Application

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µSPEed | Application Note 2018

PFAS's by Automated mixed-mode µSPEed cartridges on ePrep Environmental Application - Contaminated Surface Water

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INTRODUCTION

Perfluoroalkyl substances (PFAS) are a family of synthetic fluorine containing chemicals that consist of a fluorinated hydrocarbon chain bonded to a charged group. PFAS have many desirable chemical properties for commercial and industrial applications, such as protective coatings for fabrics, manufacture of surfaces for non-stick cookware and as flame retardants in fire-fighting foams.

PFAS are ubiquitous and persistent and contaminate soil and water resources, the local environment, and are detected across the entire earth, even in very remote areas. Animal studies, primarily performed in rodents, have shown links between perfluoro-octane sulfonate (PFOS) and perfluoro-octanoic acid (PFOA) exposure and increased liver weight, behavioural and developmental changes in offspring, negative reproductive effects and tumour growth. Large scale studies of human exposure have also linked PFOS and PFOA to high cholesterol, thyroid disease, autoimmune disease, and testicular and kidney cancer.

Food Standards Australia New Zealand (FSANZ) recommend that drinking water should contain less than 70 and 560 ng L^{-1} (parts per trillion) for PFOS and PFOA, respectively[1]. Solid phase extraction (SPE) is the preferred method[2] for the clean-up and pre-concentration of PFAS contaminated water samples. While effective, SPE is labour and time intensive and requires large sample volumes to achieve the regulatory limits of detection specified by FSANZ.

The introduction of Eprep's Sample Preparation Workstation offers an innovative alternative to traditional SPE techniques, eliminating labour intensive processes to vastly increase precision and accuracy. This unit is designed for automated standard and sample dilution, and micro solid phase extraction (µSPE). The high pressure µSPEed Cartridges is a significant advancement over current SPE cartridges as 3µm sorbents are packed into an 8µl (4.2mg) bed volume, providing enormous separation power and high concentration factors in µl volumes.

This application note demonstrates the utility of the Sample Preparation Workstation for the sample preparation of perfluoroalkyl carboxylates and sulfonates that were extracted from contaminated surface water using mixed-mode PFAS µSPEed cartridges ***in less than 5 min***[3].

METHODS

The µSPEed is a unique design of SPE cartridge for automated sample preparation in conjunction with the ePrep Sample Preparation Workstation (Figure 1). Typical operation involves loading a sample from a designated vial by drawing the sample into the syringe

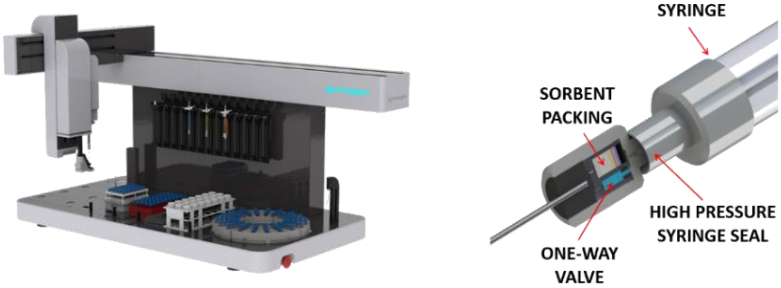
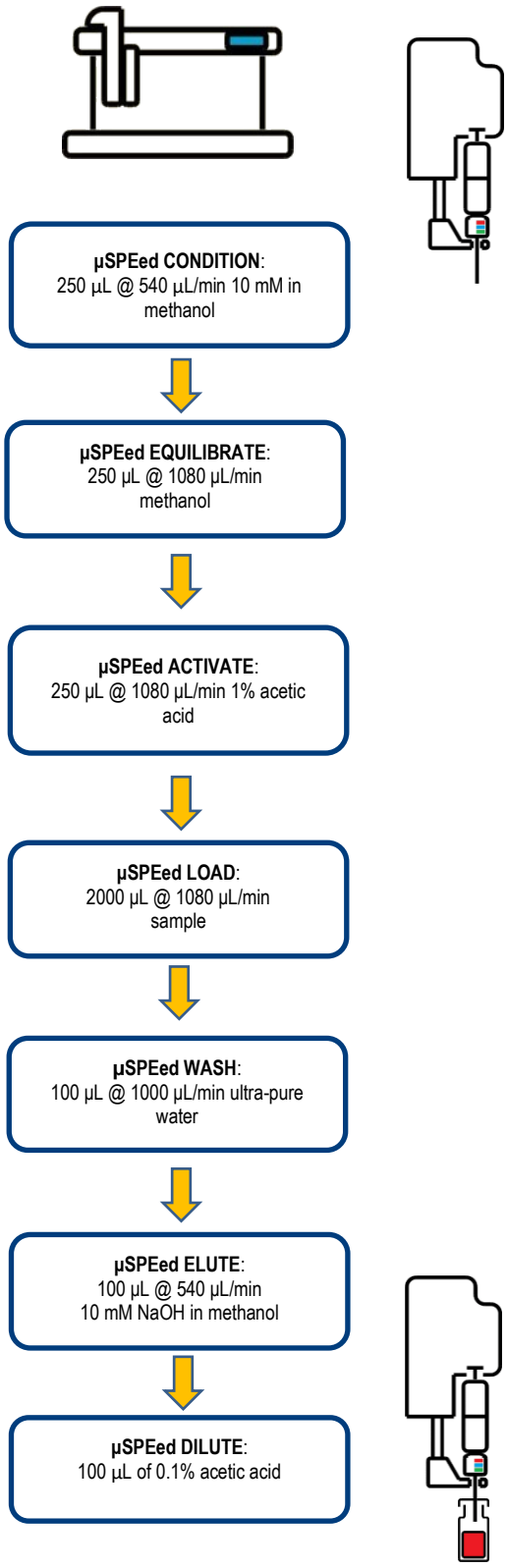


