DIRECT INJECTION SCREENING METHOD FOR PER-AND-POLYFLUOROALKYL SUBSTANCES IN DRINKING WATER USING A PROTOTYPE BENCHTOP MULTI-REFLECTING TIME-OF-FLIGHT

Hania Khoury-Hollins[1]; Stuart Adams[1]; Jayne Kirk[1]; Richard Lock[1]; Lance Nicolaysen[2]

[1]Waters Corporation, Stamford Avenue, Altrincham Road, Wilmslow, Cheshire, SK9 4AX, UK, [2]Waters Corporation, 34 Maple Street, Milford, MA 01757, USA

INTRODUCTION

The widespread use of per and polyfluoroalkyl substances (PFAS) in industrial processing and manufacturing over the last decades has led to global environmental and health concerns. As the number of these compounds continues to increase[1], it is becoming a challenging task to monitor PFAS using the traditional targeted methods. Screening workflows using high resolution mass spectrometry (HRMS) is an ideal bridge for monitoring the regulated PFAS and detecting non-regulated PFAS.

In this work, PFAS a screening method is tested by direct injection of 10 µL of samples and standards. Samples were analyzed using an ACQUITY™ Premier UPLC™ system coupled to a benchtop multi-reflecting time of flight (MRT) mass spectrometer. Data were acquired in negative ionization mode using the MS^E acquisition mode and processed using waters_connect™.

The mass accuracy, mass resolution, sensitivity and dynamic range of the Xevo™ MRT were evaluated with a dynamic range for all compounds spanning over three orders of magnitude. Drinking water samples were spiked and analyzed. PFOS was detected with mass measurement accuracy of ± 100 ppb at 30 ng/L.

LIQUID CHROMATOGRAPHY (LC)

1 LC system

Waters ACQUITY Premier Liquid chromatography system modified with PFAS solution installation kit (p/n: 176004548)

Vials: Polypropylene autosampler vial and sealed with a polyethylene cap (p/n: 186005230)

Column: ACQUITY Premier BEH™ C18, 1.7 µm, 2.1 x 100 mm, 90 Å (p/n:186009453)

Column temp.: 35°C

Sample temp.: 6°C

Injection volume: 10 µL

Chromatographic gradient

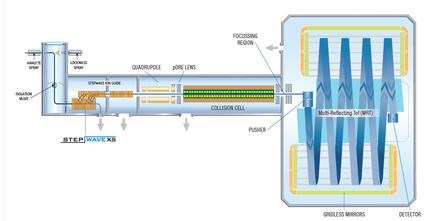
Mobile phase A: 95:5 water:methanol with 2 mM ammonium acetate

Mobile phase B: 100% methanol with 2 mM ammonium acetate

Time (min)	Flow rate (mL/min)	%A	%B	Curve
0	0.3	100	0	Initial
1	0.3	80	20	6
6	0.3	55	45	6
13	0.3	20	80	6
14	0.3	5	95	6
17	0.3	5	95	6
18	0.3	100	0	1
22	0.3	100	0	1

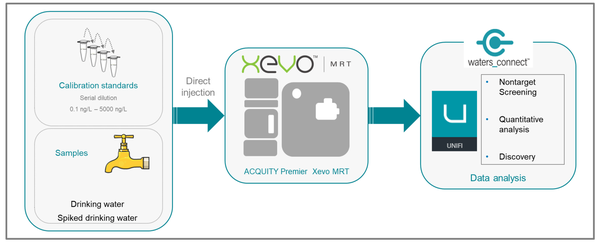
MASS SPECTROMETER

2 MS System Xevo™ MRT mass spectrometer



Scheme 1: Schematic of the benchtop multi-reflecting time of flight mass spectrometer. For PFAS analysis, the instrument was operating in the negative ion mode in the m/z range from 50-1200 Da at 10 Hz. Data were acquired using MS^E, a data independent acquisition mode.

3 Workflow



Scheme 2: Drinking water was collected in 15 mL tubes and spiked in duplicate with PFAS standards at two different calibration levels. The calibration standards and the samples were then analyzed using an ACQUITY Premier liquid chromatography system coupled by Xevo MRT. Data acquisition and processing was performed using the waters_connect software platform and UNIFI™ application.

