Poster Reprint

ASMS 2023
Poster number MP 219

Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Food Using a Novel Simplified Sample Preparation Method Followed by LC/MS/MS Detection

Limian Zhao and Mathew Giardina

Agilent Technologies Inc., Wilmington, DE, 19808

Introduction

Per- and polyfluoroalkyl substances (PFAS) are a group of synthetic organic compounds consisting of a hydrophobic fluorinated alkyl chain and a hydrophilic functional group. PFAS have been widely used in consumer products and industrial applications since 1940s. Due to the extreme persistence and widespread use, PFAS have been detected in the environment, animal and humans, and shown to bioaccumulate in the food chain. The need to analyze PFAS in food has gained more and more attention recently. Especially after the newly released regulation [1], the sub-ppt detection levels make analytical method development challenging. This study investigated a novel simplified sample preparation method followed by LC/MS/MS detection of 30 required PFAS compounds analysis in seven different food matrices. The method demonstrates improved target recovery, efficient food matrix cleanup, and acceptable LOQs meeting the sub-ppt MRLs regulation.

Instrument Detection

LC conditions (Agilent 1290 Infinity II)

Columns	Agilent ZORBAX Eclipse Plus C18, 2.1 x 100 mm, 1.8 µm column (p/n 959758-902) Agilent InfinityLab PFC delay column, 4.6 x 30 mm, (p/n 5062-8100)		
Flow Rate	0.4 mL/min		
Column Temp.	55 °C	Injection volume	20 µL (with water sandwiched injection)
Mobile Phase	A: 5 mM ammonium acetate in water B: MeOH		
Needle Wash	IPA, ACN, water		

Gradient	Time (min)	%B	Flow (mL/min)
	0	2	0.4
	2	2	0.4
	2.5	55	0.4
	6.5	70	0.4
	8.0	80	0.4
	13	100	0.4
	16	100	0.4
	16.1	2	0.4

Stop Time	16.1 min	Post time	3 min

QQQ conditions (Agilent 6470B LC/MS system)

Drying Gas	230 °C, 4 L/min	Sheath Gas	250 °C, 12 L/min
Nebulizer Gas	15 psi		
Capillary Voltage	2500 V	Nozzle Voltage	0 V
Polarity	NEG	Acquisition	dMRM

Sample Preparation

Food sample preparation procedure For PFAS Analysis

- Weigh 5-10 g of grinded sample into a 50 mL tube
- For dry or fatty food, add 5-10 mL of water. Vortex 10-15 mins
- Add 10 or 15 mL of ACN w/ 1% acetic acid. Vortex 20 sec for mixing
- Add QuEChERS EN or AOAC extraction salt and two ceramic homogenizers
- Cap and shake the sample on Gino Grinder @ 1500 rpm for 5 mins
- Centrifuge tubes @ 5000 rpm for 5 mins
- Transfer 5 mL of supernatant mixture (w/ or w/o 10% water) into Captiva EMR-PFAS 6 mL cartridges and elute by gravity
- Collect the eluent and dry @ 50 °C in the CentraVap
- Dry the cartridges for 5 minutes at a vacuum pressure of 15-20 in Hg
- Reconsititute the dried sample with 500 µL MeOH
- Vortex 3 mins, and sonicate 10 mins. Samples are ready for analysis

	Baby food	Grape	Soybean	Infant formula	Egg	Tuna
Sample size	10 g	10 g	5 g	5 g	10 g	5 g
Extraction solvent	10 mL	10 mL	15 mL	15 mL	10 mL	15 mL
QuEChERS salts	EN salt	EN salt	AOAC salt	AOAC salt	EN salt	AOAC salt
Matrix cleanup	EMR-PFAS 1	EMR-PFAS 1	EMR-PFAS 2	EMR-PFAS 2	EMR-PFAS 2	EMR-PFAS 2
Pre-mix w/ 10% water	N	N	Y	Y	Y	Y

