

Application News

MALDI-8030 EasyCare

Detection of PFAS in Aqueous Samples by Matrix Assisted Laser Desorption Ionisation Time-of-Flight (MALDI-TOF) Mass Spectrometry

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User Benefits

- ◆ Obtain results indicative of PFAS in aqueous samples within minutes for further study.
- ◆ Minimal sample preparation required prior to acquisition.
- ◆ Method can be applied to numerous sample types following additional preparation.

Introduction

Per- and polyfluoroalkyl substances (PFAS) are persistent environmental contaminants which accumulate in water, soil and living organisms. PFAS negatively impact human health with links to cancer, immune system depression and hormone disruption, amongst others, already being established. Worldwide, concern regarding the exposure of biological organisms to environmental PFAS continues to grow.

PFAS contamination in water is a particular focus for both regulations and research. Widespread water contamination has been reported, and removal continues to be difficult and expensive.

We developed a simple, cost-effective method for the detection of PFAS in aqueous samples using an entry-level benchtop linear MALDI-TOF mass spectrometer (Fig. 1).



Fig. 1 The MALDI-8030 EasyCare Benchtop linear MALDI-TOF mass spectrometer

Sample Preparation

PFOA or PFOS solutions were prepared using a standard sample (Sigma, UK). A 1 µg/mL (ppm) stock solution was prepared in methanol with dilutions prepared in water.

Samples were tested with a variety of matrices (α-cyano-4-hydroxycinnamic acid (CHCA), 2,5-dihydroxybenzoic acid (DHB), 2',6'-dihydroxyacetophenone (DHAP), 1,5-diaminonaphthalene (DAN), norharmane and 1,8-bis(tetramethylguanidino)-naphthalene (TMGN)), with norharmane and TMGN identified as suitable for further development.

The samples were mixed with 1 mg/mL norharmane or 5 mg/mL TMGN (Sigma, UK) in Methanol:Water, 70:30 (v/v). Blank samples of ultra high quality (UHQ) water were prepared to ensure no contamination was present. 1 µL was then spotted onto a MALDI target and the sample was analysed using a MALDI-8030 MALDI-TOF mass spectrometer (Shimadzu Corporation). The sample preparation scheme is shown in Fig. 2. Analysis conditions are shown in Table 1. Peaks at m/z 314.1 and m/z 499.1 were monitored for PFOA and PFOS respectively. $^{13}\text{C}_8\text{PFOS}$ (m/z 507.1) was used as an internal standard for PFOS samples.

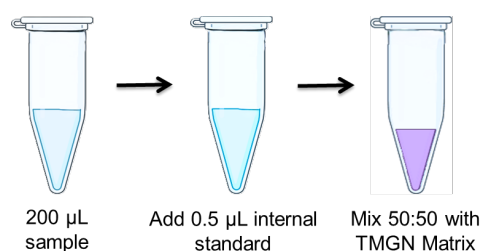


Fig. 2 Sample preparation scheme used in this study: The addition of internal standard and matrix is all that is required for sample analysis

Imaging analysis using MALDI-TOF (MALDI-MSI) was used to assess spot homogeneity during optimisation of acquisition parameters and limits of detection for the chosen matrix were established.

Results

Following optimisation of parameters using both norharmane and TMGN, MALDI-TOF MS spectra of PFOS and PFOA for both matrices showed similar results (Fig. 3). The final acquisition parameters for both matrices are shown in Table 1.

