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Application News

MALDI-8030 EasyCare

Feasibility for a PFAS Screening Protocol by Matrix-Assisted Laser Desorption/Ionisation Time-of-Flight (MALDI-TOF) Mass Spectrometry

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User Benefits

- Screen/identify high concentration samples before they enter the analytical workflow, thereby reducing the risk of contamination in sensitive LC-MS/MS equipment.
- Minimal sample preparation prior to acquisition.
- Fast pre-screen allows suitable dilution of sample to achieve LC-MS/MS results on first acquisition.

■ Introduction

Following the development of a simple, cost-effective method for the detection of PFAS in aqueous samples using an entry level linear benchtop MALDI-TOF mass spectrometer[1], here we evaluate the use of MALDI-TOF mass spectrometry as a PFAS sample screening tool to assist in preventing contamination of highly sensitive LC-MS/MS systems by detecting high PFAS concentrations in samples prior to LC-MS/MS analysis.

For the development of a viable screening method, it must be possible to determine which samples are too concentrated with a good degree of accuracy. This requires approximate determination of concentration by peak intensity or peak area relative to either a standard calibration curve or as a simple ratio to an internal standard peak.

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

■ Sample Preparation

FlexiFocus™ slides (Shimadzu Corporation) were used to improve spot homogeneity and identify potential improvements in the LOQ. To investigate the optimal parameters for LOQ values, initial experiments with PFOS were performed.

Standard samples were prepared at multiple concentrations by dilution in H_2O from a 500 µg/mL stock solution in MeOH. 5 mg/mL 1,8-bis(tetramethylguanidino)-naphthalene (TMGN) and 1 mg/mL norharmane (NRM) matrices were prepared in 1.5 mL amber Eppendorf vials and diluted to lower concentrations with either 70:30 ACN:H_2O (TMGN) or 100% MeOH (NRM).

$^{13}C_8$-PFOS was used as an internal standard. A 50 µg/mL stock solution was diluted 1:49 and 3 µL was added to 300 µL of analyte to give a final sample containing 10 ng/mL of the internal standard. Samples were then aliquoted and mixed with equal volumes of the matrices, yielding 30 different spotting mixtures.

Each mixture was spotted in triplicate (1 µL and 0.5 µL) on a 96 well FlexiFocus slide. A total of 180 spots were analysed and analyte/internal standard intensity and area values were compared.

■ Results

Analysis was performed on a benchtop linear MALDI-TOF mass spectrometer (MALDI-8030, Shimadzu Corporation) (Fig. 1). The optimised acquisition parameters for both NRM and TMGN are shown in Table 1.

Table 1 Analysis Conditions using the MALDI-8030

System	: MALDI-8030
Polarity	: Negative
Mass Range	: *m/z* 250-1000
Acquisition	: 5 shots per profile @ 200Hz
Blanking	: 200
Pulsed Extraction	: 450
Profiles	: 196

Spectra for PFOS using NRM and TMGN showed similar results, with concentrations of 0.5 mg/mL TMGN and 0.1 mg/mL NRM being optimal for use with FlexiFocus slides. Calibration curves were plotted for both, which showed a difference in the linearity range between the two matrices (Fig. 2, 3).

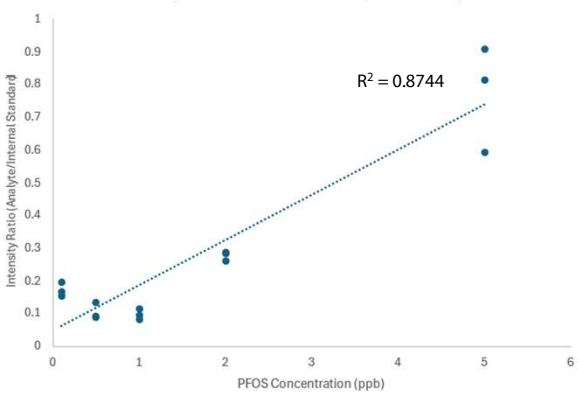

Fig. 2 Calibration curve for PFOS (100 ppt – 5 ppb) in NRM (0.1 mg/mL)

