



Analysis of Perfluorinated Alkyl Substances (PFAS) in River Water Samples Using Online SPE-LC-MS

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INTRODUCTION

Perfluorinated alkyl substances (PFAS) are a class of man-made chemicals that are widely used in many different applications from non-stick cookware to waterproof coatings. PFAS are sometimes referred to as “forever chemicals”(1) due to their high resistance to degradation in the environment. This property has led to their build up in many different areas including in soils, water systems, plants and animals, including humans(2).

There is increasing evidence that exposure to PFAS can lead to a number of adverse health effects. These include cancer, hormone disruption, effects on the immune system and low birth weights in infants(1). For these reasons there is growing interest in measuring the levels of PFAS in environmental samples, but currently instrumentation and methods are lacking. To this end we have developed a portable online solid phase extraction—liquid chromatography coupled with mass spectrometry (SPE-LC-MS) based method that can bring the lab to the sample.

EXPERIMENTAL

An automated online SPE and LC Pump System was used for the loading and separation of the PFAS samples, coupled with Microsaic’s 4500 MiD® compact Mass Spectrometer for the detection of PFAS. The SPE-LC-MS system was set up in two different formats; an in-lab setup in an air conditioned lab running on mains power, and a remote in-field setup outside running on a generator with max power output .0 kW, and N₂ bottle.

TABLE 1. SPE and LC conditions

SPE Cartridge	Strata-X-AW 33µm polymeric weak anion exchange 20 x 2.0 mm
LC Column	Phenomenex Gemini 3 mm C18 110 Å 50 x 2 mm
LC Flow Rate	0.3 ml/min
Column Temp.	25°C
Sample Volume	50 ml
Mobile Phase A	H ₂ O + 0.4% ammonium hydroxide
Mobile Phase B	MeOH + 0.4 % ammonium hydroxide
Analysis Time	38 min

The LC gradient runs concurrently with the SPE, though the sample is not eluted from the SPE until 22.15 min. The gradient is held at 90% B for the first 10 min to prevent build up of contaminant PFAS from the system, and the gradient brought to starting conditions before the elution to ensure equilibration of the column.

The water samples were collected in 250 ml polypropylene bottles. They were spiked with 200 ppt of PFAS standards and/or stable isotope labelled internal standards and filtered through a 0.5 µm glass fibre filter using polypropylene syringes followed by a 0.20 µm cellulose membrane filter. After sample loading onto the SPE cartridge there is an automated wash step followed by a second wash step using the LC flow before elution of the PFAS by increasing the amount of organic mobile phase.



FIGURE 1 Full system shown for the work presented. Left: Automated Online SPE-LC Pump System, middle: Column Thermostat, Right: Microsaic 4500 MiD® Mass Spectrometer. The resulting small footprint allows for it to be fully deployable and at the point-of-need.

TABLE 2. MS settings

Scan mode	SIM (Single Ion Monitoring)
Scan rate	1 Hz
Step	0.2
SIM	PFOA m/z 412.8, M2PFOA (IS) m/z 414.8, PFOS m/z 498.8, MPFOS (IS) m/z 502.8
Ion mode	Negative
Gas flow	1.5 l/min

APPLICATION NOTE 017



RESULTS AND DISCUSSION

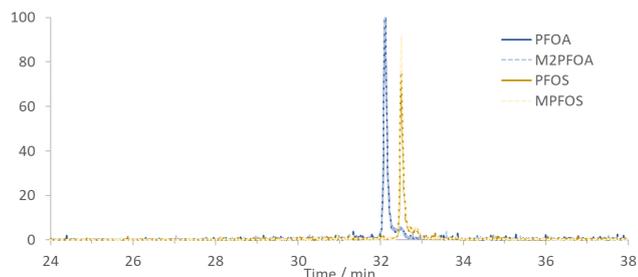


FIGURE 2. Chromatogram showing SIM traces of 200 ppt PFOA and PFOS standards in HPLC grade water with internal standards, M2PFOA and MPFOS, analysed using the in-field setup

