Application Note

Food Testing & Agriculture

A Study of Method Limit of Quantitation for 30 PFAS in Food

Using Captiva EMR PFAS food passthrough cleanup by LC/MS/MS detection

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Abstract

This application note presents a study for the method limit of quantitation (LOQ) determination for 30 per- and polyfluoroalkyl substances (PFAS) targets in foods using a newly developed method of QuEChERS extraction followed by Agilent Captiva EMR PFAS Food cartridge passthrough cleanup, then LC/MS/MS detection. The $LOQ_{spiking}$ was determined as the lowest validated spiking level in food matrices, with acceptable method accuracy and repeatability results. The LOQ_{cal} was calculated based on the standard deviation of $LOQ_{spiking\text{-}A}$ following the procedure published in 40 CFR Appendix B to Part 136.[1] Both $LOQ_{spiking\text{-}A}$ and $LOQ_{cal\text{-}A}$ from this method were compared against the required LOQ_{AOACr} from the AOAC SMPR 2023.003 guideline.[2] The $LOQ_{cal\text{-}A}$ results from this method were also compared to $LOQ_{cal\text{-}F}$ from the U.S. Food and Drug Administration (FDA) method[3], which uses the same calculation method to determine method LOQ_{cal}. The results showed that the newly developed method provided acceptable LOQs meeting the AOAC SMPR guideline requirements. The new method $LOQ_{cal\text{-}A}$ results were lower than the $LOQ_{cal\text{-}F}$ from the FDA method for foods in the same category.

Introduction

Determination of PFAS residues in food is an emerging topic that has gained significant attention over the last several years. In April 2023, the European Commission enforced regulations for four PFAS compounds, namely perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), and perfluorohexane sulfonic acid (PFHxS) in eggs, fish, seafood, meat, and edible offal.[4,5] In November 2023, AOAC released the Standard Method Performance Requirements (SMPR) 2023-003 for the analysis of 30 PFAS in produce, beverages, dairy products, eggs, seafood, meat products, and feed.[2] The FDA has released their updated method (version 3.0) for the determination of 30 PFAS in food and feed.[3]

A new method, using QuEChERS extraction followed by Enhanced Matrix Removal (EMR) mixed-mode passthrough cleanup on Captiva EMR PFAS Food cartridges for sample preparation and LC/MS/MS detection for sample analysis, was developed and validated in multiple food matrices. Method validation was strictly implemented based on the AOAC SMPR guideline in 15 food matrices, including infant formula, milk, eggs[6], baby food[7], beef, tuna, shrimp[8], carrots, grapes, mushrooms, lettuce, tomatoes, orange juice[9], bovine kidney[10], and dry soybeans[11].

The most challenging LOQ requirements are on the four critical PFAS targets – PFHxS, PFOA, PFNA, and PFOS – where the required LOQs are 10x lower than those for other PFAS targets. Considering the various requirements on method LOQs for different PFAS targets in different food matrices by the AOAC SMPR guideline and EU regulation, multiple levels of quality control (QC) samples were prepared by pre-spiking the food matrix blank with PFAS standards at different concentrations. The method $LOQ_{spiking}$ was decided based on the acceptance criteria through the actual spiking test. However, the method $LOQ_{spiking}$ may not reflect the true method LOQ due to multiple contributions arising from the complexity of PFAS analysis in food.

In this work, a case study of method LOQs for PFAS analysis in food was implemented based on raw data generated in previous work. The calculation of method LOQ_{cal} and method detection limit (MDL) were based on the procedure published in 40 CFR Appendix B to Part 136.[1] The calculated results were also compared to the AOAC SMPR 2023.003 guideline requirements[2] and results reported by FDA method C-010.03[3] for the corresponding food category.

Experimental

Method MDL and $LOQ_{cal\text{-}A}$ for 30 PFAS in food using this method were calculated using Equations 1 and 2 based upon data obtained from $LOQ_{spiking}$ measurements in previous studies.[6–11]

Equation 1.

$$MDL_A = SD_{LOQspiking\text{-}A} \times 3.14$$

Equation 2.

$$LOQ_{Cal\text{-}A} = SD_{LOQspiking\text{-}A} \times 10$$

where:

- MDL_A is the method detection limit using the Aglient method
- $LOQ_{cal\text{-}A}$ is the method calculated LOQ using the Agilent method
- $SD_{LOQspiking\text{-}A}$ is the standard deviation at the validated $LOQ_{spiking\text{-}A}$ level using the Agilent method

The determination of $LOQ_{spiking\text{-}A}$ was based on the lowest spiking QC level samples that met the AOAC SMPR guideline criteria on target recovery, repeatability, and selectivity.[2]

A total of 15 food matrices were included in this study, where three groups were classified based on the required LOQ level for the PFAS targets. These food matrices are listed in Table 1 with the AOAC SMPR guideline and EU regulation requirements on method LOQs.

In addition, the method $LOQ_{cal\text{-}A}$ also needs to be within the established calibration range (Table 2). The method calibration range in food matrix (µg/kg) is determined by the neat standard calibration range (ng/L) corrected by the concentration or dilution factor introduced during sample preparation. For the calculated $LOQ_{cal\text{-}A}$ below the lowest calibration range, the lowest calibration level was reported as $LOQ_{cal\text{-}A}$.

Table 1. Evaluation food matrices and their requirements on method LOQs based on AOAC SMPR guideline and EU regulation.

