An Integrated Solution for Over 100 PFAS Compounds in Drinking and Surface Water by Triple Quadrupole LC/MS

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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.[1] US EPA, ASTM and ISO standard methods continue to expand target lists to incorporate emerging compounds as more is learned about the impact of these compounds. These changes put laboratories under pressure to develop expanded methods quickly to stay relevant. Here, a comprehensive workflow using solid phase extraction (SPE) and LC/MS/MS was developed based on Agilent PFAS MRM Database for the analysis of more than 100 native and isotopically labelled PFAS in water matrices.

Experimental

Calibration Standards

Native and isotopically labeled PFAS analytical standards were purchased as individual stock solutions, solution mixes, or powdered standards from Wellington Laboratories Inc. (Guelph, ON, Canada) and Toronto Research Chemicals (Toronto, 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. Isotopically labeled analogues mixture was added to each calibration standard.

Experimental

Instrumentation

Chromatographic separation was achieved using an Agilent ZORBAX RRHD Eclipse Plus C18, 2.1 × 100 mm, 1.8 µm column installed on an Agilent 1290 Infinity II UHPLC system with the Agilent PFC-Free HPLC Conversion Kit to minimize background PFAS contamination. This kit includes substitutes for all critical LC system parts containing organic fluorine compounds and a newly developed PFC delay column for delaying potential per- or polyfluorochemicals impurities from the mobile phases.

A 12-minute gradient elution was performed with 5 mM ammonium acetate in water (mobile phase A) and methanol (mobile phase B) at 0.4 mL/min with a total run time of approximately 18 minutes (injection to injection).

Dynamic MRM (dMRM) analysis was performed using a 6470 LC/TQ with an Agilent Jet Stream (AJS) ion source operated in negative ionization mode. The LC/TQ autotune was performed in unit mode.

Sample Preparation

Solid phase extraction (SPE) was performed using Agilent SampliQ Weak Anion Exchange (WAX), 6 mL, 150 mg cartridges (part number 5982-3667), which were conditioned with different solvents. To prepare matrix spike samples, an appropriate amount of native PFAS spike mix solution was added at low concentration spike level (5 to 50 ng/L) and high spike level (20 to 200 ng/L). Unspiked matrix samples (matrix blank) were prepared by omitting the addition of PFAS spike mix solution. Sample preparation is illustrated in Figure 1.

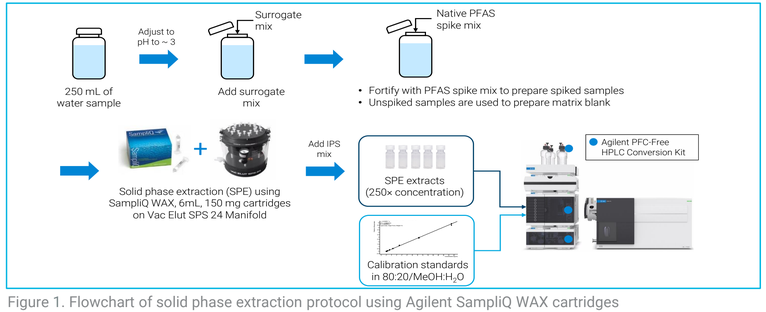

Figure 1. Flowchart of solid phase extraction protocol using Agilent SampliQ WAX cartridges

Results and Discussion

Agilent PFAS MRM Database for LC/TQ

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 14 PFAS groups for all current Agilent LC/TQ models (Figure 2).
- Retention time information derived from an optimized chromatographic method (Figure 3).

In this study, the MRM transitions and optimized MS parameters of all 108 analytes were exported from this database using the MassHunter LC/MS Data Acquisition software to create the acquisition method. 71 native PFAS were set up as targeted analytes, the rest were used as surrogates or internal standards.

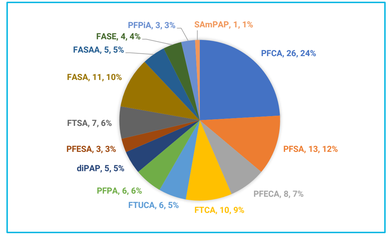

Figure 2. Classification of the analytes in the database (denoted by group, number of PFAS and % of total PFAS).

Background interference

In this study, the use of the Agilent PFC-Free HPLC Conversion Kit effectively reduced the background PFAS contamination as the routine analyses of instrument blank (gradient program with no injection) and solvent blanks (80:20 methanol:water) had no detectable PFAS peaks. In addition, evidence of low system background is demonstrated by injecting a laboratory reagent blank (LRB) immediately after the highest calibration standard.

The LRB is prepared from 250 mL of ultrapure water spiked with surrogate mix and processed using the same SPE protocol as the matrix blank samples. Trace levels of a few PFAS were seen in the LRB, but their concentrations were all below MDLs. Thus, demonstrating that there was minimal contamination from lab equipment, reagents, glassware, or extraction apparatus.

