QUECHERS EXTRACTION OF PER-AND POLYFLUOROALKYL SUBSTANCES (PFAS) FROM EDIBLE PRODUCE WITH SENSITIVE ANALYSIS ON XEVO TQ-XS

Hannah Willmer[1], Kari Organtini[2], Simon Hird[1], Stuart Adams[1]
[1]Waters Corporation, Wilmslow, United Kingdom; [2]Waters Corporation, Milford, MA, USA

INTRODUCTION

The environmental impact of per- and polyfluoroalkyl substances (PFAS) is readily known from the prevalent usage of these compounds in everyday products. They have been used extensively for decades in manufacturing processes, consumer products, and firefighting foams, leading to the release of these pollutants into the environment.

Often, environmental issues also impact our food sources. Cultivating produce using PFAS contaminated water and soils can lead to the uptake of these compounds into the edible fruits and vegetables portions of plants. Studies show that edible plants do uptake PFAS, with higher uptake of short chain PFAS (PFBA and PFPeA) in the edible portions and a wider range of PFAS uptake in the roots and stalks/stems of the plants. Since irrigation water is most typically also drinking water or ground water, contamination can be introduced through any of the environmental contamination pathways (manufacturing discharge, firefighting foam, landfill leachate, etc). Soil contamination can occur from similar mechanisms, but the use of biosolids as fertilizers has become a major concern for crop contamination.

Although some countries impose regulatory or advisory limits on the concentration of PFAS in water, limits for PFAS have yet to be set in biosolids or food. The most recent report published in 2020 by the European Food Safety Authority (EFSA) concluded that, of the 27 PFAS evaluated, fish, fruit, and eggs contributed the highest levels of exposure. The US Food and Drug Administration (FDA) monitor contaminants in highly consumed foods in their Total Diet Study, and have begun to include PFAS in their market basket studies of food commodities.

Thus, it is beneficial to have a straightforward method to monitor the occurrence of PFAS in produce. For this work, the FDA C-010.01 method based on the QuEChERS extraction method was implemented for extraction of PFAS using DisQuE dispersive solid phase extraction (dSPE) products followed by highly sensitive LC-MS/MS analysis.

The method was evaluated in five different commodity types including lettuce, strawberry, cranberry, carrot, and potato. With a few minor adjustments to the FDA method, this approach to PFAS analysis in produce proved to be accurate and robust for a range of 30 PFAS compounds of varying chemistry classes.

SAMPLE PREPARATION METHOD

QuEChERS (Quick, Easy, Cheap, Effective, Rugged, Safe) is a widely used extraction technique first created for extraction of pesticides from food and is often adopted for determination of other contaminants. This technique uses salts and acetonitrile to extract compounds of interest through a salting out and phase separation mechanism.

Produce samples were purchased at a local grocery store. Strawberries, cranberries, romaine lettuce, whole carrots, and russet potatoes were used in this study. The edible portions of each produce item were homogenized using a Ninja kitchen blender. Samples were stored in a freezer (-20°C) and thawed in a refrigerator (4°C) overnight prior to extraction.

5 grams of each sample were extracted using DisQuE AOAC QuEChERS salts. A suite of 20 isotope labeled standards purchased from Wellington Laboratories (MPFAC-24ES + M3HFPO-DA) were spiked into each 5-gram sample as surrogates prior to extraction at a concentration of 1 ng/g. MPFAC-C-IS was spiked into each sample prior to injection as an internal standard at a final concentration equal to 1 ng/g (0.5 ng/mL in vial).

LC-MS/MS METHOD

LC-MS/MS quantification of PFAS analogues was performed using a Waters Xevo™ TQ-XS triple quadrupole Mass Spectrometer (ESI-).

Chromatographic separation was achieved using an ACQUITY™ I-Class UPLC™ PLUS system fitted with the PFAS Analysis Kit, an ACQUITY UPLC BEH C18 2.1 x 100 mm, 1.7 µm column (35 °C) with a gradient flow rate.

Mobile phases: Water: Methanol (95:5) containing 2 mM ammonium acetate (Mobile Phase A)Methanol containing 2 mM ammonium acetate (Mobile Phase B).

Total analysis time was 22 minutes, with MRM conditions for each PFAS compound optimized using MassLynx™ Software and the QuanOptimize tool.