Group	Evaluated Food Matrix	Food Category	Requirements on Method LOQ (µg/kg)		
			PFOS, PFOA, PFNA, and PFHxS	PFBA and PFPeA	Other PFAS
I	Baby food	Food for infants and young children	≤ 0.01 for all (AOAC) ≤ 0.015 for PFHxS (EU) ≤ 0.005 for PFNA (EU) ≤ 0.01 for PFOA and PFOS (EU)	≤ 1	≤ 0.1
	Infant formula				
	Carrot, grape, mushroom, lettuce, and tomato	Produce			
	Orange juice	Beverage			
I-A	Milk	Milk	≤ 0.01 for all (AOAC) ≤ 0.02 for PFOS (EU) ≤ 0.01 for PFOA (EU) ≤ 0.005 for PFNA (EU) ≤ 0.015 for PFHxS (EU)	≤ 1	≤ 0.1
II	Beef	Fish and meat of terrestrial animals	≤ 0.1 for all (AOAC, EU)	≤ 1	≤ 1
	Tuna				
III	Eggs	Eggs	≤ 0.3 for all (AOAC, EU)	≤ 3	≤ 3
	Shrimp	Seafood			
	Bovine kidney	Edible offal	≤ 0.4 for all (AOAC) ≤ 0.5 for all (EU)	≤ 4	≤ 4
	Dry soybean	Feed	≤ 0.5 for all (AOAC)	≤ 5	≤ 5

Table 2. Method calibration range for 30 PFAS in food.

Evaluated Matrix	Concentration or Dilution Factor	Method Calibration Range (µg/kg)		
		PFBA	PFPeA	Other 28 Targets
Carrot, Grape, Mushroom, Lettuce, Tomato, Orange Juice, and Baby Food	10x Concentration	0.01 to 5	0.005 to 2.5	0.001 to 1
Infant Formula	5x Concentration	0.02 to 10	0.004 to 2	0.002 to 1
Milk and Eggs	10x Concentration	0.02 to 10	0.004 to 2	0.002 to 1
Beef, Tuna, Shrimp, and Dry Soybean	5x Concentration	0.04 to 20	0.008 to 4	0.004 to 2
Bovine Kidney	10x Dilution	2 to 1, 000	0.4 to 200	0.2 to 100

Results and discussion

Method $LOQ_{spiking}$

The validated method $LOQ_{spiking}$ in the representative food matrices shown in Table 3 was determined based on the lowest spiking level with acceptable criteria, including method accuracy (recovery), repeatability (RSD%), and selectivity. For food matrices with the positive detection of targets, the $LOQ_{spiking}$ has to be higher than the calculated LOQ based on the target quantitation in replicated matrix blank samples using Equation 3 based on AOAC SMPR.[4]

Equation 3.

$$LOQ = 10 \times S_s$$

where S_s is the sample standard deviation of the replicate matrix blank samples.

Figure 1 shows the method accuracy (recovery %) at $LOQ_{spiking\text{-}A}$ in all tested food matrices, and Figure 2 shows the method repeatability (RSD%) at $LOQ_{spiking\text{-}A}$ in all tested food matrices.

Results show that all the targets in all matrices meet the required LOQs with acceptable method accuracy, repeatability, and selectivity, except 4:2 FTS, 6:2 FTS, PFOS in carrot, PFOA in infant formula, 6:2 FTS in milk, and PFOS in beef. The significant positive detection of these targets in the specific food matrices resulted in a raised method $LOQ_{spiking\text{-}A}$.

Table 3. The validated method LOQ$_{spiking\text{-}A}$ for 30 PFAS targets in food.

