TOTAL WORKFLOW FOR THE SENSITIVE ANALYSIS OF PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS) IN FISH, MEAT, EDIBLE OFFAL AND EGGS

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INTRODUCTION

Rising concerns about the long-term impacts of human exposure to per- and polyfluoroalkyl substances (PFAS) have propelled the scope of PFAS analysis from just environmental matrices into the field of food analysis as well. Over the last decade, cases of PFAS contamination being found in foods such as, but not limited to, eggs, milk, chocolate cake and fast-food have become more prominent in the media. In order to protect the public and understand dietary exposure, analytical methods for the analysis of a large variety of food products are required. Complex food commodities such as fish, meat, edible offal, and eggs require a comprehensive sample extraction and clean up. To accommodate these types of samples, an alkaline digestion and extraction was implemented followed by Weak Anion Exchange (WAX) SPE to produce a suitable sample for analysis. The method was evaluated in six different commodity types including salmon, tilapia, ground beef, beef liver, beef kidney, and chicken eggs. This approach proved to be accurate, sensitive and robust for a range of 30 PFAS compounds of varying chemistry classes to match the challenging concentrations published in reports by EFSA and the FDA.[1,2]

METHOD

Samples of frozen salmon, frozen tilapia, ground beef, beef liver, beef kidney, and whole chicken eggs were purchased from local grocery stores. Fish and meat were homogenized using a kitchen blender. After removing from the shell, the egg white and yolk were mixed before subsampling. Samples were prepared using the method detailed in **Figure 1**.

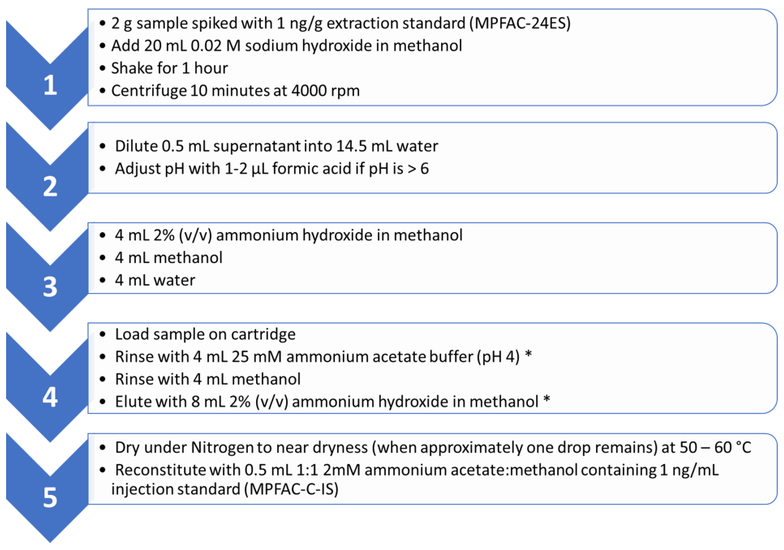

Figure 1. Sample preparation procedure for all food samples tested.

LC-MS/MS Conditions

LC System:	ACQUITY™ UPLC™ I-Class Plus System fitted with PFAS Kit
Column:	ACQUITY BEH™ C18 2.1 x 100 mm, 1.7 µm Column
Column Temp:	35 C
Sample Temp:	10 C
Injection Volume:	10 µl
Mobile Phase A:	Water + 2 mM ammonium acetate
Mobile Phase B:	Methanol + 2 mM ammonium acetate
MS System:	Xevo™ TQ-XS Mass Spectrometer
Ionization Mode:	ESI-
Capillary Voltage:	0.5 kV
Desolvation Temp:	350°C
Desolvation Gas Flow:	900 L/hr
Cone Gas Flow:	150 L/hr
Source Temperature:	100°C