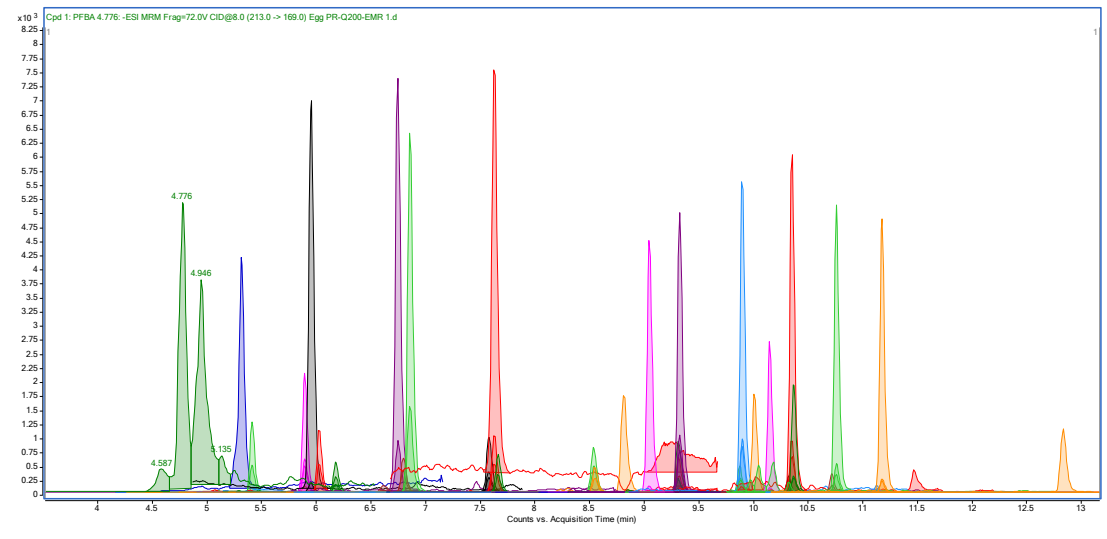


Figure 1. LC-QQQ chromatogram (dMRM) for egg sample fortified at 100 ng/kg of PFAS.

