EVALUATION OF DESI MOUNTED ON Q-TOF AND TQ MASS SPECTROMETERS TO IMAGE PFAS COMPOUNDS IN DIFFERENT MATRICES

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INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are a well-known group of chemicals that have a variety of commercial and consumer uses. They have been found to be highly persistent and can accumulate in humans, animals and the environment.

Traditionally, analysis of PFAS has focused on determination with LC-MS/MS. Often laborious SPE techniques are required before analysis of solid matrices, such as food, plants or animal tissue to assess exposure routes. Furthermore, samples are homogenized, and therefore the information of where the PFAS accumulate is not available.

Here we evaluate mass spectrometry imaging (MSI) to detect PFAS directly from sample surfaces.
A desorption electrospray ionization (DESI) source combined with two types of Q-Tof mass spectrometers operating in full scan MS (with and without, and a high performance tandem quadrupole mass spectrometer operating in targeted multiple reaction monitoring (MRM) mode were used to evaluate limits of detection (LODs) of several PFAS compounds.

METHODS

Sample preparation

A mixture of PFAS compounds (PFAC30PAR, Wellington Laboratories) containing among others PFHxS, PFOS, PFOA, PFNA, PFDA, FBSA, 6.2FTS, PFBS, FOSA, was used to evaluate LODs between different systems mass spectrometers.

The mixture was diluted in 50:50 MeOH/H_2O to prepare the dilution series from 1 ng/mL (ppb) up to 500 ng/mL with 1 µL spotted onto porcine liver sections, as well as a blank solution. Thin sections such as porcine liver were cut with a cryostat and stored at -80°C.

Lentils were grown in wet cotton balls containing 1 mL of 100 ng/mL of PFAS mixture. Clean pure water was used to keep the cotton wet for 7 days.

Mass spectrometry

Three types of experiments were performed for this study in negative ionization mode:

1) MRM using a tandem quadrupole mass spectrometer Xevo™ TQ Absolute for high sensitivity and specificity
2) Full scan MS using a SELECT SERIES™ MRT spectrometer (a multi -reflecting Q-ToF) with a mass resolution >300,000 FWHM across the lipid mass range and a mass accuracy <500 ppb
3) TOF full scan MS and IMS full scan MS using a SELECT SERIES™ Cyclic IMS spectrometer with scaling ion mobility and IMS^n capability.

The DESI XS source was used on both mass spectrometers with the High-Performance sprayer (HPS) for improved sensitivity, spray focus, robustness and ease-of-use.

The MSI method combined a DESI source with spray conditions set at 2 µL/min, 95:5 MeOH:H_2O (with 100 pg/µL Leu-enkephalin for Q-Tof systems) and 10 psi N_2 nebulizing gas. Capillary voltage was optimized between 0.55 kV and 0.75 kV.

Data management

DESI imaging datasets were mined using MassLynx™ , DriftScope™ as well as processed and visualized using High Definition™ Imaging Software (HDI™) v1.8 (Waters).

RESULTS

A) Dilution series to evaluate LODs of PFAS

To establish the LODs, a dilution series of the PFAS mixture was prepared from 1 ng/mL up to 500 ng/mL with 1 µL spotted onto porcine liver sections. Samples were analyzed using a multi-reflecting Q-Tof (MRT), a Cyclic IMS Q-Tof (in TOF and IMS modes) and a Xevo TQ Absolute MS in negative ionization mode.

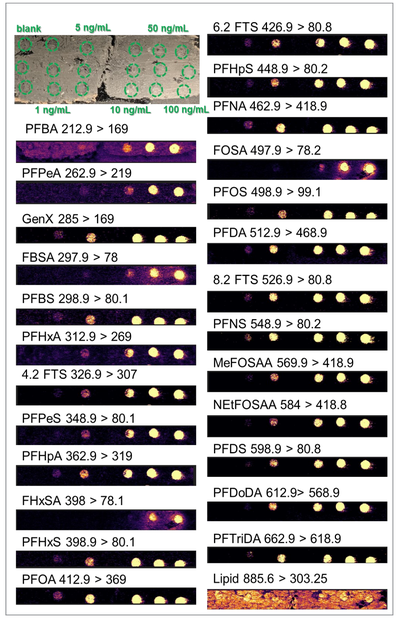

*Figure 1. Ion images of PFAS mix dilution series spotted on porcine liver tissue section from 1 ng/mL up to 100 ng/mL acquired using DES XS on the **Xevo TQ Absolute MS in targeted MRM acquisition mode.***