RESULTS

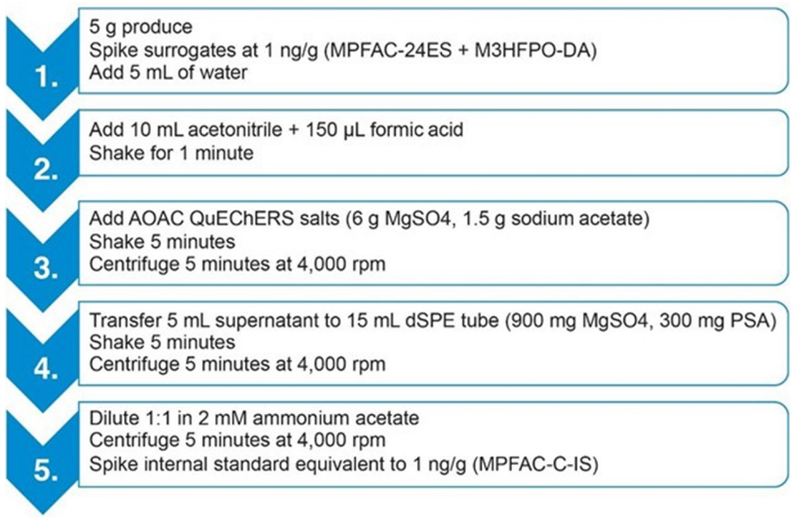

Figure 1. Full QuEChERS method for extraction of PFAS from produce samples using DisQuE AOAC salts (p/n: 186006812) and 15 mL dSPE tubes (p/n: 186008077).

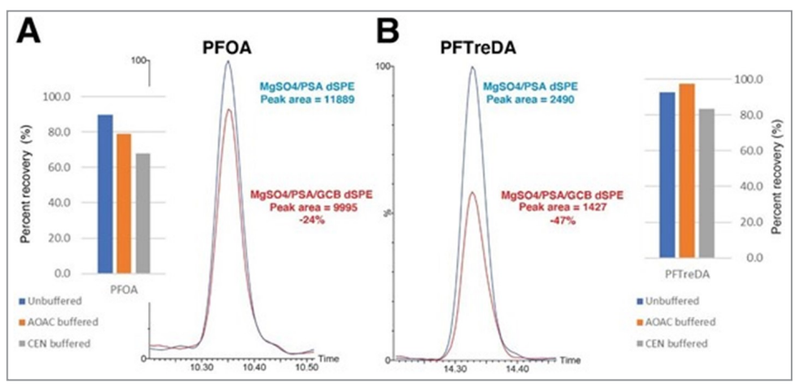

Figure 2. Evaluation of different QuEChERS salts represented as recovery in bar graphs and the effects of including GCB in the dSPE cleanup shown in peak overlays. (A) results for PFOA and (B) PFTreDA.

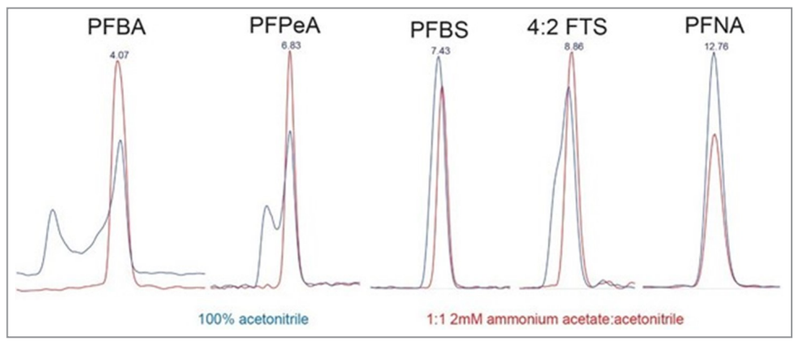

Figure 3. Demonstration of the peak shape correction gained from sample dilution. Blue peaks are undiluted samples and red peaks are diluted 1:1 with 2 mM aqueous ammonium acetate.