Figure 1: ePrep Sample Preparation Workstation and µSPEed cartridges with one-way check valves.



Scheme 1: Sample clean-up and pre-concentration

through the one-way check valve. The sample is loaded by reversing the direction of flow by depression of the syringe, where the check valve is closed directing the sample to flow through the sorbent. The sample is eluted with an eluting solvent by repeating this process.

Solutions:

- 10 mM NaOH in methanol
- methanol
- 1% acetic acid
- ultra-pure water
- 0.1% acetic acid

Sample Preparation

Prior to extraction 10 ml aliquots of samples were acidified to approximately pH 3 with 100 µl of glacial acetic acid to aid in the retention of short chain PFASs. Samples were then spiked with 100 ng L^{-1} of the internal standard mixture.

Calibration

A seven-point calibration curve ranging from 10 to 9 000 ng L^{-1} was prepared with the ePrep Workstation and used to determine the linearity and instrumental limits of detection (LODs) for the analytes

UHPLC

Gradient separation of the 13 PFAS compounds was performed on a Shimadzu Nexera MP using a Phenomonex Luna Omega 2.1 x 50 mm, 1.6 µm C18 column. Mobile phases consisted of ultra-pure water (A) and methanol (B), each with 2 mM ammonium acetate. Initial conditions of 20% B were held for 0.2 min before being raised to 70% at 2.4 min, then 95% at 5 min. The gradient was then held at 95% for 2 min before returning to the initial conditions and equilibrated for 4 min. A flow rate of 0.6 ml min^{-1} and column temperature of 50 °C were used throughout the run.

MS/MS

Detection was performed using a Shimadzu LCMS-8060 triple quadrupole mass spectrometer operated in negative ionisation mode. The interface voltage and temperature were optimised to -0.5 kV and 300 °C. Nebulising, heating and drying gas flows were set at 3, 10 and 10 L min^{-1} respectively and collision gas was operated at a pressure of 270 kPa. Multiple reaction monitoring (MRM) mode using the parameters in **Error! Reference source not found.** was used and optimised for transitions from the $[M-H]^-$ ion using the LabSolutions software. Where possible, both a quantification and identification ion were used for each compound however some compounds, such as PFBA, exhibit only one significant fragmentation.

Table 1. Multiple reaction monitoring parameters used during analysis.