From the analyses using the DESI MRM TQ system, 1-3 transitions were set for 26 of the most important PFAS compounds in the mixture solution to evaluate the best MRM transition for further MSI experiments.
Acquisitions were performed at 50 µm pixel size, with 20 MRM transitions and with an acquisition speed of 5 Hz.
Only PFTrDS compound was not detected at the highest level of 100 ng/mL.
77% of the PFAS compounds that were monitored with the targeted MRM acquisition were detected at 1-10 ng/mL (figure 1 and table 1).

In full scan MS on the DESI source on the MRT instrument and Cyclic IMS instrument in TOF and IMS mode (one pass in the cyclic device), data were acquired at 100 µm pixel size and with an acquisition speed of 1 Hz.. Respectively, **61% and 54%** of the PFAS compounds were detected lower or equal than 10 ng/mL (figure 2&3 and table 1).

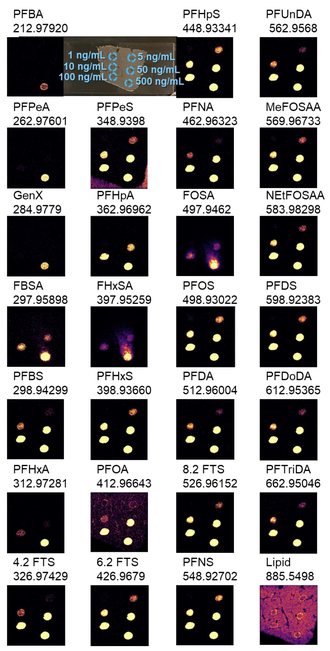

*Figure 2. Ion images of PFAS mix dilution series spotted on porcine liver tissue section from 1 ng/mL up to 500 ng/mL acquired using DES XS on the **SELECT SERIES MRT MS in TOF full scan MS**.*

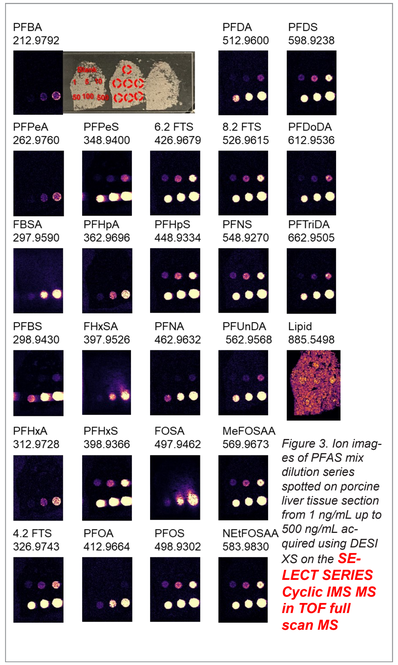

*Figure 3. Ion images of PFAS mix dilution series spotted on porcine liver tissue section from 1 ng/mL up to 500 ng/mL acquired using DESI XS on the **SELECT SERIES Cyclic IMS MS in TOF full scan MS***

B) Advantage of ion mobility separation for PFAS analysis using SELECT SERIES Cyclic IMS.

Interestingly the PFAS compounds have a much faster arrival time by ion mobility separation compared to singly charged tissue or solvent background ions, as seen in figure 4,A), enhancing the overall S/N as seen in figure 4,B for several PFAS compounds such as FHxSA, FBSA, FOSA and PFDS.

Furthermore, several PFAS compounds showed multiple arrival times in the IMS dimension, corresponding in different conformation in the gas phase, putatively corresponding to a linear and branched molecular arrangements (figure 5).

