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Application of a MRM Database for the Quantitation of Per- and Polyfluoroalkyl Substances (PFAS) in Water Extracts

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Introduction

Per- and polyfluoroalkyl substances (PFAS) are chemicals widely used in consumer products and industry due to their unique and desirable chemical properties. Due to widespread usage and environmental persistence, legacy PFAS are ubiquitous in the environment and new fluorochemicals are being found in the environment frequently. Currently, there are disparate standard methods such as USEPA 533 and 537 for drinking water; and USEPA 8327, ASTM 7979 and ISO methods for non-potable waters. Furthermore, the rapidly evolving and diverse regulatory initiatives across various regions and countries have made it more challenging for laboratories to keep up with these changes while trying to develop comprehensive analytical methods for analysis in different types of matrices. Hence, three MRM databases were developed for the simultaneous analysis of more than 100 native and isotopically labelled PFAS compounds on Ultivo LC/TQ, 6470B LC/TQ and 6495C LC/TQ.

Experimental

Optimization of MRM and Source Parameters

For each PFAS, MRM parameters such as collision energies and fragmentor voltages were optimized using the Optimizer tool in the Agilent MassHunter LC/MS Data Acquisition software. The AJS source parameters were optimized using the Source Optimizer tool.

Calibration Standards

Majority of the PFAS analytical standards and isotopically labeled analogues were purchased from Wellington Laboratories Inc. (Guelph, ON, Canada). The analytical standards were combined to a final mixture in methanol and diluted with 80:20/methanol:water to prepare 12 levels of calibration standards with concentrations mostly ranging from 0.01 to 100 ng/mL. Isotopically labeled analogues mixture was added to each calibration standard to a final concentration of 5 or 40 ng/mL.

Post-spiked Water Matrix Extracts

250 mL of unfortified drinking water, surface water or wastewater was extracted using the protocol described in EPA Method 537.1. The dried extracts were reconstituted with 80:20/methanol:water, spiked with the analytical standard mixture to a final analyte concentration of 2, 8 or 20 ng/mL. Isotopically labeled analogues mixture was added to each sample at same concentrations as the calibration standards.

Experimental

Reducing PFAS Background Contamination

Fluoropolymers such as PTFE and PFA are used in all major (U)HPLC systems and can be a potential source of PFAS contamination. To minimize background contamination, the Agilent PFC-Free HPLC Conversion Kit (P/N 5004-0006) was installed on all the UHPLC systems. This easy-to-install conversion kit includes substitutes for all critical LC system parts containing organic fluorine compounds and a newly developed delay column for delaying potential PFC impurities from the mobile phases.

Instrumental Analysis

All samples were analyzed using Agilent 1290 Infinity II UHPLC systems which were coupled to an Ultivo LC/TQ, 6470B LC/TQ or 6495C LC/TQ operated in negative ionization mode. The injection volumes are 5, 3 and 2 µL, respectively. Chromatographic separation was achieved using an Agilent ZORBAX RRHD Eclipse Plus C18, 2.1 x 100 mm, 1.8 µm column (P/N 959758-902).

Figure 1. Databases are fully integrated with the MassHunter LC/MS Data Acquisition software to facilitate quick development of data acquisition method and expansion of the analyte list.

Results and Discussion

Development of a PFAS MRM Database

- The curated database includes:
  - Intrinsic properties and identifiers such as compound name, molecular formula and CAS number.
  - MRM parameter settings for the acquisition of 72 native and 36 isotopically labelled analytes from several PFAS groups (Figure 2).
  - Retention time information derived from an optimized chromatographic method (Figure 3).
- The database allows for the customization of MRM sub-methods based on a target list of interest or standard methods such as the EPA drinking water methods.
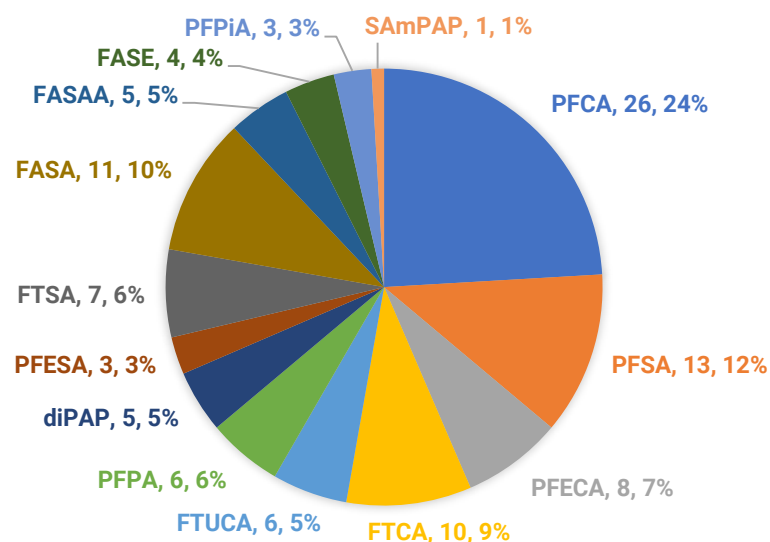