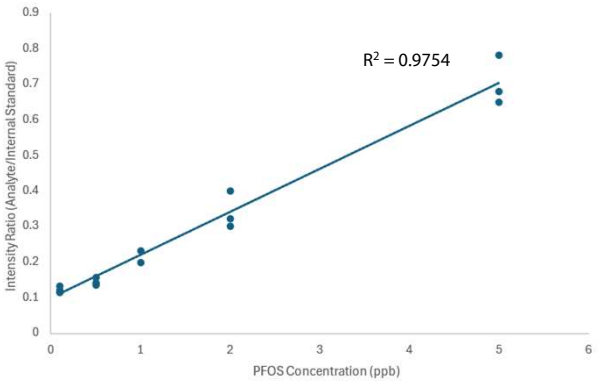

Fig. 3 Calibration curve for PFOS (100 ppt – 5 ppb) in TMGN (0.5 mg/mL)

TMGN showed better linearity in comparison to NRM, with the limit of quantification at approximately 500 ppt (See Fig. 3). Concentrations below 500 ppt displayed an unexpected levelling of the intensity (See Fig. 4). This may be because PFAS gravitate towards the surface of the water sample due to their hydrophobic tail and hydrophilic end group[2]. This would cause unreliable measurements of PFOS concentrations directly in water samples. Direct measurements could vary depending on position of the pipette for sampling, volume of sample and the size of sampling container.

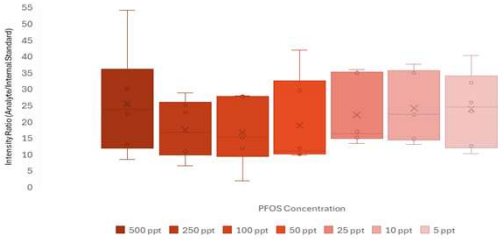

Fig. 4 Box plot showing intensities of low concentration PFOS in water samples (n=6)

Due to the limitations of this method, believed to be caused by the sample diluent, further experiments were conducted using samples and matrices prepared in 100% methanol. This would still allow a possible screening solution for samples following solid phase extraction (SPE), which is part of the accepted protocol for PFAS analysis of water samples.

The use of FlexiFocus slides allows for the use of pure methanol as a solvent in both the sample and the matrix as the hydrophilic anchor and hydrophobic surround prevents the sample spot spreading excessively during drying.

To determine the approximate LLOQ, PFOS samples were prepared across a 1 ppt – 10 ppb range in 100% methanol. The samples were premixed with a 0.5 mg/mL TMGN solution and 1 µL was spotted onto a 96 well FlexiFocus slide and the calibration curves were plotted (Fig. 5, Fig. 6).

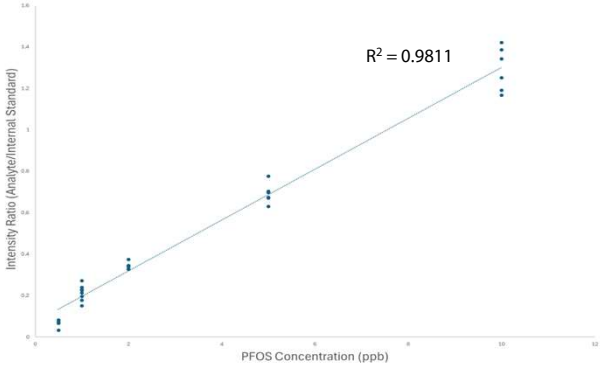

Fig. 5 Calibration Curve for PFOS (500 ppt – 10 ppb) in 0.5 mg/mL TMGN

Below 500 ppt, no linearity could be seen (1 ppt – 500 ppt range, Fig. 6).

