Automated µSPE for the determination of PFAS compounds

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Introduction: Perfluoroalkyl substances (PFASs) are a group of synthetic fluorine containing chemicals that possess a number of highly desirable properties including low surface tensions and high stability. Since the introduction of PFASs in the late 1940s their widespread use has led to global dispersion and contamination. An increased understanding of the potential health and environmental impact of these chemicals has resulted in the creation of increasingly stringent regulations.[1] Current techniques for the analysis of PFASs use solid-phase extraction (SPE), a laborious and time intensive method of extraction, to prepare samples for analysis.[2] Micro-SPE (µSPE) has been developed with the potential to reduce both the time and labour required to analyse PFAS contaminated samples.

Experimental: PFAS standards were obtained from Wellington Laboratories (Ontario, Canada) and water samples provided by EnvrioLabs (Chatswood, Australia). Extractions were performed using the ePrep µXact[3] digital syringe driver, PFAS µSPEed® cartridges (Figure 1) and according to the workflow in Table 1. Chromatographic separations used a 50x2.1 mm, 1.6 µm Phenomonex Luna Omega C18 Column. Analyses were performed on a Shimadzu Nexera MP UHPLC coupled to a Shimadzu LCMS-8060 equipped with an electrospray ionisation source, operated in negative ion and multiple reaction monitoring (MRM) modes.

Table 1. µSPE extraction workflow.

	Volume (µL)	Reagent	Flow rate (µL/min)
Activation	250	Methanol	600
Equilibration	250	10 mM HCl	600
Load	2000	Sample, adjusted to pH 2	450
Wash	100	Ultra-pure water	600
Elute	100	10 mM NaOH in methanol	220
Dilution	Extract diluted to 200 µL with 10 mM HCl		

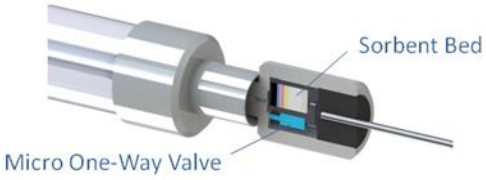

Figure 1. ePrep µSPEed cartridge.

Tandem mass spectrometry conditions and MRM transitions were automatically optimised using the Shimadzu LabSolutions software while electrospray voltages and temperatures (0.5 kV, 300 °C) were optimised using injections of a mixed standard. Low responses for the perfluoroalkyl carboxylates were observed at high interface temperatures and voltages due to increased fragmentation of the $[M - H]^-$ ion within the source (Figure 2 and Figure 3).

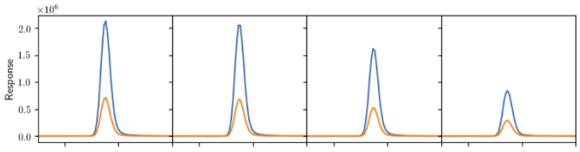

Figure 2. Response of PFOA ions at various interface temperatures. From the left: 250, 300, 350 and 400 °C.

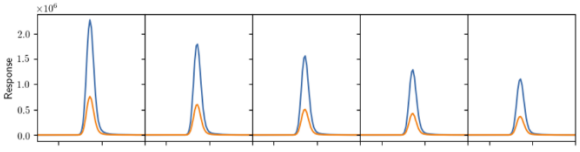

Figure 3. Response of PFOA ions at various interface voltages. From the left: 0.5, 0.8, 1, 2 and 3 kV.

Results & Discussion: The extraction method detailed in Table 1 was applied to a selection of five PFAS contaminated surface water samples. 2 mL aliquots of each sample were acidified to approximately pH 2 (to aid in the retention of short chain PFASs), spiked with 100 ng/L of the internal standard mix and extracted. The accuracy of the method was evaluated using spiked recoveries from the surface water samples.