Target	Method LOQ$_{spiking\text{-}A}$ in Food (µg/kg)														
	Baby Food	Carrot	Grape	Mushroom	Lettuce	Tomato	Orange Juice	Infant Formula	Milk	Beef	Tuna	Eggs	Shrimp	Bovine Kidney	Dry Soybean
PFBA	1.0	0.2	0.1	1.0	0.2	1.0	0.2	0.1	0.1	0.4	0.4	0.2	0.4	2.0	5.0
PFPeA	0.01	0.01	0.01	0.005	0.01	0.005	0.01	0.02	0.02	0.04	0.04	0.02	0.04	0.4	0.1
PFBS	0.1	0.01	0.01	0.004	0.002	0.01	0.004	0.01	0.01	0.02	0.02	0.01	0.02	0.2	0.05
4:2 FTS	0.002	0.2	0.1	0.001	0.1	0.1	0.004	0.01	0.01	0.02	0.02	0.01	0.02	0.4	0.05
PFHxA	0.004	0.004	0.01	0.004	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.4	0.05
PFPeS	0.002	0.02	0.01	0.004	0.01	0.002	0.002	0.01	0.01	0.02	0.02	0.01	0.02	0.4	0.05
HFPO-DA	0.001	0.004	0.004	0.004	0.1	0.004	0.002	0.01	0.01	0.02	0.02	0.01	0.02	0.2	0.05
PFHpA	0.002	0.01	0.004	0.004	0.002	0.002	0.004	0.01	0.01	0.02	0.02	0.01	0.02	0.2	0.05
PFHxS	**0.002**	**0.01**	**0.01**	**0.004**	**0.01**	**0.004**	**0.004**	**0.01**	**0.01**	**0.02**	**0.02**	**0.01**	**0.02**	**0.2**	**0.05**
DONA	0.001	0.1	0.002	0.002	0.002	0.002	0.001	0.01	0.1	0.02	0.02	0.01	0.02	0.2	0.5
6:2 FTS	0.002	0.2	0.004	0.01	0.1	0.004	0.02	0.01	0.2	0.02	0.02	0.01	0.02	0.4	0.1
PFOA	**0.002**	**0.01**	**0.002**	**0.01**	**0.004**	**0.004**	**0.01**	**0.02**	**0.01**	**0.02**	**0.02**	**0.01**	**0.04**	**0.4**	**0.05**
PFHpS	0.004	0.002	0.002	0.01	0.002	0.002	0.001	0.01	0.01	0.02	0.02	0.01	0.02	0.2	0.05
PFNA	**0.002**	**0.004**	**0.002**	**0.01**	**0.002**	**0.004**	**0.004**	**0.01**	**0.01**	**0.4**	**0.02**	**0.01**	**0.1**	**0.4**	**0.05**
PFOS	**0.002**	**0.02**	**0.002**	**0.001**	**0.002**	**0.001**	**0.004**	**0.01**	**0.01**	**0.02**	**0.04**	**0.1**	**0.1**	**0.4**	**0.05**
9Cl-PF3ONS	0.002	0.001	0.002	0.001	0.002	0.001	0.001	0.01	0.01	0.02	0.02	0.01	0.02	0.2	0.05
8:2 FTS	0.001	0.002	0.001	0.002	0.001	0.002	0.001	0.01	0.01	0.02	0.02	0.01	0.04	0.4	0.05
PFDA	0.001	0.002	0.004	0.002	0.001	0.002	0.002	0.01	0.01	0.02	0.02	0.01	0.1	0.4	0.05
PFNS	0.001	0.002	0.002	0.01	0.001	0.004	0.001	0.01	0.01	0.02	0.02	0.01	0.02	0.2	0.05
PFDS	0.01	0.004	0.004	0.004	0.01	0.004	0.002	0.01	0.01	0.02	0.02	0.01	0.02	0.2	0.05
PFUnDA	0.002	0.004	0.002	0.01	0.002	0.002	0.001	0.01	0.01	0.02	0.04	0.01	0.4	0.4	0.05
PFOSA	0.004	0.02	0.004	0.002	0.1	0.004	0.002	0.01	0.01	0.02	0.02	0.01	0.02	0.2	0.05
11Cl-PF3OUdS	0.004	0.002	0.001	0.001	0.001	0.001	0.02	0.01	0.01	0.02	0.02	0.01	0.02	0.2	0.05
PFUnDS	0.01	0.004	0.01	0.004	0.002	0.004	0.01	0.01	0.01	0.02	0.02	0.01	0.02	0.2	0.05
PFDoDA	0.004	0.004	0.002	0.01	0.002	0.004	0.001	0.01	0.01	0.02	0.04	0.01	0.04	0.4	0.05
10:2 FTS	0.002	0.002	0.004	0.002	0.004	0.001	0.001	0.01	0.01	0.02	0.02	0.01	0.02	1.0	0.05
PFDoS	0.01	0.02	0.002	0.004	0.004	0.002	0.01	0.01	0.01	0.02	0.1	0.01	0.02	0.2	0.05
PFTrDA	0.002	0.001	0.001	0.004	0.004	0.002	0.001	0.01	0.01	0.02	0.02	0.01	0.4	0.2	0.05
PFTrDS	0.02	0.01	0.004	0.01	0.02	0.02	0.01	0.01	0.01	0.02	0.4	0.01	0.02	0.2	0.05
PFTeDA	0.004	0.002	0.002	0.004	0.001	0.001	0.001	0.01	0.01	0.02	0.02	0.01	0.1	0.4	0.05

Bold: Highlights for four critical PFAS targets, i.e. PFHxS, PFOA, PFNA, and PFOS, and their results.
Red: Outlier due to significant positive detection of target in sample matrix blank.