Figure 2. Classification of the analytes in the database (denoted by group, number of PFAS and % of total PFAS).
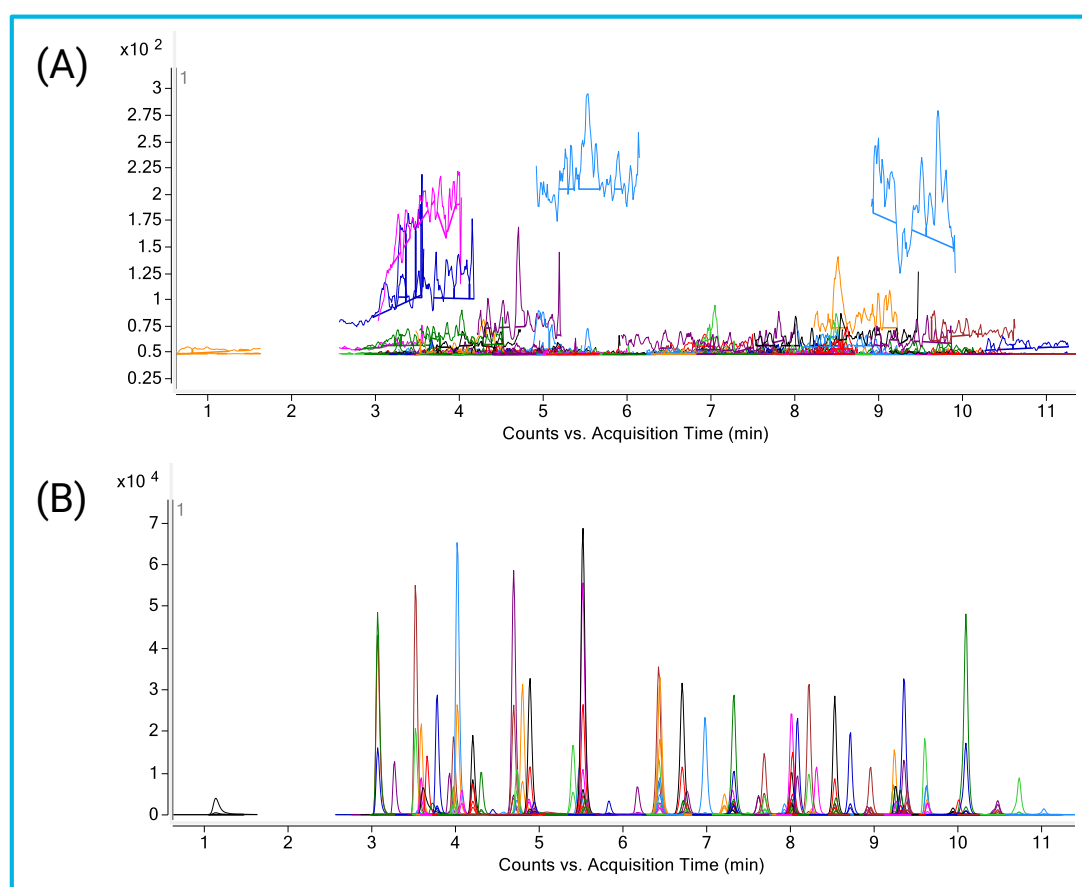

Figure 3. MRM chromatograms of (A) blank solvent (80:20/methanol:water) and (B) drinking water extract post-spiked with 2, 8 or 20 ng/mL of native PFAS.