A chromatographic separation of the 18 compounds was completed in just over 4 minutes. Instrumental limits of detection (LODs) ranged from 1 to 10 ng/L for all the compounds and when coupled with the ten times µSPE pre-concentration, far exceeded the lowest Australian guidance value for drinking water (70 ng/L PFOS).[1]

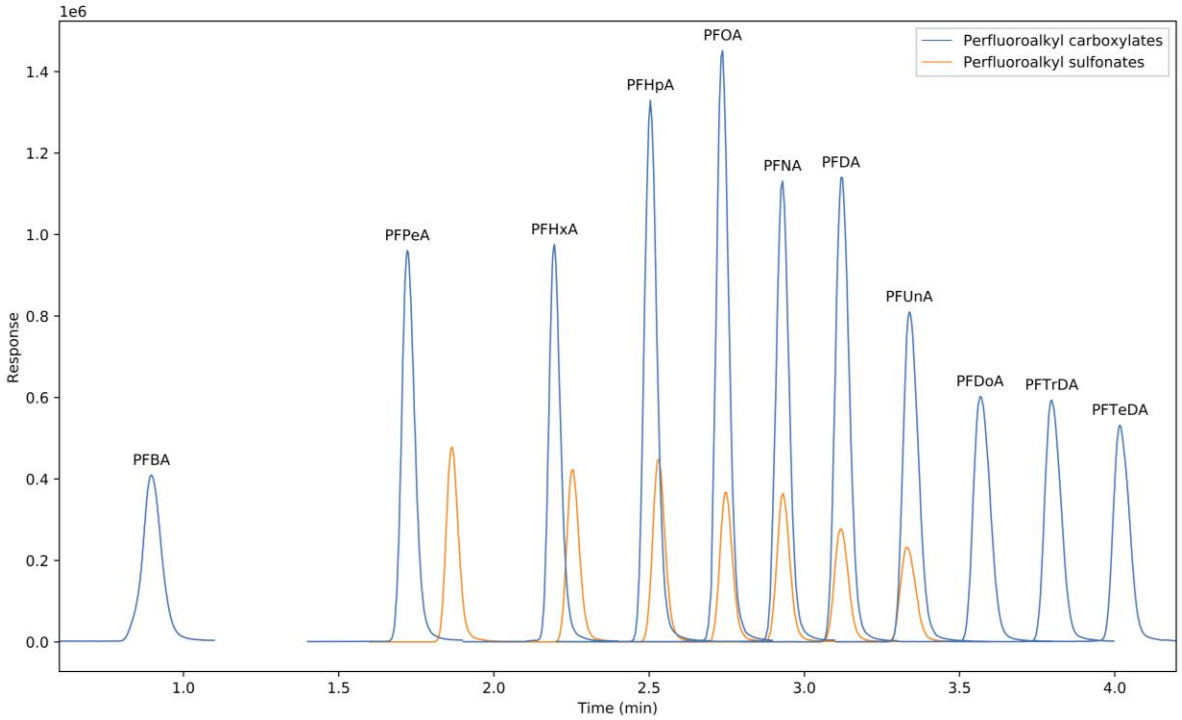

Figure 4. TIC of a calibration standard showing the separation of the 18 compounds.

Concentrations of the PFASs detected in the five samples ranged from below the LOD to approximately 3000 ng/L. Quantification was performed using the total area of all structural isomers detected in the samples (Figure 5). Spiked recoveries typically ranged from 90 to 110% with low %RSDs (Table 2).

Table 2. Percent recovery of the five spiked water samples.

	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	*PFTrDA	PFTeDA
% Recovery	103	94	98	104	93	106	91	99	104	75	65
% RSD	**9	9	13	4	2	8	15	15	4	44	27
	PFBS	***PFPeS**	**PFHxS**	***PFHpS**	**PFOS**	***PFNS**	***PFDS**				
% Recovery	103	117	107	83	105	72	74				
% RSD	2	6	**11	9	**7	6	17				

* No isotopically labelled internal standard available.
** N=4, as one sample above calibration range.