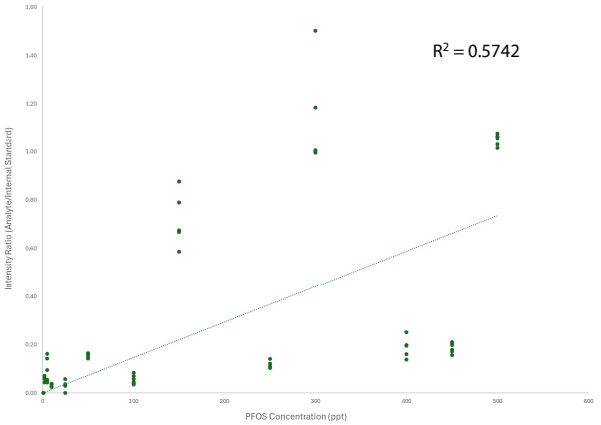

Fig. 6 Calibration Curve for PFOS (1 ppt – 500 ppt) in 0.5 mg/mL TMGN

To determine if the linearity would extend beyond the ULOQ for LC-MS/MS (62.5 ppb from EPA1633, Table 4), thus allowing screening to identify samples requiring additional dilution, PFOS samples were prepared across a 500 ppt – 100 ppb range in 100% methanol. The samples were premixed with a 0.5 mg/mL TMGN solution and 1 µL was spotted onto a 96 well FlexiFocus slide and the calibration curve was plotted (Fig. 7). Representative spectra are shown in Fig. 8.

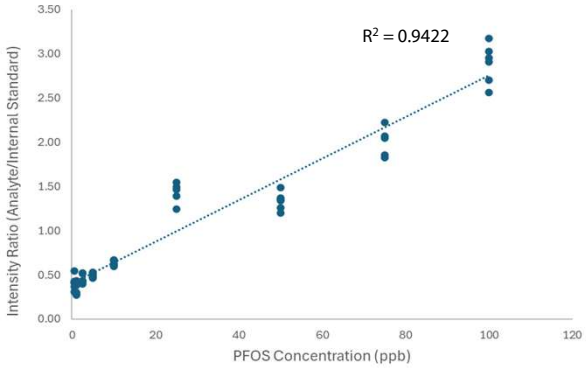

Fig. 7 Calibration Curve for PFOS (500 ppt – 100 ppb) in 0.5 mg/mL TMGN

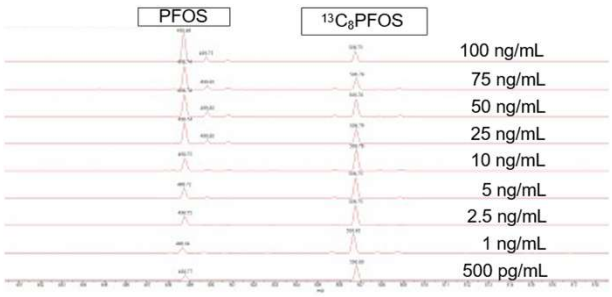

Fig. 8 Representative spectra for PFOS (500 ppt – 100 ppb) in 0.5 mg/mL TMGN

The ULOQ for LC-MS/MS screening (62.5 ppb from EPA1633, Table 4) falls within the linear range for PFOS which allows for semi-quantitative determination of samples requiring additional dilution prior to LC-MS/MS analysis. The R^2 value of 0.94 allows for a good level of confidence in the correct identification of those samples which could potentially result in instrument contamination and downtime, impacting the laboratory throughput.

■ Analysis of PFOA

PFOA was selected for analysis to provide further evidence for the suitability of this method. PFOA samples were prepared across a 1–100 ppb range in 100% methanol. The samples were premixed with a 0.5 mg/mL TMGN solution (100% methanol) and 1 µL was spotted onto a 96 well FlexiFocus slide. When calculating the calibration curve, it was apparent that, at concentrations below 5 ppb, linearity was lost (Fig. 9).