Analytical range and accuracy

- Majority of the analytes demonstrated a wide analytical range of 3 to 4 orders of magnitude (Figure 4).
- For 6470B LC/TQ and 6495C LC/TQ, all 72 native PFAS had linear calibration curves with $R^2 > 0.99$.
- For Ultivo LC/TQ, all analytes had linear calibration curves with $R^2 > 0.99$ except 10:2 FTCA ($R^2 = 0.98$).
- The accuracy of each point included in the calibration curve range from 71 to 129%, meeting the EPA requirement of 70 to 130%.
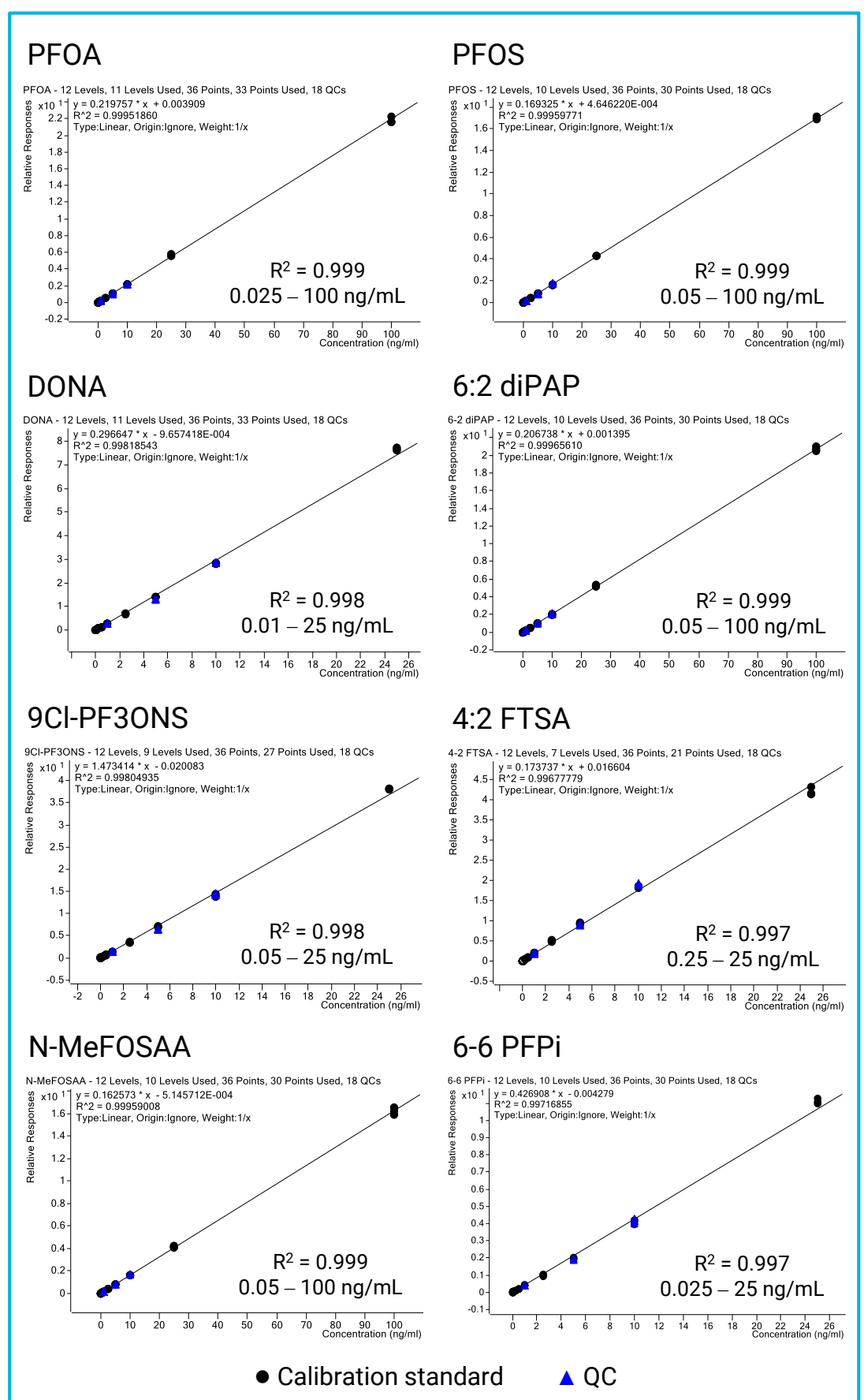

Figure 4. Linear calibration curves (3 injections per CAL) for eight of the PFAS analyzed by 6470B LC/TQ.

Results and Discussion

Instrument detection limits

- Instrument detection limits (IDLs) of the native PFAS were calculated from the 7 repeated injections at the lowest calibration concentration with area RSD ≤ 20%[1].

- IDLs ranged from 3.5 to 7456, 4.9 to 9210 and 2.3 to 250 fg on-column for Ultivo LC/TQ, 6470B LC/TQ and 6495C LC/TQ, respectively.