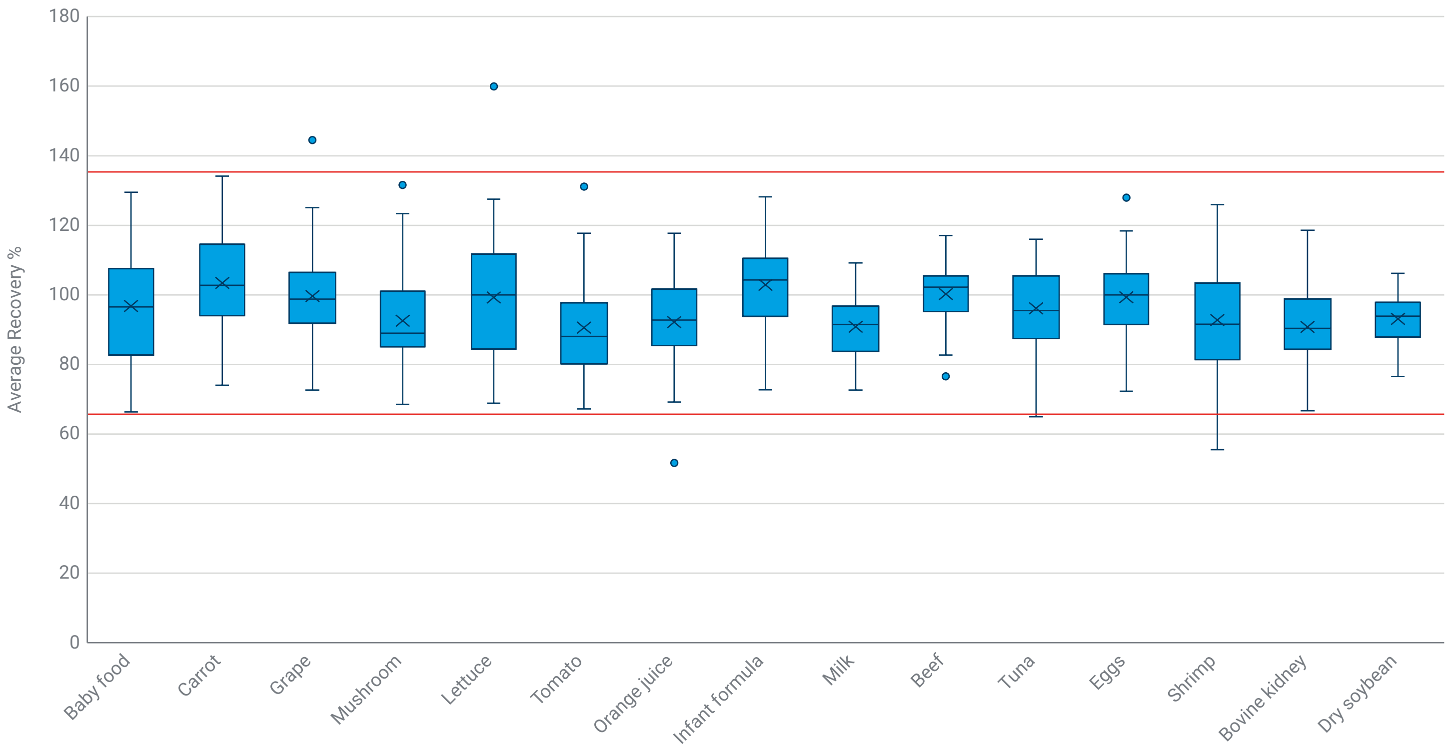

Figure 1. Method recovery at $LOQ_{spiking\text{-}A}$ level for 30 PFAS targets in food (refer to Table 3 for $LOQ_{spiking\text{-}A}$ level details).

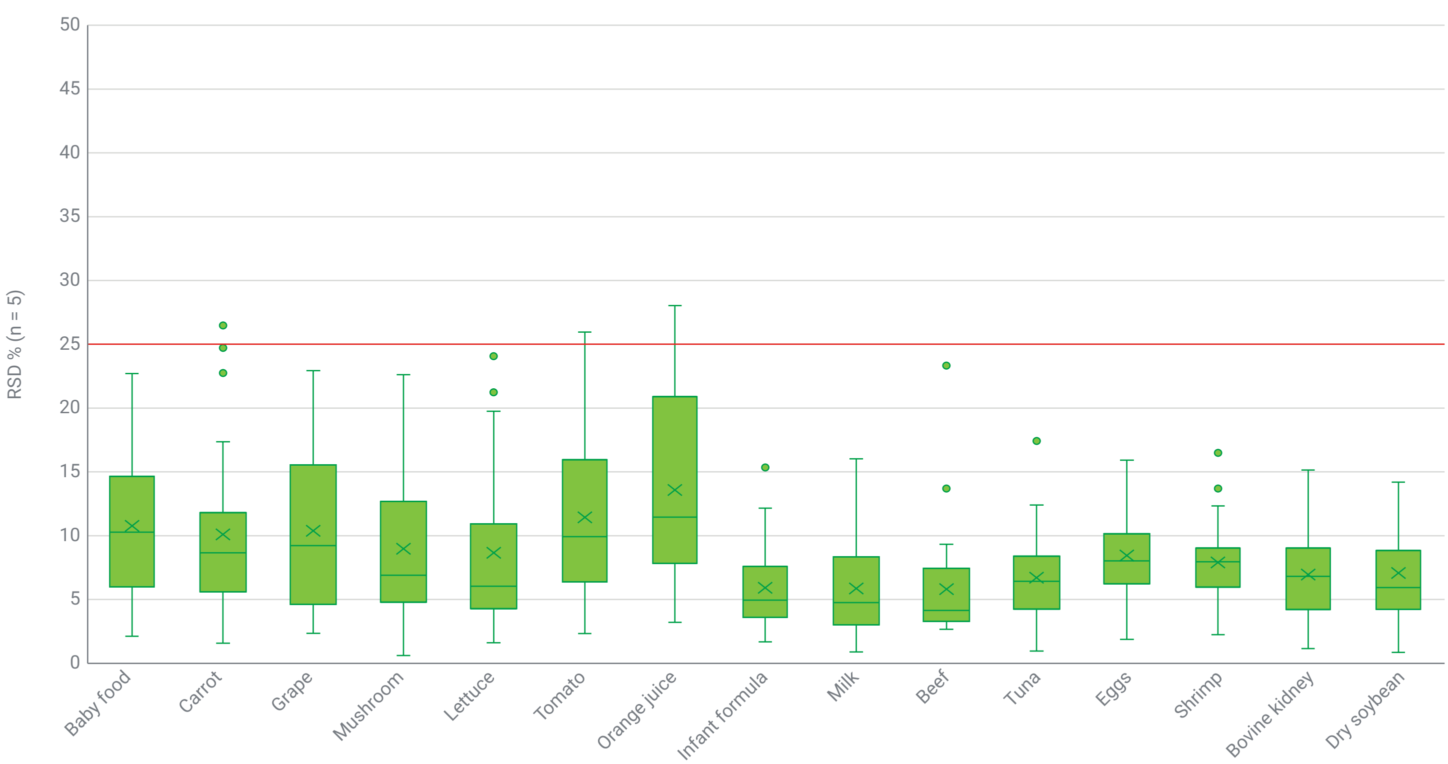

Figure 2. Method repeatability (RSD%) at $LOQ_{spiking\text{-}A}$ level for 30 PFAS targets in food (refer to Table 3 for $LOQ_{spiking\text{-}A}$ level details).