Analytical range and accuracy

For each PFAS compound except FTSAs, the calibration curve was generated using linear regression by forcing it through the origin with 1/x weighting. (Quadratic regression was used for FTSAs.)

- Majority of the analytes demonstrated a wide analytical range of 3 to 4 orders of magnitude (Figure 3).
- All 71 analytes had linear calibration curves with $R^2 > 0.99$ on 6470 LC/TQ
- The accuracy of each point included in the calibration curve range from 71 to 129%, meeting the EPA requirement of 70 to 130%.

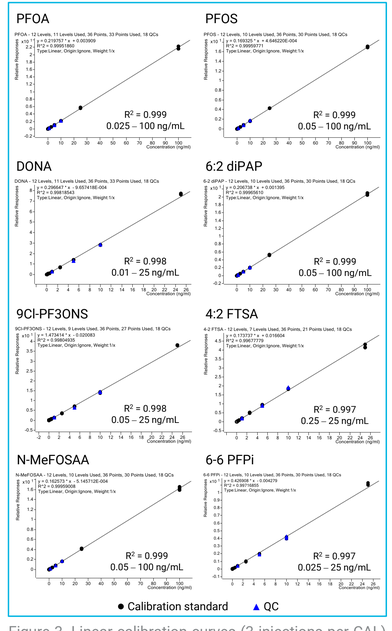

Figure 3. Linear calibration curves (3 injections per CAL) for eight of the PFAS analyzed by 6470 LC/TQ.

Results and Discussion

Method sensitivity

The method sensitivity was assessed by calculating method detection limits (MDLs) based on the procedure described in 40 CFR Part 136 Appendix Revision 2. [2]

- Method detection limits (MDLs) of the native PFAS were calculated from the 7 seven replicates of 250 mL of ultrapure water spiked with a PFAS spike mix solution containing native PFAS at 1 to 25 ng/L with area RSD ≤ 20%.
- MDLs ranged from 0.14 to 14 ng/L for 60 PFAS on 6470 LC/TQ as shown in Figure 4.

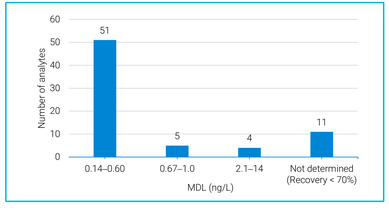

Figure 4. Distribution of the MDLs for all PFAS in ultrapure water samples on 6470 LC/TQ system.

Figure 5 shows the overlay of the MRM chromatograms of seven technical replicate analyses of pre spiked samples with 1 ng/L of PFOS and HFPO-DA, which demonstrates good overall sensitivity despite compromising on source parameters for some analytes.

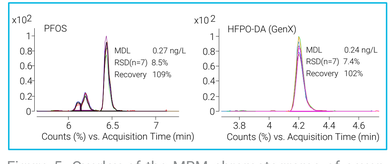

Figure 5. Overlay of the MRM chromatograms of seven technical replicate analyses of pre spiked samples with 1 ng/L of PFOS and HFPO-DA

Interbatch method precision and recovery

The interbatch precision and recovery for 60 PFAS analytes in drinking water were within the acceptable limits of 2.9 to 16.7% RSD and 76 to 119%, respectively. The interbatch precision for 60 PFAS in surface water ranged from 1.6 to 19.9% RSD with recovery of 72 to 120%.

Method robustness

Method robustness was assessed by analyzing 300 continuous injections of high spike surface water samples (20 to 200 ng/L) across a continuous batch spanning 93 hours on the unattended instrument. Ten analytes were selected to represent nine different PFAS groups. A good response ratio reproducibility RSD of ≤3.1% and RT RSD of ≤0.10% was observed for the ten analytes, demonstrating the sustainable performance of the LC/TQ method for day-to-day operation (Figure 6).

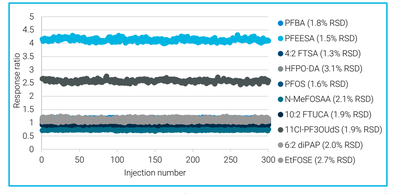

Figure 6. Response ratio of the 10 PFAS, over 93 hours of continuous injections of high spike surface water sample.

Conclusions

- Target quantitative method was developed based on Agilent PFAS MRM database for the analysis of more than 100 native and isotopically labelled PFAS on 6470 LC/TQ.
- The study showed that the developed LC/TQ method demonstrated good linearity, precision and sensitivity where most analytes had MDLs at low to sub-ng/L concentrations in water matrices. The method is available as an eMethod: *PFAS in Drinking and Surface Water by LC/TQ* (part number G5285AA).

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. US EPA. Definition and Procedure for the Determination of the Method Detection Limit, Revision 2. EPA 821-R-16-006, December 2016.

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