Results and Discussion

Equivalent QuEChERS buffered extraction

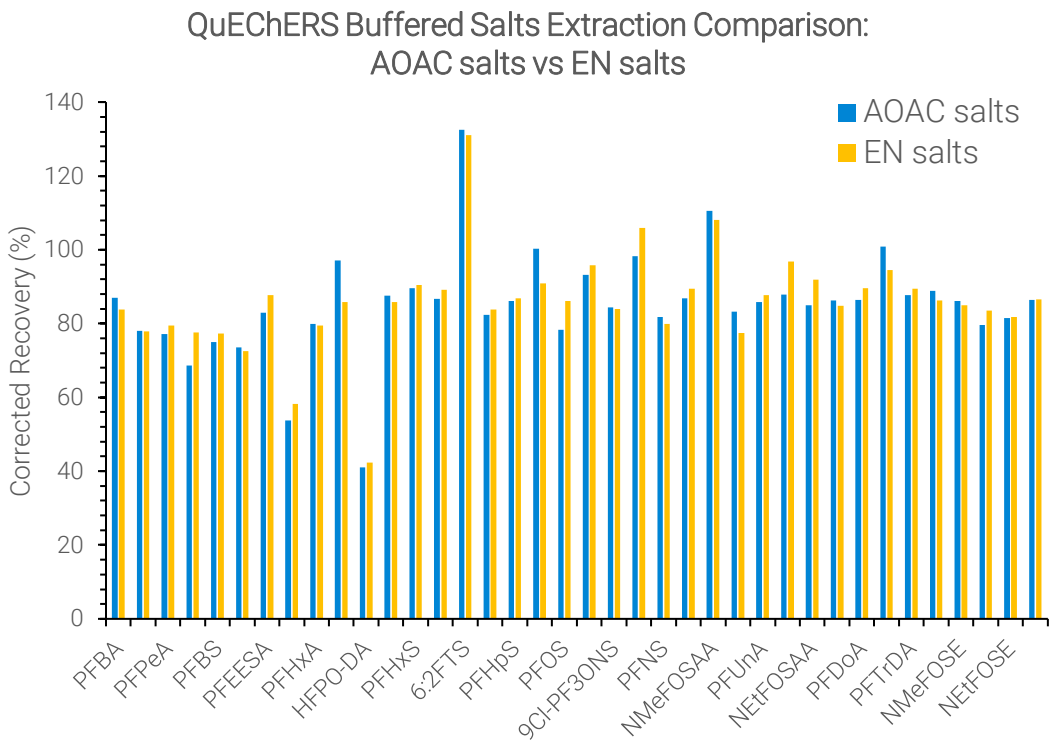
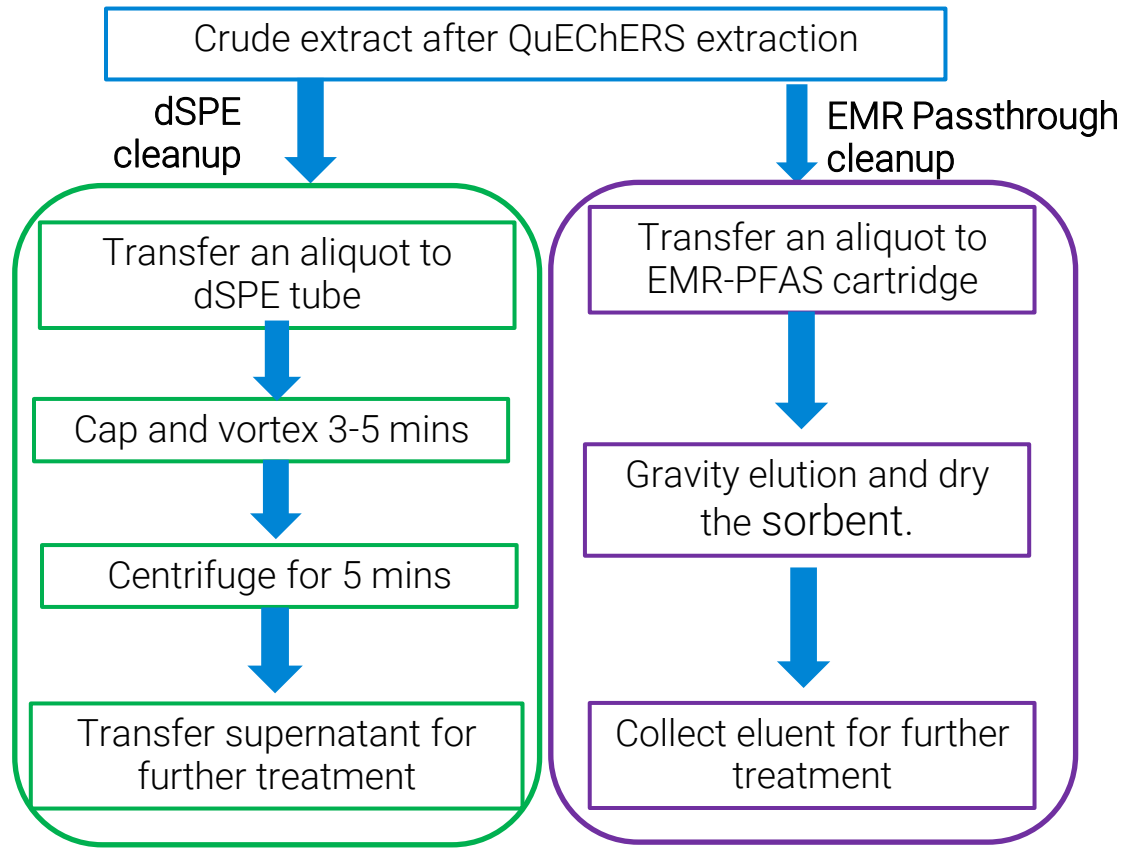


Figure 2. QuEChERS extraction recovery comparison for PFAS in lettuce (100 ng/kg fortified).