Method MDL and LOQ_{cal}

Agilent methods MDL_A and $LOQ_{cal\text{-}A}$ were determined based on validated method $LOQ_{spiking\text{-}A}$, using the aforementioned equations. Table 4 shows Agilent method MDL_A, and Table 5 shows Agilent method $LOQ_{cal\text{-}A}$. The results were compared to those from FDA method C-010.03[3] for targets in the representative food matrices from the same category, including lettuce, milk, eggs, fish, and feed. Since data for PFBA and PFPeA are not available for FDA method C-010.03, the comparison is limited to the remaining 28 PFAS targets. The results are shown in Figure 3.

The calculated $LOQ_{cal\text{-}A}$ were comparable to the $LOQ_{spiking\text{-}A}$ levels, with many of $LOQ_{cal\text{-}A}$ below the $LOQ_{spiking\text{-}A}$. When the LOQ_{cal} was calculated below the lowest calibration level, the lowest calibration level was considered as method LOQ_{cal} instead and differentiated in italics. Based on calculation, LOQ_{cal} for all targets in all matrices were shown to be below the required LOQ that met both the AOAC SMPR guideline and EU regulation for required LOQs. The only two exceptions, 4:2 FTS in carrot and PFNA in beef (highlighted in red), were caused by the significant positive detection of targets in the sample matrices. For four critical targets – PFHxS, PFOA, PFNA, and PFOS – the results are highlighted in bold. Comparing the targeted LOQ suggested in the EU regulation[4,5] for the four critical PFAS targets, the Agilent method $LOQ_{cal\text{-}A}$ satisfied the EU-targeted LOQs in milk, which are ≤ 0.01 µg/kg for PFOS and PFOA, ≤ 0.02 µg/kg for PFNA, and ≤ 0.04 µg/kg for PFHxS. For these four targets, the ultralow EU-targeted LOQs in fruits, vegetables, and food for infants and young children are significantly challenging, i.e., ≤ 0.001 µg/kg for PFOA and PFNA, ≤ 0.002 µg/kg for PFOS, and ≤ 0.004 µg/kg for PFHxS. The matrix background was the biggest barrier for the method to achieve these ultra-low LOQ levels in real food matrices. However, the Agilent method still met these ultra-low LOQs for the critical four targets in some food matrices with cleaner matrix background, which included 0.001 µg/kg $LOQ_{cal\text{-}A}$ for PFOA in grape and tomato, 0.001 µg/kg $LOQ_{cal\text{-}A}$ for PFNA in grape, 0.002 µg/kg (and below) $LOQ_{cal\text{-}A}$ for PFOS in grape, mushroom, lettuce, and tomato, and 0.004 µg/kg (and below) $LOQ_{cal\text{-}A}$ for PFHxS in baby food, mushroom, and lettuce. These results demonstrate that the Agilent method can reach ultra-low LOQ levels, given an acceptably clean food matrix.

The LOQ_{cal} comparison between the Agilent method ($LOQ_{cal\text{-}A}$) and FDA method C-010.03 ($LOQ_{cal\text{-}F}$) is based on careful selection of food matrices, covering produce, milk, eggs, fish, and feed categories. For the produce category, lettuce was used in both method validations. For the eggs category, egg was used in both methods. Therefore, the comparison in these two matrices was quite straightforward. For the milk category, whole milk was used in the Agilent method validation, while chocolate milk was used in the FDA method. For the fish category, salmon was used in the FDA method, while canned tuna was used in the Agilent method. For the feed category, corn was used in the FDA method, while soybean was used in the Agilent method. Even with the slight differences in these food matrices, they are considered comparable sample matrices, and thus were also chosen for method comparison. Including these food matrices also expands the method comparison for more complicated and challenging food categories. The calculation of $LOQ_{cal\text{-}A}$ was based on validated $LOQ_{spiking\text{-}A}$, while $LOQ_{cal\text{-}F}$ was based on results from a 0.05 µg/kg spiking level using the FDA method.[3]

The results summarized in Figure 3 show that Agilent method $LOQ_{cal\text{-}A}$ levels are overall below $LOQ_{cal\text{-}F}$ using the FDA C-010.03 method, with few exceptions due to the matrix positive detection impacts. The significantly lower $LOQ_{spiking\text{-}A}$ is attributed to the much more simplified sample preparation method procedure, where improved matrix removal efficiency allows the collection of validated data at low $LOQ_{spiking\text{-}A}$ levels. The higher matrix removal efficiency also allows the use of larger sample sizes for extraction, results in a higher concentration factor, and reduces matrix effect for target determination. This also contributes to the lower $LOQ_{cal\text{-}A}$ using the Agilent method. Even with the equivalent spiking level for method $LOQ_{spiking}$ (0.05 µg/kg) in the feed matrix comparison, the $LOQ_{cal\text{-}A}$ by the Agilent method still ranges lower than that of the FDA method. This confirms that the reduced matrix effect and larger sample size can improve method LOQs overall.