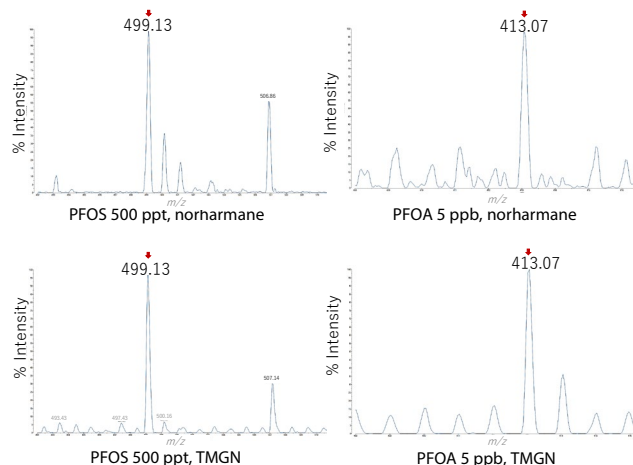


Fig. 3 MALDI-TOF MS spectra of PFOS (500 ppt) and PFOA (5 ppb) using TMGN (5mg/ml) or norharmane (1mg/ml) as a matrix

Table 1 Analysis Conditions of MALDI-8030

System	: MALDI-8030
Polarity	: Negative
Mass Range	: m/z 100-1000
Acquisition	: 5 shots per profile @ 200Hz
Blanking	: 200
Pulsed Extraction	: 400
Profiles	: 196

To gain a better understanding of analyte distribution within the samples, MALDI-MSI spot imaging was performed and the data was processed using the IonView™ software package (Shimadzu Corporation). MALDI-MSI spot imaging revealed higher intensities of PFAS towards the outer perimeter of the spots, particularly with norharmane (Fig. 4). This was variable between PFOS and PFOA.

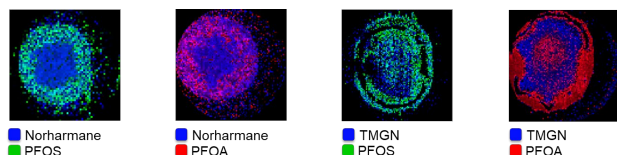


Fig. 4 MALDI MSI spot imaging of PFOS and PFOA using norharmane or TMGN as a matrix

Implementing an annular raster strategy for analysis of norharmane spots produced spectra with an improved signal to noise ratio as expected (Fig. 5). However, use of an annular raster should be combined with either manual positioning or, for higher throughput, combined with alternative strategies to control the location of the spot e.g. FlexiFocus™ slides. An alternative to this strategy would be to use the data quality feature within the *Data Acquisition* software to ensure a minimum level of signal for peaks of interest at each data point acquired.

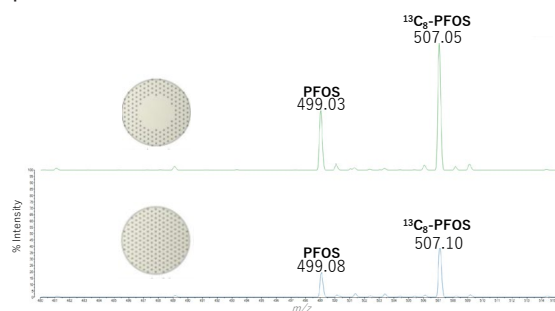


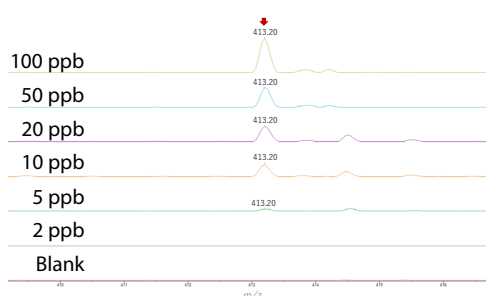
Fig. 5 MALDI mass spectra of PFOS by annular or general raster strategies with norharmane

Spots with TMGN matrix showed a more optimal distribution and work was continued with this matrix. This distribution of the sample to matrix was achieved using 5 mg/mL TMGN in 70% acetonitrile mixed 50:50 (v/v) with the sample prepared in 100% UHQ water.