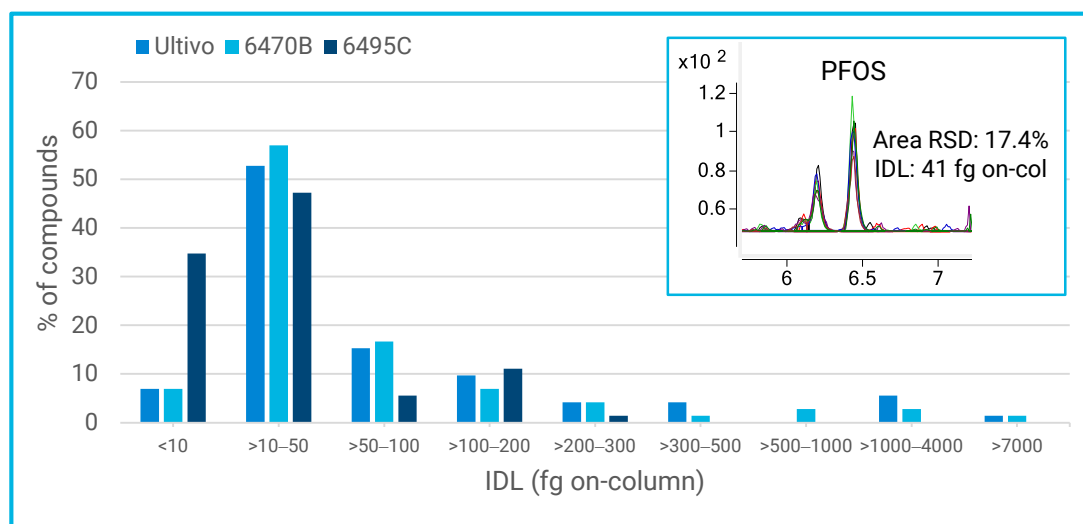- Most IDLs were below the limits of 50 to 5000 fg on-column reported by Gremmel et al.[2] (Figure 5).

Figure 5. Distribution of the IDLs for 72 PFAS in solvent for the three LC/TQ systems. The inset shows the overlay of 7 repeated injections of PFOS at 0.025 ng/mL for calculating its IDL (analyzed by 6470B LC/TQ).

MRM Method Precision

- MRM method precision was assessed by calculating the relative standard deviation (RSD) of retention times (RT) and areas from 10 repeated injections of the post-spiked water matrix extracts.

- RT RSD of the 72 native PFAS in all post-spiked matrix extracts is 0 to 0.82% for the three LC/TQs.

- For drinking water and surface water, area RSDs for all PFAS are 1.9 to 18.5% for the three LC/TQs (Figure 6). In wastewater, area RSDs for most PFAS were less than 18% except for 6 compounds.