Table 4. Method MDL_As for 30 PFAS targets in food.

Target	Method MDL_A (µg/kg)														
	Baby Food	Carrot	Grape	Mushroom	Lettuce	Tomato	Orange Juice	Infant Formula	Milk	Beef	Tuna	Eggs	Shrimp	Bovine Kidney	Dry Soybean
PFBA	0.282	0.078	0.018	0.044	0.027	0.163	0.149	0.019	0.008	0.042	0.099	0.026	0.041	0.159	0.974
PFPeA	0.002	0.001	0.002	0.002	0.002	0.002	0.006	0.004	0.002	0.006	0.011	0.004	0.015	0.081	0.010
PFBS	0.011	0.002	0.004	0.001	0.001	0.003	0.002	0.004	0.001	0.003	0.005	0.001	0.005	0.047	0.010
4:2 FTS	0.001	0.065	0.014	0.001	0.008	0.013	0.002	0.002	0.001	0.006	0.006	0.001	0.005	0.070	0.007
PFHxA	0.001	0.001	0.003	0.002	0.002	0.012	0.002	0.005	0.002	0.005	0.009	0.001	0.004	0.124	0.015
PFPeS	0.001	0.001	0.003	0.002	0.001	0.002	0.002	0.001	0.001	0.004	0.008	0.001	0.005	0.086	0.007
HFPO-DA	0.001	0.005	0.002	0.002	0.047	0.002	0.002	0.001	0.001	0.007	0.005	0.003	0.003	0.088	0.015
PFHpA	0.001	0.005	0.002	0.001	0.001	0.001	0.001	0.002	0.002	0.005	0.005	0.002	0.010	0.031	0.021
PFHxS	**0.001**	**0.003**	**0.003**	**0.001**	**0.001**	**0.002**	**0.003**	**0.002**	**0.002**	**0.005**	**0.004**	**0.001**	**0.006**	**0.024**	**0.007**
DONA	0.001	0.016	0.001	0.001	0.001	0.001	0.001	0.001	0.022	0.004	0.005	0.001	0.005	0.018	0.065
6:2 FTS	0.002	0.011	0.001	0.001	0.014	0.001	0.002	0.007	0.006	0.005	0.004	0.002	0.006	0.111	0.029
PFOA	**0.002**	**0.003**	**0.001**	**0.001**	**0.001**	**0.001**	**0.001**	**0.005**	**0.003**	**0.001**	**0.005**	**0.003**	**0.008**	**0.072**	**0.016**
PFHpS	0.001	0.001	0.001	0.003	0.001	0.001	0.001	0.003	0.002	0.005	0.002	0.002	0.005	0.076	0.008
PFNA	**0.001**	**0.002**	**0.001**	**0.002**	**0.003**	**0.002**	**0.001**	**0.002**	**0.002**	**0.059**	**0.005**	**0.003**	**0.031**	**0.113**	**0.015**
PFOS	**0.002**	**0.004**	**0.001**	**0.001**	**0.001**	**0.001**	**0.002**	**0.001**	**0.001**	**0.005**	**0.008**	**0.011**	**0.031**	**0.122**	**0.009**
9Cl-PF3ONS	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.006	0.006	0.001	0.005	0.036	0.007
8:2 FTS	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.001	0.003	0.005	0.003	0.009	0.103	0.004
PFDA	0.001	0.001	0.002	0.001	0.001	0.001	0.001	0.002	0.003	0.008	0.013	0.003	0.052	0.097	0.008
PFNS	0.001	0.001	0.002	0.001	0.002	0.001	0.001	0.003	0.001	0.002	0.005	0.001	0.005	0.058	0.004
PFDS	0.001	0.003	0.002	0.002	0.003	0.003	0.001	0.001	0.003	0.003	0.005	0.002	0.004	0.024	0.001
PFUnDA	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.008	0.008	0.001	0.007	0.178	0.020
PFOSA	0.003	0.012	0.002	0.001	0.019	0.001	0.001	0.004	0.004	0.003	0.005	0.005	0.008	0.024	0.008
11Cl-PF3OUdS	0.001	0.001	0.001	0.001	0.001	0.001	0.014	0.001	0.002	0.004	0.005	0.001	0.004	0.053	0.003
PFUnDS	0.002	0.004	0.003	0.003	0.002	0.003	0.006	0.005	0.001	0.004	0.008	0.002	0.008	0.061	0.013
PFDoDA	0.001	0.002	0.001	0.001	0.001	0.001	0.001	0.003	0.003	0.004	0.011	0.003	0.012	0.115	0.014
10:2 FTS	0.001	0.001	0.003	0.001	0.001	0.001	0.001	0.001	0.001	0.003	0.005	0.001	0.006	0.066	0.008
PFDoS	0.006	0.005	0.001	0.003	0.002	0.001	0.005	0.002	0.003	0.003	0.005	0.001	0.004	0.071	0.021
PFTrDA	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.003	0.012	0.173	0.008	0.082	0.065	0.022
PFTrDS	0.006	0.007	0.003	0.01	0.015	0.005	0.007	0.004	0.003	0.007	0.005	0.001	0.007	0.030	0.010
PFTeDA	0.004	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.003	0.008	0.009	0.002	0.029	0.084	0.025

Bold: Highlights four critical PFAS targets, i.e. PFHxS, PFOA, PFNA, and PFOS, and their results.

Table 5. Method $LOQ_{cal\text{-}A}$ for 30 PFAS targets in food.