Simplified matrix cleanup after extraction



Improved PFAS recovery during food matrix cleanup

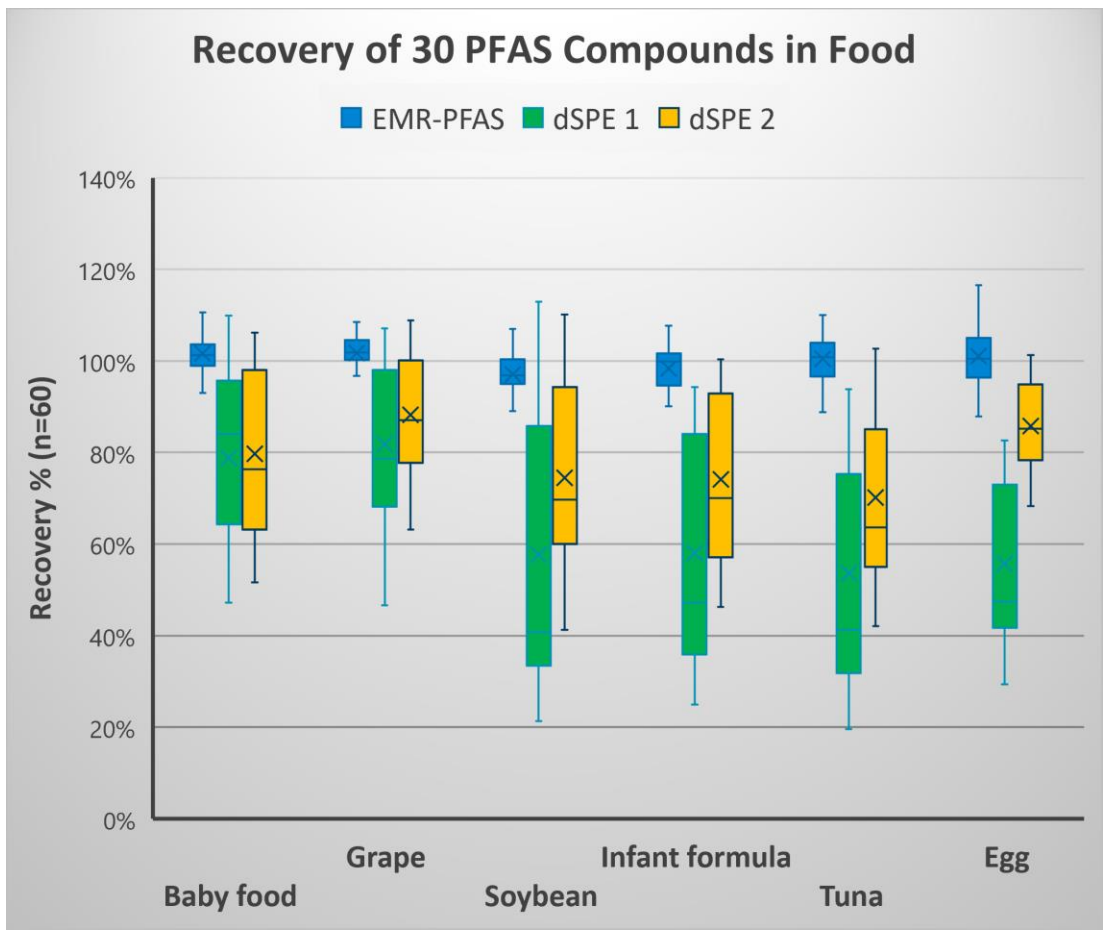


Figure 3. Recovery of 30 PFAS in seven food matrices using different matrix cleanup methods. Matrix crude extract was fortified at 200 ng/L PFAS for cleanup recovery study.

