Determination of 30 PFAS in Eggs, Produce, Seafood, Protein Powder, and Baby Food by LC-MS/MS

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1. Introduction

Foods contaminated with PFAS pose a risk to the public, particularly in products consumed in relatively high quantities like eggs and produce, as supplements, or meant for children. As PFAS have been linked to serious health effects, accurate testing methods are needed. In this work, we describe a single laboratory validation study with a rapid extraction of low concentrations of 30 PFAS in eggs, produce, seafood, protein powder and baby food. Preparation using QuEChERS was followed by analysis using the Shimadzu Nexera Liquid Chromatograph coupled to a Shimadzu LCMS-8060NX triple quadrupole mass spectrometer (Figure 1).

In this study, we spiked samples at four concentrations in triplicate. Standards were matrix-matched and extracted, spikes were quantified using isotope dilution. Recovery and precision were compared to the requirements of AOAC SMPR 2023.003. All recovery, precision, and LOQ's met the acceptance criteria of the SMPR; including the stricter requirements for EU-regulated compounds in eggs, and the strictest requirements of the SMPR in produce and baby foods.

We optimized the chromatography to achieve excellent peak shape, separation, and sensitivity within nine minutes (Figure 2). Instrument operating parameters were adjusted for maximum signal to noise of PFOA, PFHxS, PFNA, and PFOS (Figure 3).

2. Methods

Eggs, carrots and shrimp were first individually ground in dry ice before being spiked in triplicate at four concentrations. Protein powder and baby food were sampled from their original packaging to prepare for spiking. Test portions were spiked in triplicate for the calibration with 30 native PFAS and 16 isotopically labeled internal standards.

Ten-gram portions were weighed, spiked with target analytes and internal standards, and 10 mL of acetonitrile was added. The samples were shaken and a QuEChERS packet was added. After cooling and centrifugation, an aliquot of the acetonitrile layer was transferred to a tube and diluted with PFAS-free reagent water. The sample was passed through WAX Solid Phase Extraction (SPE) cartridge and the PFAS were eluted with basic methanol. For greater sensitivity, the extract was concentrated in a methanol-water mixture. All samples were prepared as outlined. Details of sample preparation are further described in application news dedicated for each sample type.

Fig. 1 Nexera™ and LCMS™ -8060NX

Mass spectrometry was performed on a Shimadzu LCMS-8060NX with heated electrospray ionization in negative mode. Chromatography was adjusted to provide sufficient separation of PFOA from potential cholic acid interferences, and to provide baseline resolution of isomers.

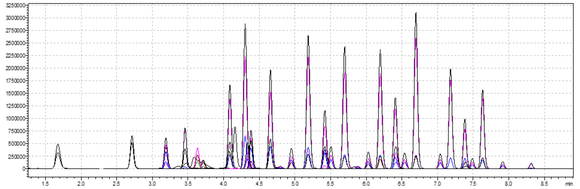

Fig. 2 Chromatogram of 0.55 ng/g PFAS in a seafood matrix with separation of all peaks in nine minutes.

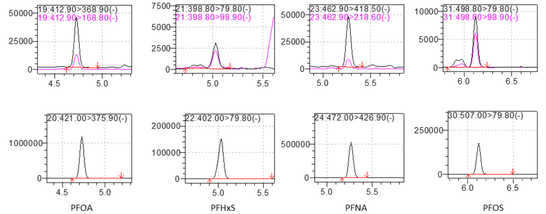

Fig. 3 LOQ peaks with internal standards in protein powder for PFOA, PFHxS, PFNA, and PFOS.

3. Results

Calibration standards were processed the same as samples. A linear model provided the best fit and best recoveries of analytes. Residuals of each point in the curve were ±25% of the expected value. Branched and linear isomers of PFHxS and PFOS were integrated together. Blank matrixes and four different concentrations ranging from below the SMPR required LOQ up to 500 times the estimated LOQ were analyzed in triplicate, depending on the matrix. Recovery and repeatability for each analyte at LOQ are given in Table 1 for eggs. Recovery and repeatability for PFOA, PFNA, PFOS and PFHxS at each spike concentration is given for baby food and produce in Table 2 and 3, respectively. These compounds are highlighted, as they have the strictest LOQ requirements in the SPMR. Recovery and repeatability data for the remaining 26 PFAS, can be found in application news corresponding to this poster.

Table. 1 Recovery and repeatability at the LOQ of PFAS in egg.