Target	Method $LOQ_{cal\text{-}A}$ (µg/kg)														
	Baby Food	Carrot	Grape	Mushroom	Lettuce	Tomato	Orange Juice	Infant Formula	Milk	Beef	Tuna	Eggs	Shrimp	Bovine Kidney	Dry Soybean
PFBA	0.899	0.247	0.056	0.139	0.085	0.519	0.474	0.061	0.025	0.134	0.316	0.082	0.130	0.506	3.103
PFPeA	0.008	*0.005*	0.006	0.005	0.006	0.007	0.018	0.011	0.005	0.019	0.036	0.014	0.047	0.258	0.033
PFBS	0.035	0.007	0.013	0.001	0.002	0.008	0.006	0.014	0.002	0.008	0.016	0.004	0.017	*0.200*	0.033
4:2 FTS	0.003	0.208	0.046	0.001	0.024	0.041	0.005	0.006	0.003	0.019	0.019	0.003	0.017	0.223	0.021
PFHxA	0.004	0.004	0.010	0.005	0.006	0.039	0.007	0.016	0.007	0.016	0.030	0.003	0.014	0.394	0.047
PFPeS	0.002	0.017	0.010	0.006	0.004	0.005	0.007	0.004	0.002	0.014	0.024	0.005	0.016	0.272	0.022
HFPO-DA	0.002	0.002	0.007	0.006	0.123	0.005	0.005	0.003	0.003	0.023	0.015	0.009	0.010	0.281	0.047
PFHpA	0.002	0.015	0.005	0.004	0.001	0.003	0.003	0.006	0.005	0.014	0.017	0.006	0.033	*0.200*	0.067
PFHxS	**0.002**	**0.010**	**0.009**	**0.004**	**0.002**	**0.006**	**0.010**	**0.005**	**0.005**	**0.016**	**0.013**	**0.004**	**0.018**	***0.200***	**0.022**
DONA	0.001	0.049	0.001	0.001	0.001	0.002	0.001	0.004	0.069	0.012	0.016	0.004	0.014	*0.200*	0.208
6:2 FTS	0.005	0.034	0.002	0.005	0.045	0.004	0.007	0.021	0.018	0.016	0.012	0.005	0.018	0.353	0.093
PFOA	**0.005**	**0.009**	**0.001**	**0.002**	**0.002**	**0.001**	**0.004**	**0.014**	**0.009**	***0.004***	**0.015**	**0.010**	**0.025**	**0.230**	**0.049**
PFHpS	0.004	0.004	0.003	0.009	0.002	0.001	0.001	0.008	0.007	0.016	0.005	0.007	0.016	0.243	0.025
PFNA	**0.002**	**0.006**	**0.001**	**0.006**	**0.005**	**0.007**	**0.003**	**0.007**	**0.007**	**0.189**	**0.017**	**0.008**	**0.100**	**0.359**	**0.047**
PFOS	**0.006**	**0.014**	**0.002**	**0.002**	**0.002**	**0.001**	**0.006**	**0.003**	**0.003**	**0.014**	**0.025**	**0.034**	**0.100**	**0.388**	**0.029**
9Cl-PF3ONS	0.002	0.001	0.001	0.001	0.001	0.002	0.001	0.003	0.003	0.018	0.019	0.003	0.017	*0.200*	0.023
8:2 FTS	0.002	0.001	0.002	0.003	0.002	0.004	0.002	0.006	0.004	0.009	0.017	0.010	0.030	0.327	0.011
PFDA	0.002	0.005	0.006	0.004	0.001	0.003	0.002	0.006	0.004	0.024	0.042	0.010	0.167	0.309	0.026
PFNS	0.002	0.003	0.005	0.003	0.005	0.003	0.002	0.009	0.003	0.006	0.017	0.004	0.015	*0.200*	0.014
PFDS	0.002	0.008	0.006	0.005	0.010	0.010	0.003	0.004	0.008	0.009	0.016	0.005	0.013	*0.200*	0.004
PFUnDA	0.002	0.001	0.001	0.004	0.003	0.002	0.001	*0.002*	0.004	0.025	0.025	0.003	0.023	0.566	0.063
PFOSA	0.008	0.038	0.006	0.003	0.061	0.004	0.001	0.014	0.014	0.008	0.017	0.015	0.027	*0.200*	0.026
11Cl-PF3OUdS	0.004	0.001	0.002	0.001	0.001	0.001	0.045	0.004	0.006	0.014	0.015	0.004	0.013	*0.200*	0.011
PFUnDS	0.007	0.012	0.012	0.008	0.005	0.010	0.019	0.015	0.003	0.012	0.026	0.005	0.025	*0.200*	0.043
PFDoDA	0.005	0.005	0.005	0.004	0.002	0.002	0.002	0.010	0.009	0.013	0.036	0.010	0.039	0.365	0.045
10:2 FTS	0.003	0.003	0.003	0.002	0.001	0.001	0.002	0.002	0.003	0.009	0.015	0.003	0.018	0.210	0.025
PFDoS	0.018	0.015	0.015	0.009	0.005	0.001	0.016	0.008	0.010	0.011	0.015	0.003	0.013	0.225	0.066
PFTrDA	0.002	0.001	0.001	0.003	0.001	0.002	0.001	0.006	0.009	0.039	0.551	0.025	0.262	0.205	0.069
PFTrDS	0.019	0.021	0.021	0.031	0.047	0.015	0.021	0.013	0.008	0.024	0.017	0.003	0.022	*0.200*	0.033
PFTeDA	0.012	0.002	0.002	0.003	0.001	0.002	0.001	0.003	0.008	0.026	0.030	0.007	0.092	0.268	0.080

Bold: Highlights four critical PFAS targets, i.e. PFHxS, PFOA, PFNA, and PFOS, and their results.
Italic blue: Highlights for $LOQ_{cal\text{-}A}$ where the calibration range lowest level was used, when calculated LOQ_{cal} was below the method calibration range.
Red: Outlier due to significant positive detection of target in sample matrix blank.