Acceptable matrix effect in multiple food matrices

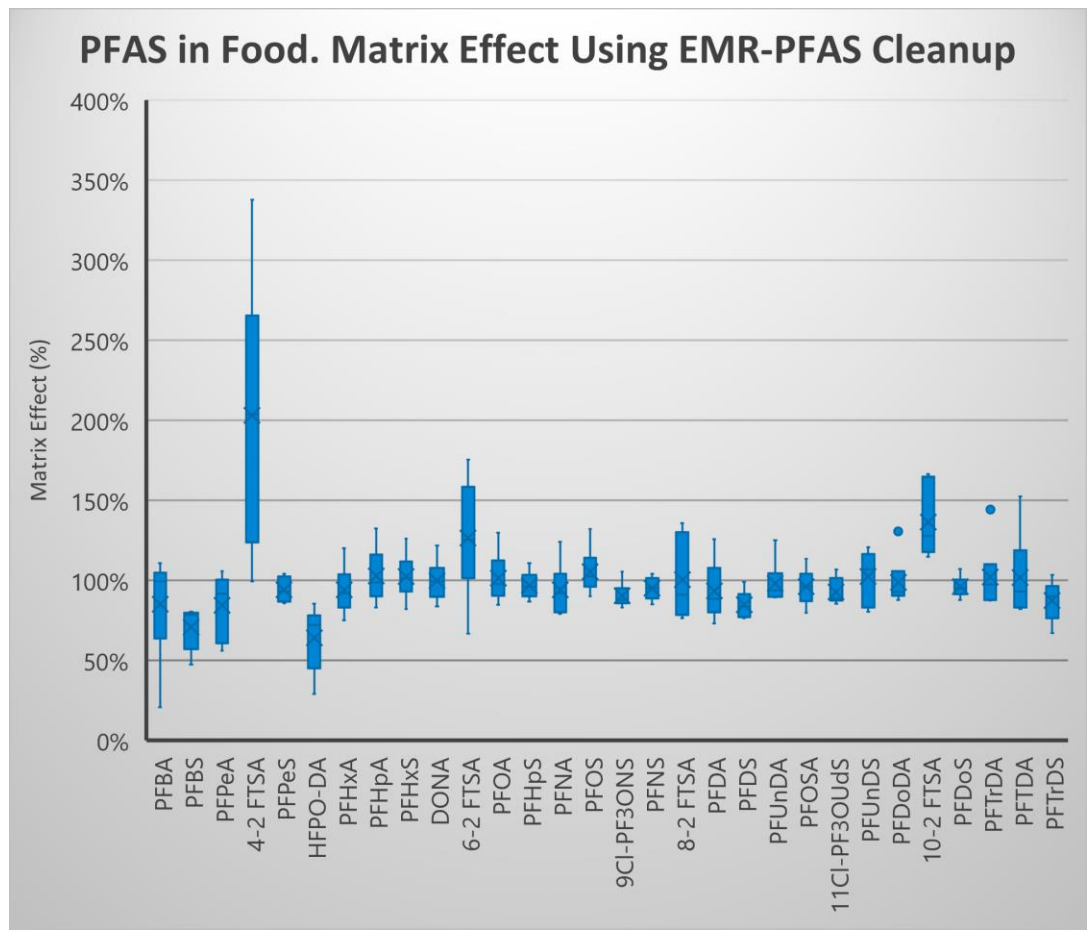


Figure 4. Matrix effect of 30 PFAS in seven food matrices using EMR-PFAS passthrough cleanup. Matrix final extract was fortified at 200 ng/L PFAS for matrix effect study.

Results and Discussion

Critical PFAS compounds: PFHxS, PFOA, PFNA, and PFOS LOQ chromatograms in baby food and infant formula