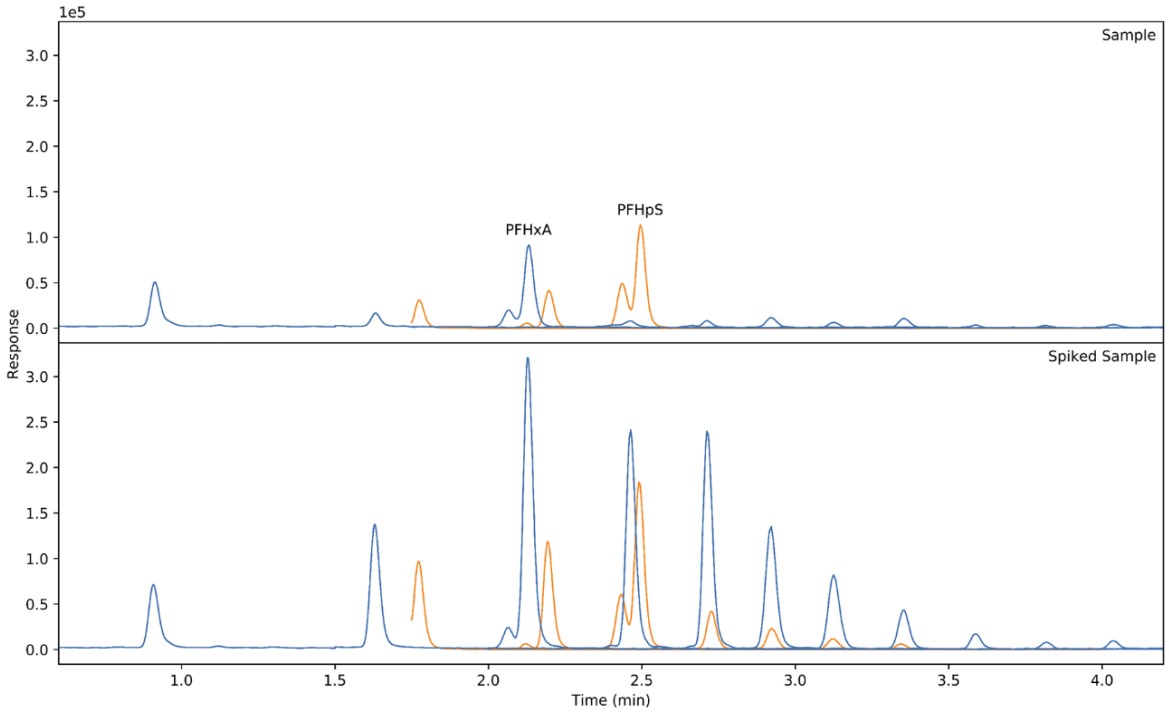

Figure 5. Comparison of a spiked (bottom) and un-spiked sample. Multiple peaks, representing multiple structural isomers, are seen for both PFHxA and PFHpS.

Conclusion: This study demonstrated the improvements of an automated µSPE method when compared against current extraction techniques. Required LODs were exceeded using only 2 mL of sample (250 mL required for EPA Method 5372[2]) and without the normal lengthy evaporation step. Samples required no additional clean-up or filtration, even for very turbid waters. Recoveries and repeatability were good for most compounds. These can be further improved by limiting the adsorption of long chain compounds to glass and metal surfaces.

Acknowledgements

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References

1) Perfluorinated chemicals in food; Food Standards Australia New Zealand, 2017.
2) Shoemaker, J. A.; Grimmett, P. E.; Boutin, B. K. METHOD 537. DETERMINATION OF SELECTED PER-FLUORINATED ALKYL ACIDS IN DRINKING WATER BY SOLID PHASE EXTRACTION AND LIQUID CHROMATOGRAPHY/TANDEM MASS SPECTROMETRY (LC/MS/MS); EPA 600/R-08/092; United States Environmental Protection Agency: Cincinnati, OH, 2009.