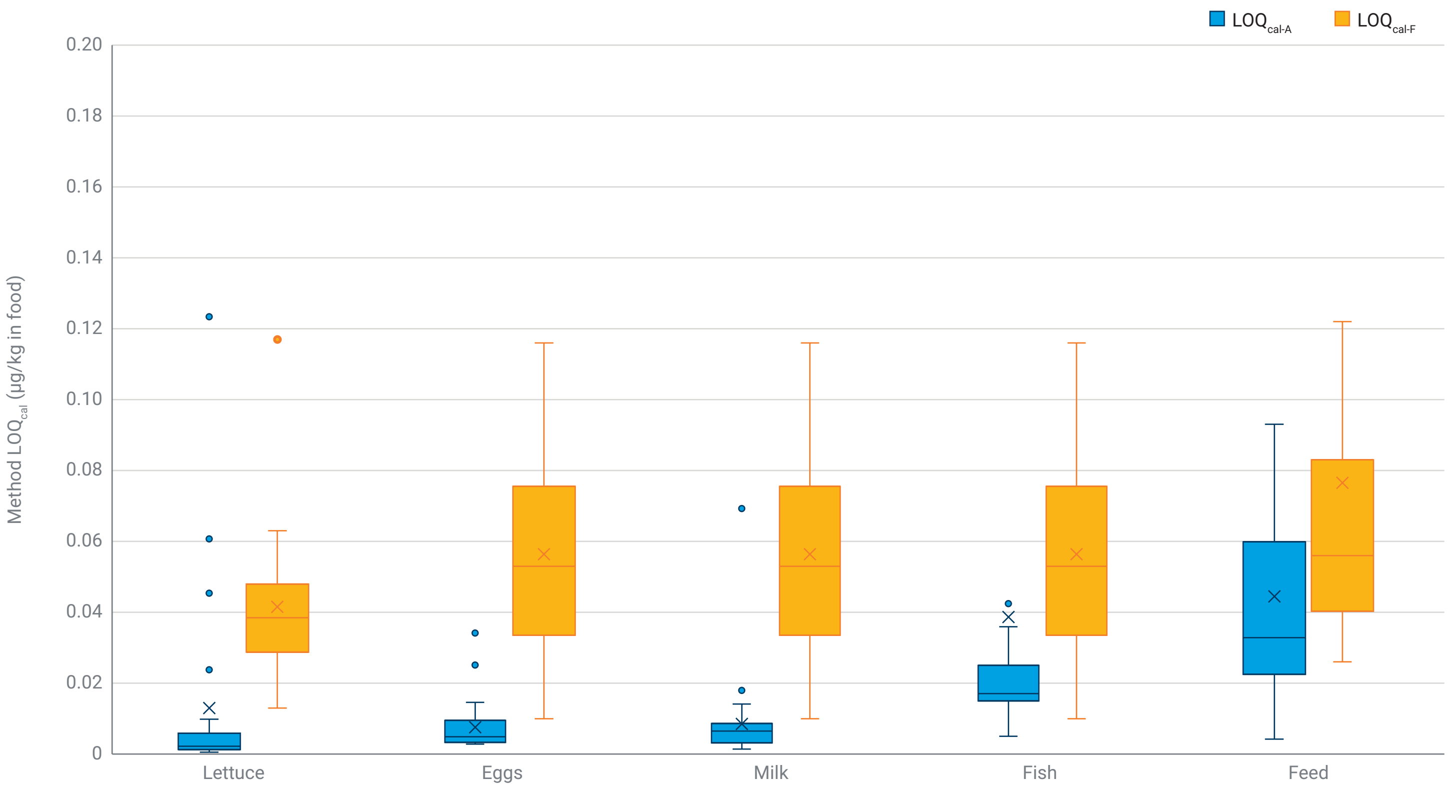

Figure 3. Method LOQ_{cal} comparison of 28 PFAS determinations in representative foods; LOQ_{cal-A} using the Agilent method versus LOQ_{cal-F} using the FDA C-010.03 method.

Conclusion

A case study on the method limits of quantitation was conducted for the validated Agilent method for 30 PFAS in food. Method $LOQ_{spiking\text{-}A}$, MDL_A, and $LOQ_{cal\text{-}A}$ were summarized for 30 PFAS targets in all 15 food matrices. Both method $LOQ_{spiking\text{-}A}$ and $LOQ_{cal\text{-}A}$ were compared to the LOQ levels required by the AOAC SMPR 2023.003 guideline and EU regulation; all met the accepted criteria, with few exceptions due to the significant positive detection of target in food matrices. Method $LOQ_{cal\text{-}A}$ results were then compared between the Agilent and FDA C-010.03 methods, demonstrating a much lower method LOQ_{cal} achieved by the Agilent method, which is attributed to the simplified method, higher matrix removal efficiency, and reduced matrix effect.

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