

Automated μ SPE for the determination of PFAS compounds

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Overview

In this study a novel micro solid-phase extraction method was developed for the analysis of perfluoroalkyl substances (PFAS) in contaminated environmental water samples. Rapid clean-up and pre-concentration of a range of PFASs (Table 1) was achieved with small sample size (i.e. 2 mL aliquots of contaminated surface water samples) and Limit of Detections (LODs) ranging from 1 to 10 ng/L by targeted tandem mass spectrometry. When compared with traditional extraction techniques the micro solid-phase extraction method is faster, requires smaller sample volumes and has greater potential for automation.

Introduction

Perfluoroalkyl substances (PFAS) are a family of synthetic fluorine containing chemicals that possess a number of highly desirable properties (e.g. oil and water repellency and temperature resistance), which are ideal for a range of industry products. 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 utilise solid-phase extraction (SPE), a laborious and time intensive method of extraction, to prepare samples for analysis.² Micro-SPE (Figure 1) has been developed with the potential to reduce both the time and labour required to analyse PFAS contaminated samples.

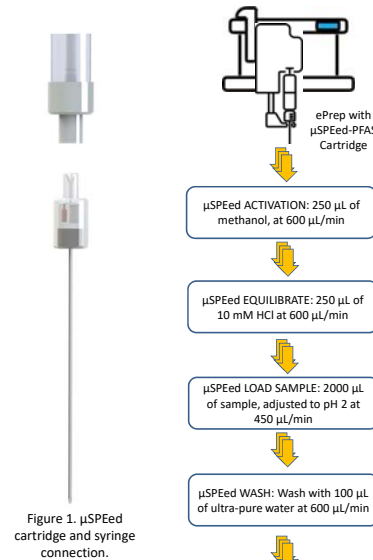


Figure 1. μ SPEd cartridge and syringe connection.

Methodology

- PFAS standards were obtained from Wellington Laboratories (Ontario, Canada) and water samples provided by EnviroLabs (Chatswood, NSW, Australia).
- Extractions were performed by the ePrep μ Xact³ Programmable Digital Syringe Driver (Figure 2) and PFAS μ SPEd[®] cartridges (Figure 3).
- Chromatography was on a 50 x 2.1 mm, 1.6 μ m Phenomenex Luna Omega C18 Column.
- Analyses were performed on a Shimadzu Nexera UHPLC coupled to a Shimadzu triple quadrupole LCMS-8060 equipped with an Electrospray ionisation (ESI) source, operated in negative ion mode and MRM (Multiple Reaction Monitoring mode).



Figure 2. ePrep Automated Sample Preparation Workstation (left) and μ Xact³ Programmable Digital Syringe Driver.

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MS/MS Method Development

Tandem mass spectrometry conditions and MRM (Table 1) transitions were automatically optimised by the Shimadzu LabSolutions software while electrospray voltages and temperatures (0.5 kV, 300 °C) were optimised manually by 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 (Figures 4, 5, 6).

Table 1. MS/MS transitions for the selected compounds.

Compound	Abbrev.	Parent Ion	Product Ion
Perfluorobutanoic acid	PFBA	213.05	169.00
Perfluoropentanoic acid	PFPeA	262.95	218.95
Perfluorohexanoic acid	PFHxA	312.95	268.90
Perfluoroheptanoic acid	PFHpA	362.95	319.00
Perfluorooctanoic acid	PFOA	412.95	369.00
Perfluorononanoic acid	PFNA	462.95	419.00
Perfluorodecanoic acid	PFDA	512.90	468.95
Perfluoroundecanoic acid	PFUnA	562.90	518.85
Perfluorododecanoic acid	PFDoA	612.90	568.95
Perfluorotridecanoic acid	PFTriDA	662.90	618.90
Perfluorotetradecanoic acid	PFTeDA	712.90	668.90
Perfluorobutane sulfonate	PFBS	298.90	80.00
Perfluoropentane sulfonate	PFPeS	348.90	80.00
Perfluorohexane sulfonate	PFHxS	399.00	80.00
Perfluoroheptane sulfonate	PFHpS	449.00	80.00
Perfluorooctane sulfonate	PFOS	499.00	80.00
Perfluorononane sulfonate	PFNS	549.00	80.00
Perfluorodecane sulfonate	PFDS	599.00	80.00

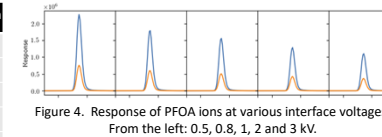


Figure 4. Response of PFOA ions at various interface voltages. From the left: 0.5, 0.8, 1, 2 and 3 kV.