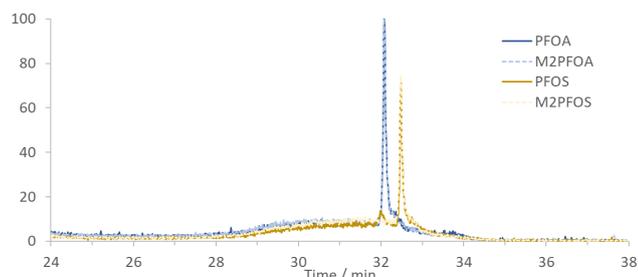


FIGURE 3. Chromatogram showing SIM traces of filtered canal water spiked with 200 ppt of the internal standards M2PFOA and MPFOS, analysed using the in-field setup

The chromatographic separation between PFOA and PFOS was unchanged between spiked HPLC water and spiked canal water (Fig. 2 and 3). In the canal water however there was evidence of background noise from matrix components (Fig. 3) which required a wash step before elution from the SPE to move the matrix components away from the PFAS peaks. The chromatography was consistent between the samples analysed in-lab and in-field. No system contamination peaks were observed (Fig. 5).

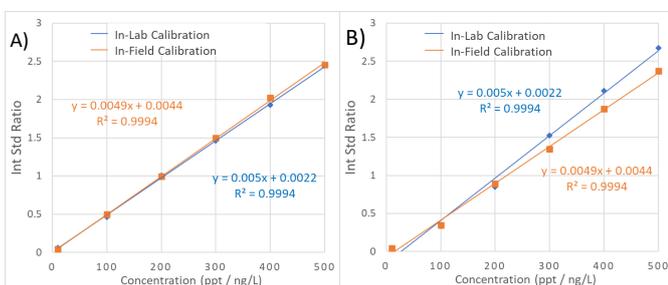


FIGURE 4. Calibration curves for PFOA vs. M2PFOA (A) and PFOS vs. MPFOS (B). Each graph shows data for the calibration curve created in-lab (shown in blue) and using the in-field set-up (shown in orange.)

Calibration curves were produced in the range of 10-500ppt with minimal deviation in the regression values and high recoveries for each in the spiked samples (Fig. 4).

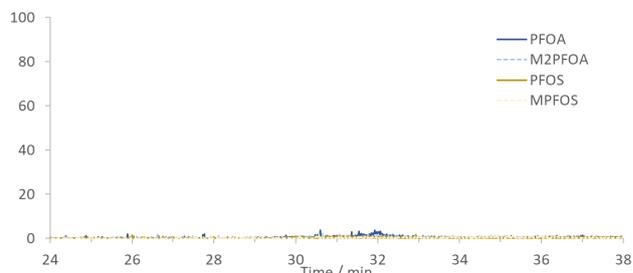


FIGURE 5. Blank chromatogram of HPLC grade water showing the lack of PFAS peaks from potential system contamination

The calibration curves for PFOA and PFOS were consistent between the in-lab and in-field analysis (Fig. 4) which allows the application of a calibration curve generated in-lab conditions to samples that have been analysed in-field, reducing the number of samples that need to be analysed whilst working remotely. Standard recovery for the spiked canal water samples were between 94–106%. The calculated concentrations and standard recoveries were also in agreement between the same samples analysed in the in-lab and in-field setups.

The use of online SPE-LC-MS for the analysis of PFAS in water samples minimises the amount of sample preparation needed. The low power consumption of the system enables the whole set-up to be run using a small generator, and the small size of the MiD 4500 makes the entire system highly portable and able to fit in the back of a car or van. There is no significant difference in results between samples analysed using a traditional lab based set-up and the remote in-field set-up.

CONCLUSION

Use of the Microsaic 4500 MiD® coupled to an automated online SPE-LC enables the first entirely remote and fully automated on-site investigation of PFAS in water, with results equivalent to lab-based setups. Moving these detection tools to the point of need for the analysis of PFAS in water allows the monitoring of whole ecosystems and mapping of these issues by geography and time.

REFERENCES

- 1) Sunderland, Elsie M., et al. "A review of the pathways of human exposure to poly-and perfluoroalkyl substances (PFASs) and present understanding of health effects." *Journal of exposure science & environmental epidemiology* 29.2 (2019): 131-147.
- 2) Beans, Carolyn. "News Feature: How "forever chemicals" might impair the immune system." *Proceedings of the National Academy of Sciences* 118.15 (2021).