4 Instrument parameters[2,3]

	Parameters	Value
Source	Capillary voltage	0.5 kV
	Cone voltage	10 V
	Source temp.	120ºC
	Desolvation temp.	250ºC
	Cone gas	100 L/h
	Desolvation gas	600 L/h
Collision energy	Low collision energy	4 V
	High collision energy	Ramp 20- 70 V
Transmission Settings	StepWave RF	100 V
	Body gradient	5 V

The source and transmission parameters were described in application notes 720008118-en and 720008198-en[2,3].
These parameters were optimised in order to increase the transmission of the different classes of PFAS.

RESULTS

1 A summary of the nontarget screening (NTS) workflow using UNIFI

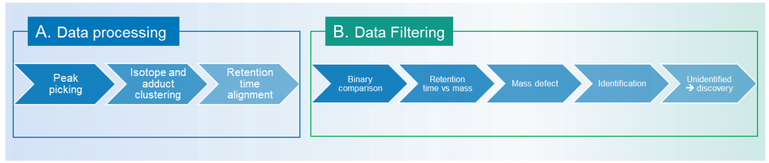


Figure 1: NTS workflow can be defined in two steps: data processing (figure 1 A) and data filtering (Figure 1 B). The data processing includes peak picking, isotope and adducts clustering, and retention time alignments. The data filtering corresponds to a set of parameters to display a list of the components that fit the user defined criteria. For example, a filter for viewing components eluting between 3-5 minutes, with m/z above 500 Da, and are within the mass defect defined for PFAS.

2 Identification of PFAS using Waters PFAS library[4]

Compounds are identified using accurate mass (< 500 ppb), retention time and fragment ions.

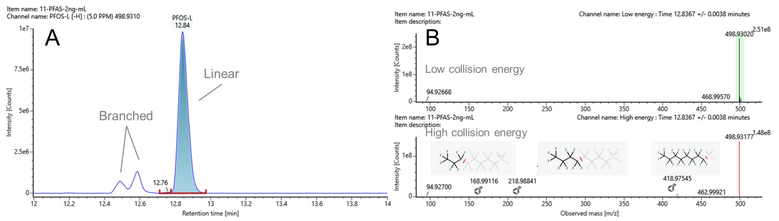


Figure 2: Identified perfluorooctanesulfonic acid (PFOS) in a standard mix at 2000 ng/L as $[M+H]^+$ with mass measurement accuracy < 36 ppb. Figure 2A: Extracted ion chromatogram (XIC) of PFOS (linear and branched). Figure 2B: Mass spectra of linear PFOS at low and high collision energy (upper and lower panels, respectively).

3 Identification and quantification of PFAS in drinking water by direct injection[5]

PFOS is identified and quantified in spiked drinking water with mass measurement accuracy 107 ppb.

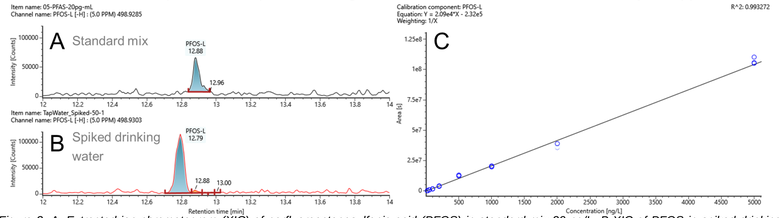


Figure 3: A: Extracted ion chromatogram (XIC) of perfluorooctanesulfonic acid (PFOS) in standard mix 20 ng/L, B XIC of PFOS in spiked drinking water. PFOS is identified in spiked drinking water at m/z 498.9303 with mass measurement accuracy ± 100 ppb and Signal-to-noise ratio ± 17. The signal-to-noise is calculated using peak-to-peak method. B: calibration curve from the ion response at low collision energy. The linear regression is fitted with 1/X weighting with coefficient of determination R^2 = 0.99327. PFOS response is linear from 20 ng/L to 5,000 ng/L.)

CONCLUSION

- **NTS workflow using the UNIFI application in waters_connect is a single software solution for nontarget screening, discovery, and quantitative analysis.**
- **The UNIFI screening and discovery workflows offer numerous options from mass defect filtering, mass retention time filtering for PFAS homologues, and online database and library searches.**
- **The benchtop Xevo MRT instrument demonstrated accuracy < 300 ppb and high mass resolution < 75K for *m/z* 556.2765 (Leu-enkephalin).**
- **Direct injection methods for the identification and quantification of PFAS help circumvent the limitations of sample preparation using SPE and the need for commercially available standards for identification using conventional targeted methods.**
- **To increase sensitivity there is also the option of increasing injection volume.**
- **The data set generated was used for targeted quantitative approaches and can be mined retrospectively for identification and discovery workflows using different library sources.**

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