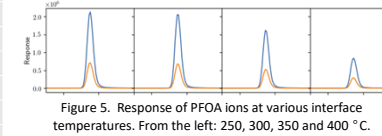


Figure 5. Response of PFOA ions at various interface temperatures. From the left: 250, 300, 350 and 400 °C.



Figure 6. Examples of the common fragmentation patterns seen for perfluoroalkyl carboxylates and sulfonates.

A chromatographic separation of the 18 compounds was completed in just over 4 minutes (Figure 7). Instrumental limits of detection (LODs) ranged from 1 to 10 ng/L for all the compounds and when coupled with the ten times micro-SPE pre-concentration, far exceed the lowest Australian guidance value for drinking water (70 ng/L PFOS).¹

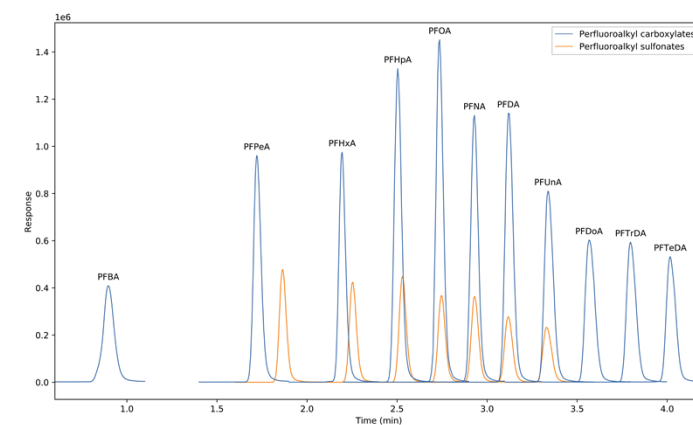


Figure 7. TIC of a calibration standard representing the HPLC MRM separation of the 18 compounds.

Micro Solid-Phase Extraction

The extraction method (Figure 3) 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. Validation was achieved by recoveries of spiked internal standards from the surface water samples.

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 8). 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	*PFTriDA	PFTeDA	PFBS	*PFPeS	PFHxS	*PFHpS	PFOS	*PFNS	*PFDS
% Recovery	103	94	98	104	93	106	91	99	104	75	65	103	117	107	83	105	72	74
% RSD	**g	9	13	4	2	8	15	15	4	44	27	2	6	**11	9	**7	6	17

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

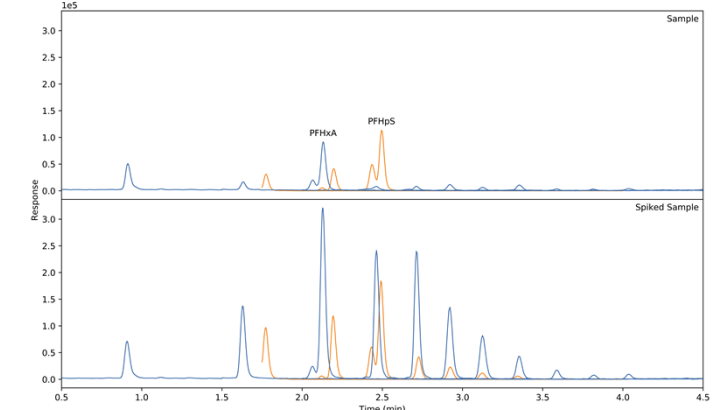


Figure 8. Comparison of spiked (bottom) and un-spiked samples. Multiple peaks, representing multiple structural isomers, are observed for both PFHxA and PFHpS.

Conclusions

This study demonstrates the improvements an automated micro-SPE method has over current extraction techniques for PFAS analysis. Required LODs were exceeded using only 2 mL of sample (250 mL required for EPA Method 537²) and without the lengthy evaporation step. Samples required no additional clean-up or filtration, even for very turbid water samples. Recoveries and repeatability were good for the majority of compounds and could be further improved by limiting the adsorption of long chain compounds.

Acknowledgements

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