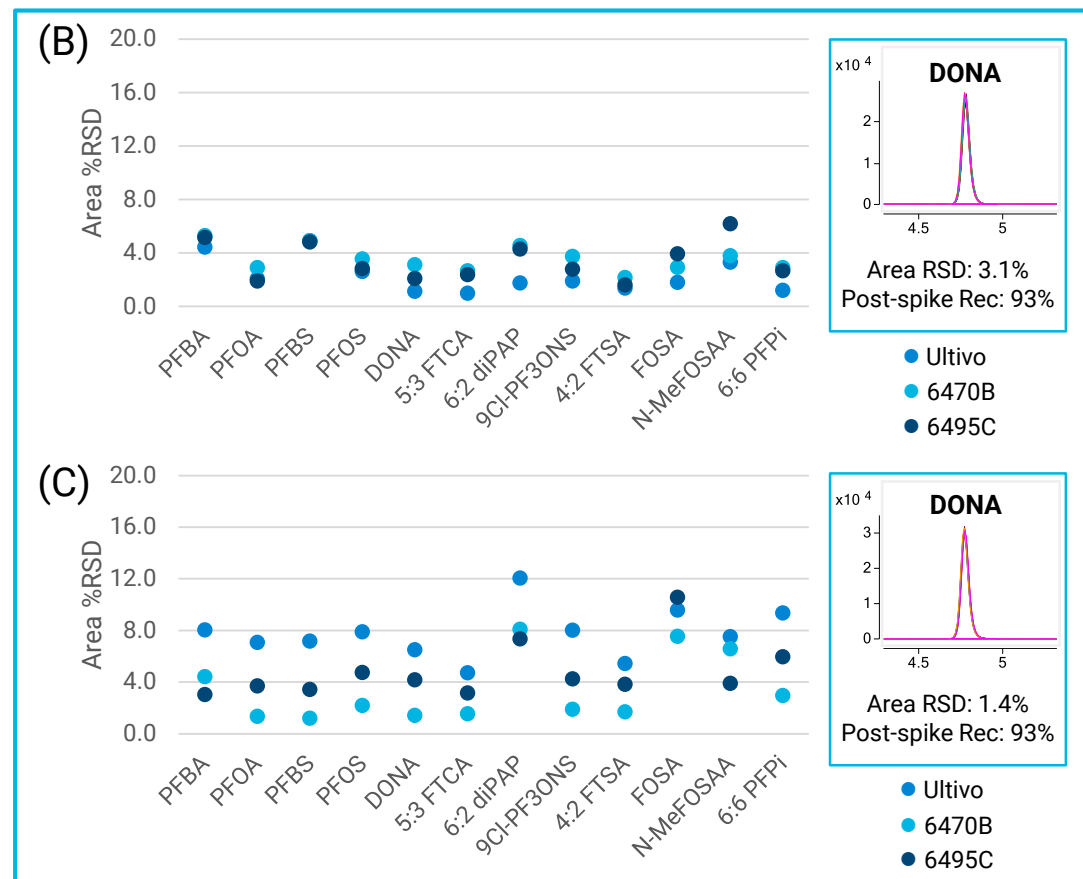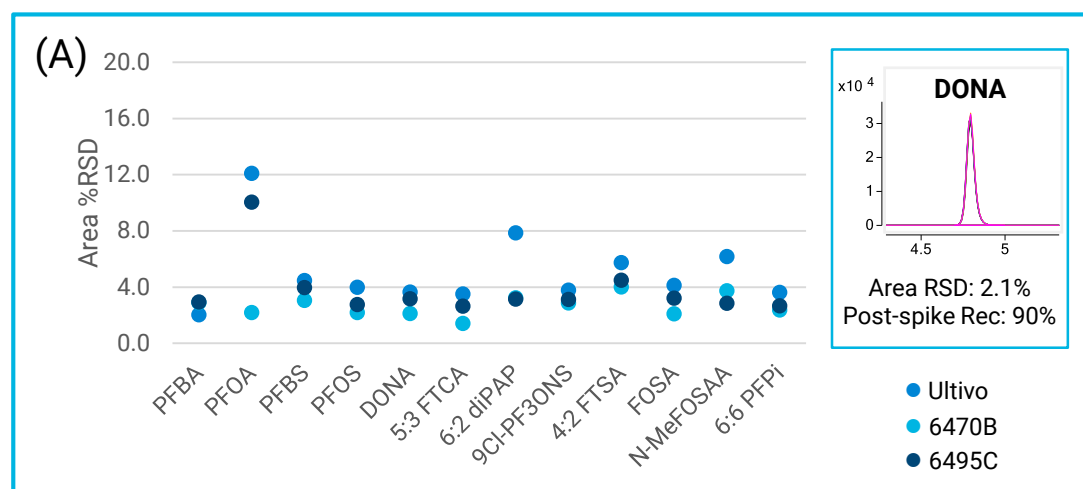- Overall, the MRM method demonstrated good RT and area precision.

Figure 6. Area RSD plot for selected PFAS in post-spiked (A) drinking water, (B) surface water and (C) wastewater extracts. The inset shows the overlay of 10 repeated injections of DONA in each extract type (6470B LC/TQ).

Conclusions

- Three MRM databases were developed for the analysis of more than 100 native and isotopically labelled PFAS on Ultivo LC/TQ, 6470B LC/TQ and 6495C LC/TQ.

- The in-house verification study showed that the developed MRM method demonstrated good sensitivity, linearity and reproducibility for the analysis of PFAS in post-spiked environmental water extracts.

- The databases could facilitate the quick creation of targeted screening or quantitative methods for a more comprehensive targeted PFAS analysis.

References

[1] Coggan LC, et al. A single analytical method for the determination of 53 legacy and emerging per- and polyfluoroalkyl substances (PFAS) in aqueous matrices. Anal Bioanal Chem. 2019, 411(16), 411(16)

[2] Gremmel C, et al. HPLC-MS/MS methods for the determination of 52 perfluoroalkyl and polyfluoroalkyl substances in aqueous samples. Anal Bioanal Chem. 2017, 409(6),1643-1655

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