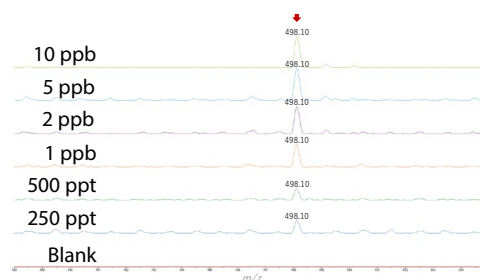
■ LODs for Representative PFAS

Four compounds were chosen to represent four subclasses of PFAS: long chain perfluorocarboxylic acids (PFOA), short chain perfluorocarboxylic acids (PFHxA), long chain perfluorosulfonic acids (PFOS) and short chain perfluorosulfonic acids (PFBS) to establish approximate limits of detection. The limits of detection established for PFOA, PFOS, PFHxA and PFBS were 5 ng/mL, 250 pg/mL, 200 pg/mL and 1 ng/mL respectively (Fig. 6).

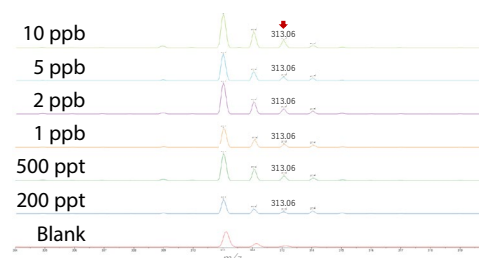
PFOA (m/z 413.20)



PFOS (m/z 498.10)



PFHxA (m/z 313.06)



PFBS (m/z 299.14)

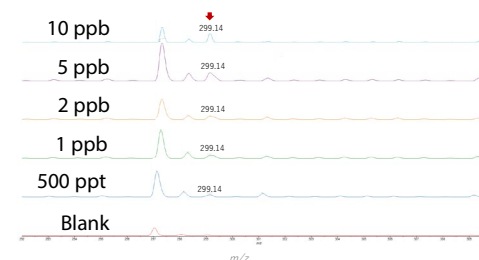


Fig. 6 Representative mass spectra showing approximate LODs for PFOA (5 ppb), PFOS (250 ppt), PFHxA (200 ppt) and PFBS (1 ppb) with TMGN used as a matrix. The red arrow is indicative of the analyte peak.

■ Analysis of Water Samples

Samples of both bottled water and pond water from different sources (labelled 1 & 2 below) were tested using the optimised method alongside a sample of UHQ water containing PFOS, PFOA, PFBS and PFHxA at 100 ng/mL (Fig. 7). Both bottled water samples contained peaks corresponding with the m/z for PFOA, with bottled water 1 also containing a peak corresponding with the m/z for PFBS. Pond water sample 1 contained no peaks corresponding to the m/z for any of the PFAS in the standards mix, whilst pond water sample 2 contained peaks corresponding with the m/z for PFHxA and PFOS.

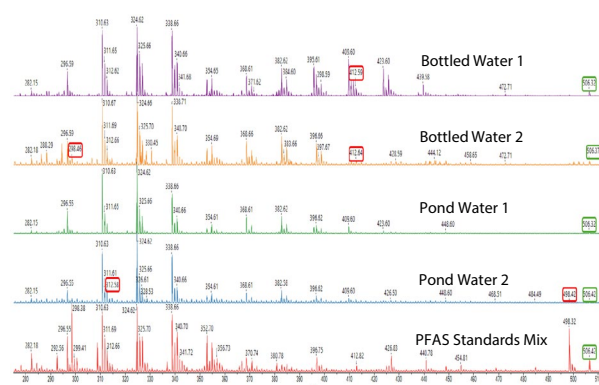


Fig. 7 MALDI-TOF MS spectra showing analysis of pond water and bottled drinking water alongside a standard PFAS sample containing PFOS, PFOA, PFBS and PFHxA at 100 ng/mL. All samples used 5 mg/mL TMGN as matrix. Small peaks were seen in some water samples with similar m/z to the known m/z of PFAS compounds have been highlighted in red. The internal standard for PFOS has been highlighted in green.

■ Q-TOF LCMS Analysis

To confirm the presence of PFAS in the water samples, solid phase extraction (SPE) was used to prepare the samples.