Compound	Abbreviation	Transition (m/z)	Q1 PreBias (V)	Collision Energy (eV)	Q3 PreBias (V)
Perfluorobutanoic acid	PFBA*	213.05 → 169.00	5	9	9
Perfluoropentanoic acid	PFPeA*	262.95 → 218.95	9	8	29
Perfluorohexanoic acid	PFHxA*	312.95 → 268.90	7	9	35
	PFHxA	312.95 → 118.90	11	19	19
Perfluoroheptanoic acid	PFHpA*	362.95 → 319.00	13	10	15
	PFHpA	362.95 → 169.05	13	17	9
Perfluorooctanoic acid	PFOA*	412.95 → 369.00	15	10	11
	PFOA	412.95 → 169.05	15	17	9
Perfluorononanoic acid	PFNA*	462.95 → 419.00	11	11	13
	PFNA	462.95 → 219.00	11	17	13
Perfluorodecanoic acid	PFDA*	512.90 → 468.95	19	11	15
	PFDA	512.90 → 268.90	19	17	13
Perfluoroundecanoic acid	PFUnA*	562.90 → 518.85	13	11	13
	PFUnA	562.90 → 319.10	9	19	21
Perfluorododecanoic acid	PFDoA*	612.90 → 568.95	15	12	11
	PFDoA	612.90 → 319.15	15	18	9
Perfluorotetradecanoic acid	PFTeDA*	712.90 → 668.90	17	13	17
	PFTeDA	712.90 → 168.85	19	26	27
Perfluorobutane sulfonate	PFBS*	298.90 → 80.00	11	32	11
	PFBS	298.90 → 99.00	11	26	5
Perfluorohexane sulfonate	PFHxS*	399.00 → 80.00	11	40	9
	PFHxS	399.00 → 99.05	13	34	5
Perfluorooctane sulfonate	PFOS*	499.00 → 80.00	9	58	9
	PFOS	499.00 → 99.05	9	40	5

* Quantification ion.

RESULTS

Six samples and sample spikes (100 ng/L) were extracted and separated via UHPLC (**Error! Reference source not found.**), and quantified. Recoveries of the PFAS were calculated to be between 86 and 111% across the six samples. Low standard deviations highlighted the reproducibility of µSPE for the extraction of PFASs from surface waters with LODs well below the regulatory limits.

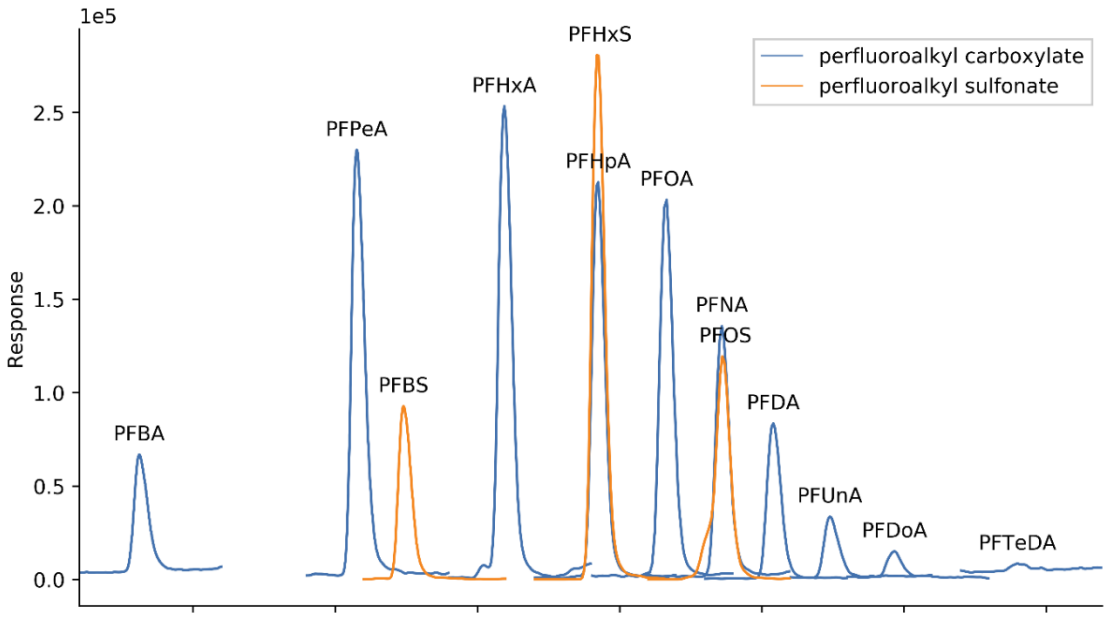


Figure 2: UHPLC separation of the 13 compounds. Perfluoroalkyl carboxylates and sulfonates are in orange and blue respectively

Table 2. Validation results for the extraction and instrument methods.