Analyte	Spike conc. (ppb)	Average conc. (ppb)	%RSD	Average Recovery %
PFBA	0.055	0.051	1.48	93.3
PFPeA	0.0055	0.006	9.67	108.4
PFHxA	0.0055	0.005	4.82	93.8
PFHpA	0.0055	0.005	4.62	94.9
PFOA	0.0055	0.005	6.19	88.9
PFNA	0.0055	0.005	1.67	99.1
PFDA	0.0055	0.005	3.91	93.7
PFUnA	0.0055	0.005	3.35	95.5
PFDoA	0.0055	0.004	16.81	71.7
PFTrDA	0.0055	0.005	10.21	90.2
PFTeDA	0.0055	0.006	21.48	112.3
PFBS	0.0055	0.004	10.25	75.4
PFPeS	0.0055	0.005	18.11	97.6
PFHxS	0.0055	0.006	19.16	111.7

Analyte	Spike conc. (ppb)	Average conc. (ppb)	%RSD	Average Recovery %
PFHpS	0.0055	0.005	2.98	98.3
PFOS	0.0055	0.006	5.28	98.1
PFNS	0.0055	0.005	11.84	86.7
PFDS	0.0055	0.005	2.47	91.3
PFUnDS	0.0055	0.005	5.03	88.9
PFDoS	0.0055	0.004	11.46	67.5
PFTrDS	0.055	0.045	2.25	82.5
PFOSA	0.0055	0.005	12.42	81.5
9Cl-PF3ONS	0.0055	0.006	6.82	100
11Cl-PF3OUdS	0.0055	0.006	4.23	116.2
HFPO-DA	0.0055	0.005	10.88	92
DONA	0.0055	0.005	3.24	100.6
4:2 FTS	0.0055	0.005	4.43	82.7

Table. 2 Recovery and repeatability for select PFAS: PFOA, PFNA, PFOS and PFHxS at each concentration level in baby food.

Analyte	Spike conc. (ppb)	Average conc. (ppb)	Standard Deviation	%RSD	Average Recovery%
PFOA	Blank	ND			
	0.01	0.01	3.04	3.07	99.3
	0.1	0.102	1.95	1.92	101.7
	0.5	0.495	0.95	0.96	99
	1	0.994	0.38	0.38	99.4
PFNA	Blank	0			
	0.01	0.011	5.44	5.13	106.2
	0.1	0.1	2.35	2.36	99.6
	0.5	0.48	2.24	2.33	96.1
	1	0.975	1.83	1.88	97.5
PFOS	Blank	ND			
	0.01	0.009	5.72	6.56	87.2
	0.1	0.099	3.74	3.78	99.1
	0.5	0.462	0.06	0.06	92.3
	1	0.943	1.66	1.76	94.3
PFHxS	Blank	0.001			
	0.01	0.011	7.99	7.45	107.4
	0.1	0.101	2.16	2.15	100.5
	0.5	0.457	2.4	2.62	91.5
	1	0.941	2.06	2.19	94.1

Table. 3 Recovery and repeatability for select PFAS: PFOA, PFNA, PFOS and PFHxS at each concentration level in produce.

Analyte	Spike conc. (ppb)	Average conc. (ppb)	Standard Deviation	%RSD	Average Recovery%
PFOA	Blank	0.001			
	0.0055	0.006	3.55	3.3	107.3
	0.055	0.055	1.16	1.16	99.8
	0.55	0.56	0.65	0.64	101.7
	5.5	5.954	0.45	0.42	108.2
PFNA	Blank	0.001			
	0.0055	0.006	1.45	1.38	104.8
	0.055	0.057	0.67	0.64	103.6
	0.55	0.592	2.73	2.54	107.7
	5.5	5.168	0.6	0.64	94
PFOS	Blank	ND			
	0.0055	0.006	3.72	3.77	98.9
	0.055	0.05	2.49	2.75	90.4
	0.55	0.511	1.08	1.16	93
	5.5	5.627	0.15	0.15	102.3
PFHxS	Blank	0			
	0.0055	0.005	6.82	7.21	94.5
	0.055	0.05	1.82	1.98	91.8
	0.55	0.514	1.02	1.09	93.5
	5.5	5.182	10.95	11.62	94.2

The LOQ for each analyte was estimated by spiking at concentrations at, or below, the required LOQs listed in SMPR. Further details, including recovery and repeatability data for seafood and protein powder, as well as LOQ for eggs, baby food and produce can be found in application news corresponding to this poster.

4. Conclusion

The Shimadzu LCMS-8060NX Triple Quadrupole Mass Spectrometer coupled with a Shimadzu Nexera Liquid Chromatograph measured 30 PFAS compounds in eggs, produce, seafood, protein powder, and baby food, meeting criteria set by AOAC SMPR 2023.003, including stricter requirements for 4 PFAS that are regulated in the EU for eggs, and the strictest requirements for baby food and produce. All matrixes were extracted using the same QuEChERS workflow followed by SPE. Cleaned-up samples were analyzed using the same instrument method. Chromatography conditions and the mass spectrometer were optimized to achieve excellent separation of all analytes in only nine minutes.

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