Chromabond WAX SPE columns (Avantor, UK) were conditioned with methanol and UHQ water. 50 mL of sample was loaded and washed with methanol:UHQ water, 5:95 (v/v). The samples were eluted in 2 mL methanol and concentrated by SpeedVac (Thermo Fisher, UK). Finally, the samples were reconstituted in 1 mL methanol:water, 80:20 (v/v).

The SPE extracts were analysed on an LCMS-9050 Q-TOF mass spectrometer (Shimadzu Corporation). Detection of the PFAS seen in the MALDI spectra was achieved by data-independent acquisition (DIA) analysis.

The obtained DIA data for the water samples were processed using LabSolutions Insight Explore™ for compound identification. Using the MS/MS library search, all potential PFAS contaminants flagged by MALDI analysis were confirmed and matched to reference spectra in the PFAS library. Library similarity scores (SI) for each compound by sample are shown in Table 2 below. Representative MS/MS spectra obtained are shown in Fig. 8 alongside library reference spectra.

Table 2 Lib. SI values for PFAS detected in water samples

	PFOS	PFOA	PFBS	PFHxA
Bottle 1	99	89	96	80
Bottle 2	100	91	---	85
Pond 1	100	89	92	85
Pond 2	98	80	81	77

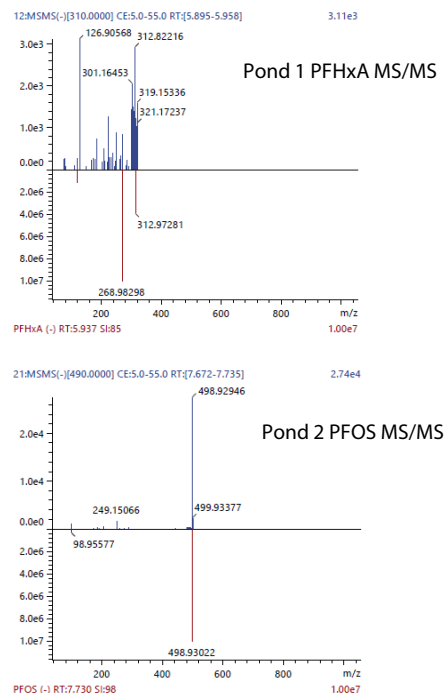


Fig. 8 Representative spectra (top) showing matches to PFAS library references (bottom) in water samples

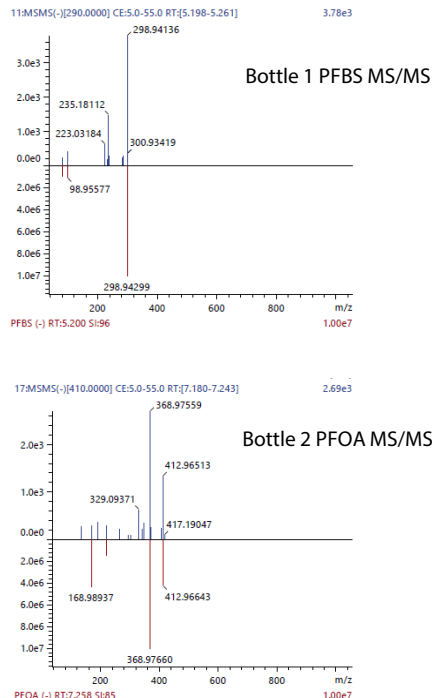
■ Conclusions

We have shown MALDI-TOF mass spectrometry applied to the detection of PFAS in aqueous samples in this proof of principle analysis.

The samples can be analysed using an entry-level MALDI-8030 linear benchtop MALDI-TOF mass spectrometer. These instruments are robust and compact in size, so could be installed with minimal resources into a wide variety of laboratories.

Spot imaging at 30 μ m spacing during method development highlights the differences in homogeneity of PFOS and PFOA spots suggesting that multiple internal standards would be necessary to pursue quantitative analysis.

Analysis of bottled and pond water samples were chosen to be representative of a significant proportion of samples in environmental research and monitoring laboratories. We were able to identify peaks corresponding to low levels of PFAS in some of these samples.



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