4.20-5.00	499.00>99.30	65	47
PFBA 12C4	0.25-1.05	217.05>172.32	17	8	PFOS 13C4	4.20-5.00	503.01>99.38	70	47
PFPeA	1.20-2.00	263.28>219.26	17	7	PFDA	4.50-5.30	512.93>468.92	21	11
PFBS	1.60-2.40	299.05>99.02	47	28	PFDA 13C2	4.50-5.30	515.05>470.13	19	11
PFHxA	2.45-3.25	312.93>268.93	19	8	PFuDA	4.80-5.60	563.29>519.30	11	21
PFHxA 13C2	2.45-3.25	315.08>270.50	19	8	PFuDA 13C2	4.80-5.60	565.04>520.10	18	11
PFHpA	3.50-4.00	362.93>318.89	17	8	PFDoA	5.05-5.95	613.2>569.22	21	11
PFHxS	3.30-4.10	399.05>99.02	57	37	PFDoA 13C2	5.05-5.95	615.05>570.13	18	11
PFHxS 18O2	3.30-4.10	403.04>103.59	56	39	PFTTrDA	5.50-6.30	663.02>619.25	21	11
PFOA	3.75-4.55	412.93>368.93	15	8	PFTeDA	5.35-6.15	713.05>669.20	21	15
PFOA 13C4	3.75-4.55	417.12>372.30	18	9	PFHxDA	5.6-6.4	813.14>769.10	21	15
PFNA	4.15-4.95	463.20>419.28	21	9	PFODA	5.6-6.4	913.01>869.30	19	16
PFNA 13C5	4.15-4.95	468.11>423.11	18	9					



Chromatography

25ngstd

Toxic Report Trace Analysis Laboratory



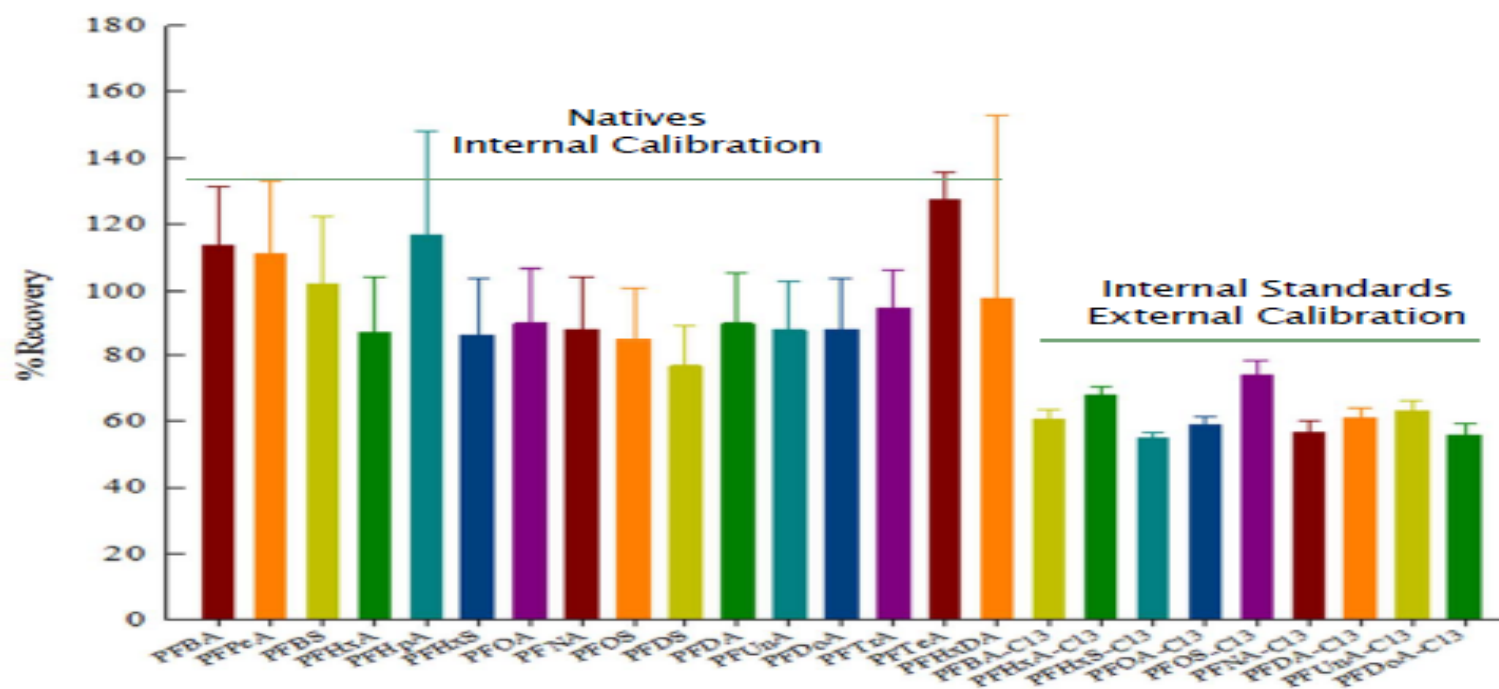
Analytical Results

Labeled Compound	Amount Spiked ng/L	Mean Percent Recovery	Background from FMS SPE
50 ng/l			
PFHxA 13C4		61%	0.068
PFHxS 18O2		77%	0.06
PFOA 13C4		88%	0.214
PFNA 13C5		74%	0.062
PFOS 13C4		72%	0.048
PFDA 13C2		84%	0.054
PFUdA 13C2		65%	
PFDoA 13C2		57%	0.011



Analytical Results

System PFC Recovery



Summary

- The FMS PFC SPE delivers sample extracts with extremely low PFC background.
- Set up and cleanup is easy and allows for unattended extraction.
- The Waters Acquity H-Class UPLC has predictable background PFC easily subtracted to give accurate results.



Flexibility and Customization

- Alternate extractions protocols.
- Weak anion exchange sorbent
- Alternate eluting solvents



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