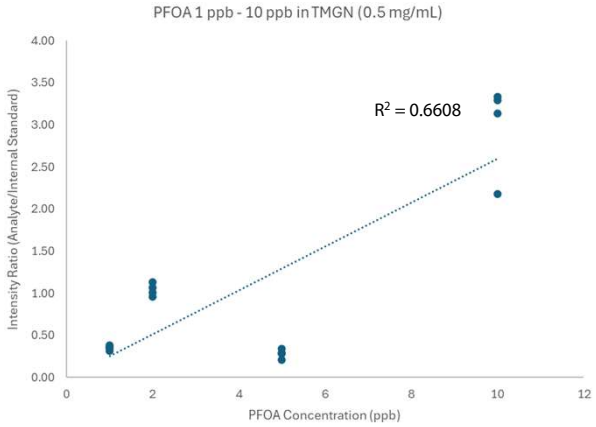

Fig. 9 Calibration Curve for PFOA (1–10 ppb) in 0.5 mg/mL TMGN

The calibration curve for PFOA was then recalculated across the range of 5–100 ppb (Fig. 10). Representative spectra are shown in Fig. 11. The R^2 value of 0.99 across this range again allows for a good level of confidence in the correct identification of those samples which could result in instrument contamination.

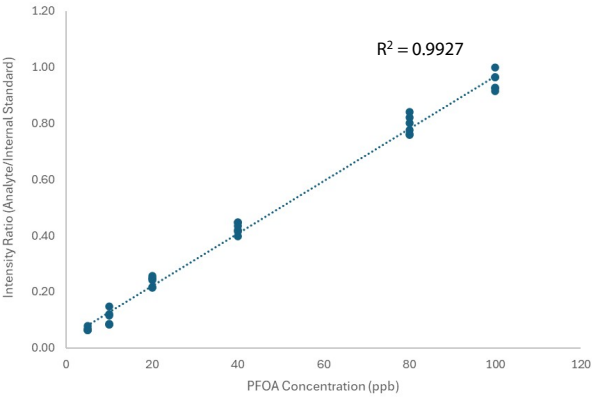

Fig. 10 Calibration Curve for PFOA (5–100 ppb) in 0.5 mg/mL TMGN

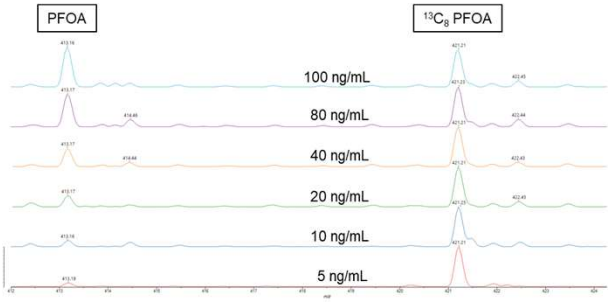

Fig. 11 Representative spectra for PFOA (5–100 ppb) in 0.5 mg/mL TMGN

■ Conclusions

We have shown that it is feasible to implement a fast and simple screening protocol using MALDI-TOF mass spectrometry following the solid phase extraction step for the analysis of PFAS samples, to prevent contamination of instrument hardware in LC-MS/MS workflows.

The use of FlexiFocus slides permits deposition of analytes and matrix primarily composed of methanol. This improves the precision of concentration estimates in comparison with aqueous preparations, although the lower limit for the concentration estimate remains unchanged due to the loss of linearity in the calibration curve.

For water samples, limited solubility introduces uncertainty in concentrations determined by MALDI-TOF mass spectrometry . Therefore, samples should be screened after solid-phase extraction when the samples are reconstituted primarily in methanol.

Whilst limits of detection are lower with the use of FlexiFocus slides, the loss of linearity in the lower concentration range prevents the implementation of screening protocols below approximately 500 ppt for PFOS and 5 ppb for PFOA.

<References>

1. Detection of PFAS in Aqueous Samples by Matrix Assisted Laser Desorption IonisationTime-of-Flight (MALDI-TOF) Mass Spectrometry Application News No. 12-MO-543-EN
2. Tighe, M *et al*, Rapid PFAS removal from water with floating polymer assisted by air bubbles, Chemosphere 377, 2025.

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