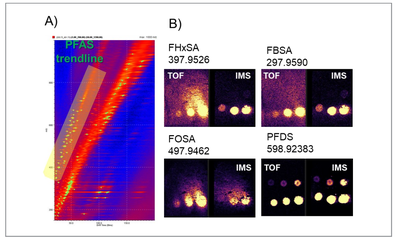

*Figure 4. **DESI Cyclic IMS** 2D plot m/z vs.Dt from Driftscope showing quicker arrival time of the PFAS compounds than other singly charged background. B) Examples of background reduction with IMS for FHxSA, FSBA, FOSA and PDFS.*

Analyte name	TQA LOD (ng/mL)	MRT LOD (ng/mL)	Cyclic IMS LOD (ng/mL)
PFBA	50	500	X
PFPeA	50	500	X
GenX	1	500	X
FBSA	50	100	100
PFBS	5	10	10
PFHxA	50	100	100
4:2 FTS	10	10	5
PFPeS	10	10	5
PFHpA	1	100	100
FHxSA	50	500	100
PFHxS	5	5	5
PFOA	1	50	50
6:2 FTS	1	10	1
PFHpS	10	5	1
PFNA	1	10	50
FOSA	10	50	50
PFOS	5	5	1
PFDA	5	10	50
8:2 FTS	5	10	1
PFNS	5	5	1
N-MeFOSAA	5	10	1
N-EtFOSAA	10	10	1
PFDS	5	10	1
PFDoDA	5	10	5
PFTriDa	1	5	5

*Table 1. LODs for each PFAS with a S/N > 3 when data was acquired on the **Xevo TQ Absolute MS**(MRM mode), **SELECT SERIES MRT MS** (TOF-MS mode) and **SELECT SERIES Cyclic IMS MS** (TOF-MS mode).*

C) PFAS contaminated lentils analyzed using targeted DESI MSI on the Xevo TQ Absolute

The seed and root parts of the 7 day-old lentils were imaged after cryosectioning using CMC at 100 µm thickness. The same number of MRM transitions used during the dilution series experiment were set for this experiment.

Ion images of some of the PFAS detected in the root and seed are displayed in figure 6. It can be seen that PFHxS (398.9 > 80.1) and FHxSA (398 > 78.1) display different accumulation and localization within both the root and the seed of the lentils, highlighting the advantages of using mass spectrometry imaging to study the impact of PFAS distribution in plants (figure 6).

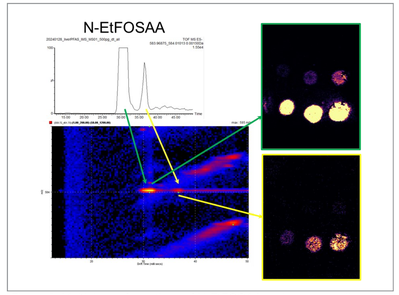

*Figure 5. Multiple conformations of N-EtFOSAA and corresponding specific drift time ion images of the dilution series. Analyzed using **SELECT SERIES Cyclic IMS MS in IMS mode** .*

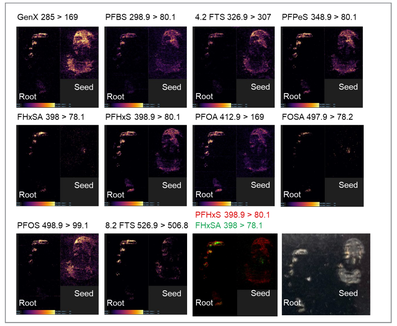

*Figure 6. Ion images of 100 ppb PFAS mixture contaminated lentil root and seed analyzed by targeted MRM using DESI XS on the **Xevo TQ Absolute MS in targeted MRM acquisition mode.***

CONCLUSION

- **61% and 55% of the PFAS compounds were detected as low as 10 ng/mL spotted on tissue when analyzed by negative mode DESI in discovery full scan MS acquisition mode.**
- **The targeted MRM acquisition mode on the DESI XS Xevo TQ Absolute MS is the most sensitive system with 77% of the PFAS compounds detected as low as 10 ng/mL spotted on tissue.**
- **PFAS compounds have a different ion mobility, with faster arrival time in the gas phase, allowing differential selection and a decrease of interference signal.**
- **Different conformations of several PFAS were detected by ion mobility with only a single pass in the cyclic device.**
- **Distinct distributions of PFAS in the seed and root of contaminated PFAS lentils were demonstrated.**

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