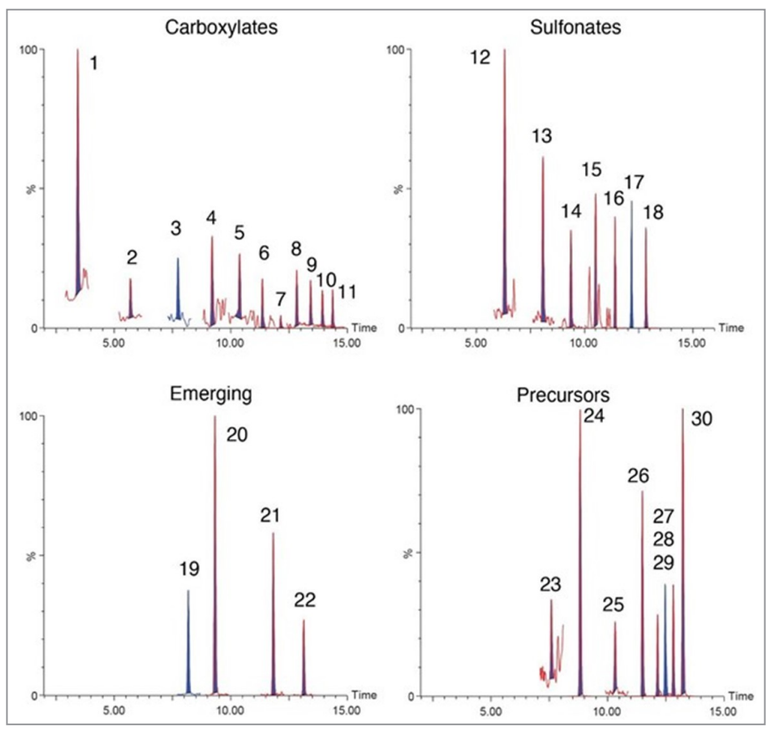

Figure 4. Extracted ion chromatograms of the quantitation ion for each PFAS in the 0.1 ng/g spike in potato

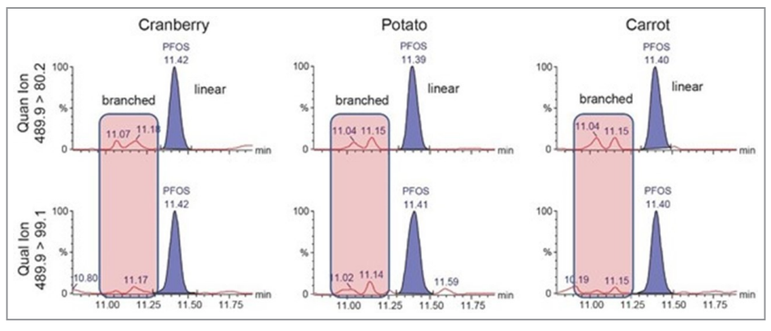

Figure 5. Detection of branched and linear PFOS isomers in 0.05 ng/g cranberry, potato, and carrot matrix.

CONCLUSIONS

- **The QuEChERS extraction was fast and easy, utilizing small sample amounts and small volumes of organic solvents.**
- **Modifications to basic FDA method were shown to improve method performance: use of buffered salts allows for use of readily available materials; removal of GCB graphitized carbon black) improves recovery of long chain PFAS: addition of a dilution step prior to analysis improves peak shape of early eluting PFAS.**
- **The suite of chemicals evaluated was successfully expanded from the 16 listed in FDA C0101-01 to 30 PFAS compounds including: Carboxylates: C4–C14; Sulfonates: C4–C10; Emerging: GenX, ADONA, 9Cl-PF3ONS, 11Cl-PF3OUdS; Precursors: FBSA, FHxSA, FOSA, NMeFOSAA, NEtFOSAA, 4:2 FTS, 6:2 FTS, 8:2 FTS.**
- **Sensitive analysis on the Xevo TQ-XS Mass Spectrometer successfully detected PFAS at sub-ng/g levels to match detected concentrations published in reports by EFSA and FDA**
- **Recovery of the target PFAS from 5 produce matrices using isotopic internal standards to correct for any matrix effects, were in the range of 62–135%, with mean recoveries of 72–113%. FDA guidance states an acceptable recovery range of 40–120% for concentrations at 1 ng/g and a maximum % RSD of 22%. The reported recoveries fall into this acceptable range, with only a few outliers above 120% at the low spiked concentration.**
- **Analysis using Xevo TQ-XS Mass Spectrometer coupled to an ACQUITY UPLC I-Class PLUS, modified with PFAS Kit for LC modification to isolate possible system and solvent contaminants ensures accurate and reliable results.**
- **The application demonstrates high confidence in results for a rapid and easy analysis of PFAS in edible produce to allow for better monitoring and understanding of the environmental impact of PFAS on our food sources.**

TO DOWNLOAD A COPY OF THIS POSTER, VISIT WWW.WATERS.COM/POSTERS