Compound	%Recovery	%RSD	Linearity	LOD (ng L^{-1})
PFBA	101	15	0.9990	3.5
PFPeA	98	10	0.9998	2.8
PFHxA	101	12	0.9999	5.2
PFHpA	106	3	0.9999	1.2
PFOA	97	8	0.9998	1.7
PFNA	107	7	0.9998	2.2
PFDA	96	18	0.9997	1.7
PFUnA	104	12	0.9995	4.4
PFDoA	103	3	0.9993	4.8
PFTeDA	86	6	0.9992	6.6
PFBS	105	4	0.9998	0.29
PFHxS	105	12	0.9997	1.3
PFOS	111	12	0.9995	2.7

CONCLUSIONS

The instrument detection limits for all compounds were less than 10 ng L^{-1}. The lowest Australian guidance value for PFASs in water is 70 ng L^{-1} (PFOS),7 making this method suitable for monitoring environmental waters with no additional clean-up required. A typical extraction took 5 minutes to perform manually, faster than conventional SPE methods such as EPA Method 537 (>30 minutes),24 and achieved similar results using a 125x smaller sample volume (2 ml vs 250 ml).25 Conventional SPE methods using larger volumes of elution solvent do obtain a higher level of pre-concentration, however this is achieved by evaporation and reconstitution of the extract (8 ml evaporated to ~0.5 ml and reconstituted in 1 ml for EPA Method 537), a process that can take several hours and may potentially lead to loss of more volatile PFASs such as fluorotelomer alcohols.26

PFAS were detected in all six of the samples, with concentrations ranging from <LOD to 898 ± 15 ng L^{-1}. Recoveries of spikes were between 95 and 110% for most compounds with %RSDs below 20%

ACKNOWLEDGEMENTS

Lockwood, T.[1]; Bishop, D.[1]; Maleknia, S.[1]; Minett, A.[2]; Dawes, P.[2]; Doble, P.[1]
[1]University of Technology Sydney - School of Mathematical and Physical Sciences, Faculty of Science.
[2]Eprep Pty Ltd, Mulgrave VIC 3170, Australia

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[1] Perfluorinated Chemicals in Food; Food standards Australia New Zealand; 2017.

[2] Shoemaker, J. A.; Grimmett, P. E.; Boutin, B. K. METHOD 537; 2009.

[3] Lockwood, T.; Bishop, D.; Maleknia, S.; Minett, A.; Dawes, P.; Doble, P. Automated μSPE for the determination of PFAS compounds, Proceedings of the 66th American Society for Mass Spectrometry Conference on Mass Spectrometry and Allied Topics, June 3-7, San Diego, USA; 2018.

µSPEed Cartridge Ordering Information

Part Number	Code	Description
µSPEed Cartridges		
01-10185	µSPEed, Cxyl-3µm/120Å (Pkt 10)	µSPEed, Customisable Microreactor Carboxyl-3µm/120Å (Pkt 10)
01-10110	µSPEed, C18RPS-3µm/120Å (Pkt 10)	3µm/ 120Å ODS spherical silica packing with high acidic resistance suitable for general organic compound applications.
01-10115	µSPEed, Silica-3µm/120Å (Pkt 10)	3µm/120Å spherical bare silica packing. High purity silica for normal and hilic applications
01-10118	µSPEed, PFAS-3µm/120Å (Pkt 10)	3µm/120Å spherical mixed PFAS packing. Turned for PFAS analysis
01-10150	µSPEed, PS/DVB -3µm/ 300Å (Pkt 10)	3µm/ 300Å spherical, crosslinked polystyrene divinyl benzene
01-10151	µSPEed, PS/DVB RP-3µm/ 300Å (Pkt 10)	3µm/ 300Å Phenyl(RP) spherical, crosslinked polystyrene divinyl benzene
01-10155N	µSPEed, PS/DVB SAX-3µm/ NP (Pkt 10)	3µm/Non-Porous SAX spherical, crosslinked polystyrene divinyl benzene
01-10156N	µSPEed, PS/DVB SCX-3µm/ NP (Pkt 10)	3µm/Non-Porous SCX spherical, crosslinked polystyrene divinyl benzene