RESULTS AND DISCUSSION

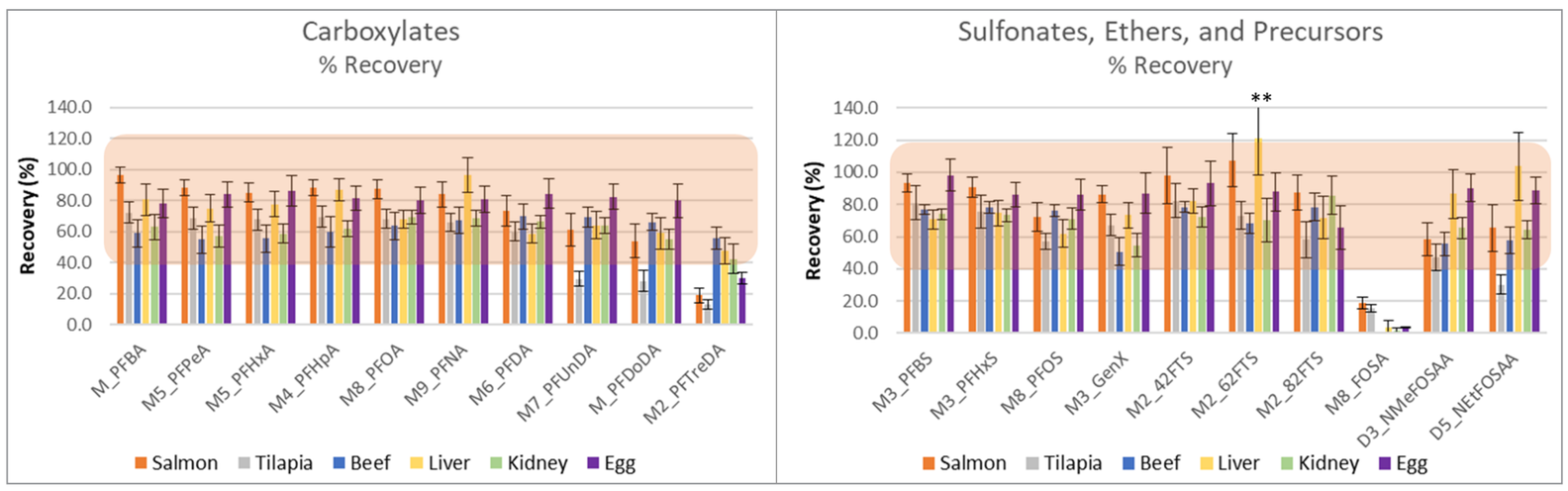

*Figure 2. Percent recovery in each matrix evaluated.**143% standard deviation shown off scale. Orange highlight demonstrates the FDA guidelines for recovery at 1 ng/g (40 – 120%).*

The method was evaluated using five replicates of each commodity spiked at 3 concentration levels; 0.1 ng/g, 1.0 ng/g, and 5 ng/g. The isotope labelled extraction standards were used to evaluate method recovery due to lack of a truly blank matrix. Recovery values are shown in Figure 2, with standard deviation for n=15 extracts. The neutral sulfonamides are not recovered using the WAX SPE protocol as they are lost to waste during the methanol wash step required to remove matrix, resulting in the low recoveries in Figure 2 for $^{13}C_8$-FOSA. Alternate SPE using the Oasis™ HLB Cartridge can be utilized if recovery of the sulfonamides is required, but is not suitable for the full range of PFAS compounds covered in this study. Besides the sulfonamides, the long chain carboxylates were difficult to recover from egg, salmon, and tilapia, resulting in recoveries below the FDA guidelines of 40%. Additionally, NEtFOSAA had recovery of 30% in tilapia. Besides these particular problematic compounds, the remaining PFAS recoveries were within the FDA recovery guidelines of 40-120%.

In addition, NIST standard reference material 1947, Lake Michigan Fish Tissue, was extracted and analyzed to gauge the accuracy of the method. This reference material reports NIST determined concentrations for four PFAS (PFNA, PFDA, PFUnDA, PFTriDA). During analysis, n=8 replicates of NIST 1947 were extracted and analyzed and the comparison data is reported in **Figure 3.** While the uncertainty values aren't available for the NIST SRM, the experimental results are not significantly different to the NIST values, further demonstrating method accuracy.

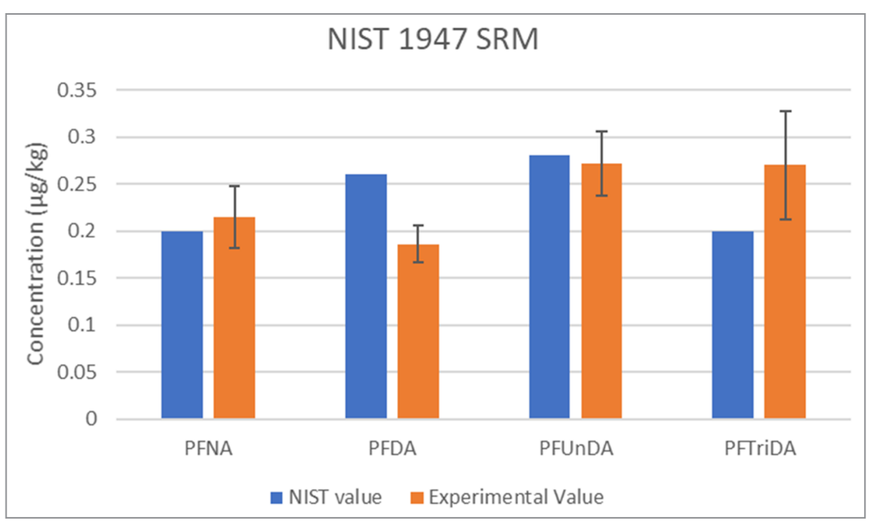

Figure 3. Comparison of NIST reported values to experimental values of four PFAS in NIST 1947 SRM, Lake Michigan Fish Tissue (n=8)

PFAS	Liver (ng/g)	Egg (ng/g)
PFOS linear	0.52	-
PFOS branched	0.24	-
PFOS (total)	0.76	-
PFPeA	-	0.18
PFHxA	-	0.25
PFHpA	-	0.29
PFOA	-	0.13

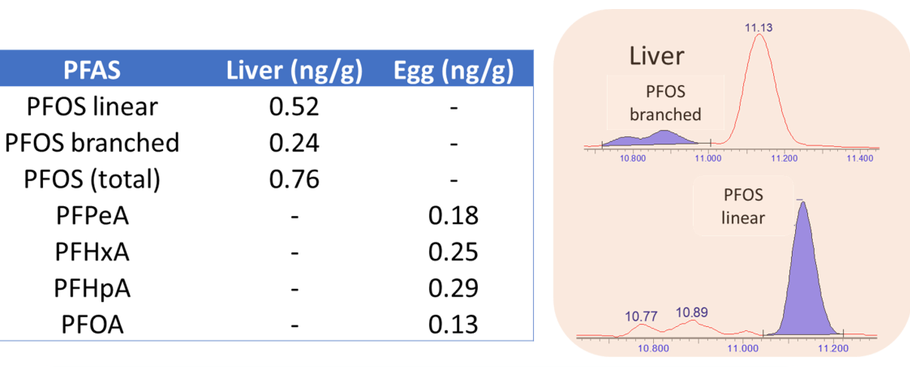

Figure 4. PFAS detected in samples of beef liver and egg purchased in local grocery stores.

Finally, there were detectable amounts of PFAS in the chicken egg and beef liver samples used in this study that were able to be confidently identified and quantified (Figure 4). Beef liver contained 0.76 ng/g PFOS (0.52 ng/g linear, 0.24 ng/g branched), whereas chicken eggs contained PFPeA, PFHxA, PFHpA, and PFOA in amounts of 0.18, 0.25, 0.29 and 0.13 ng/g, respectively.

REFERENCES

1. EFSA Panel on Contaminants in the Food Chain (EFSA CONTAM Panel), Schrenk D, Bignami M, et al. Risk to human health related to the presence of perfluoroalkyl substances in food. EFS2. 2020;18(9).
2. Food and Drug Administration. Analytical results of testing food for PFAS from environmental contamination. June 2021 [cited 2021 December 15]. Available from: https://www.fda.gov/food/chemical-contaminants-food/analytical-results-testing-food-pfas-environmental-contamination

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