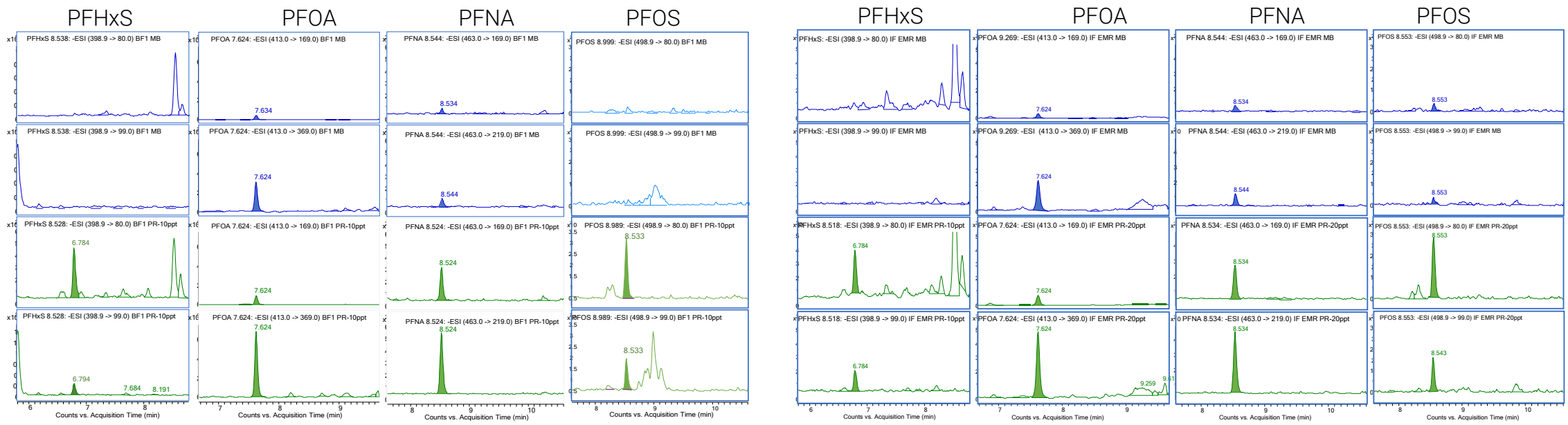


Figure 5. Chromatograms of baby food (left) and infant formula (right) for matrix blank (top two panes with two MRM transitions) and 10 **ng/kg in baby food and 20 ng/kg in infant formula (bottom two panes with two MRM transitions)**

Excellent food matrix cleanup efficiency

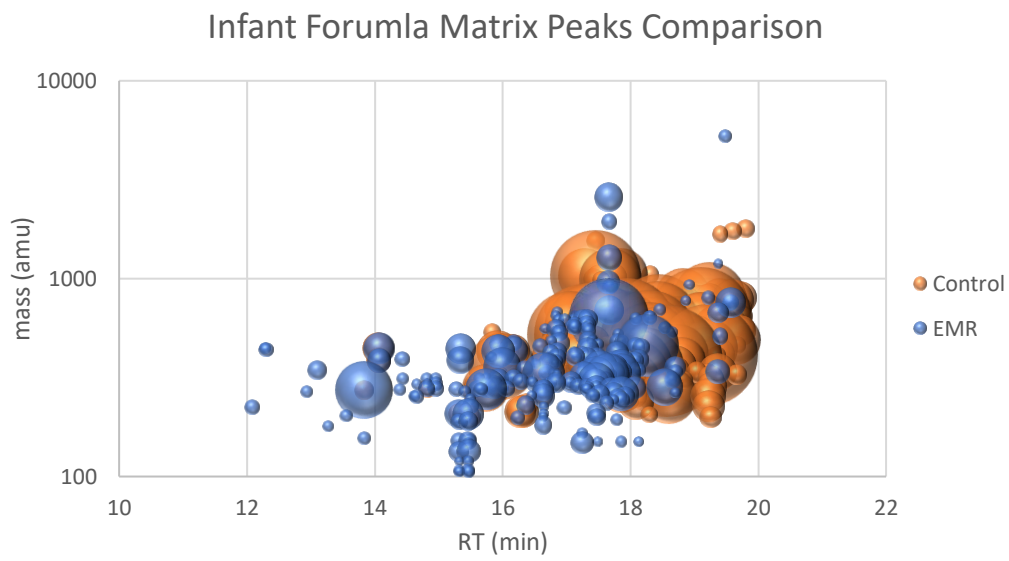


Figure 6. Molecular feature extraction from LC/Q-TOF 6546 data. Peak intensity in infant formula sample with (blue) and without (orange) EMR-PFAS passthrough cleanup.

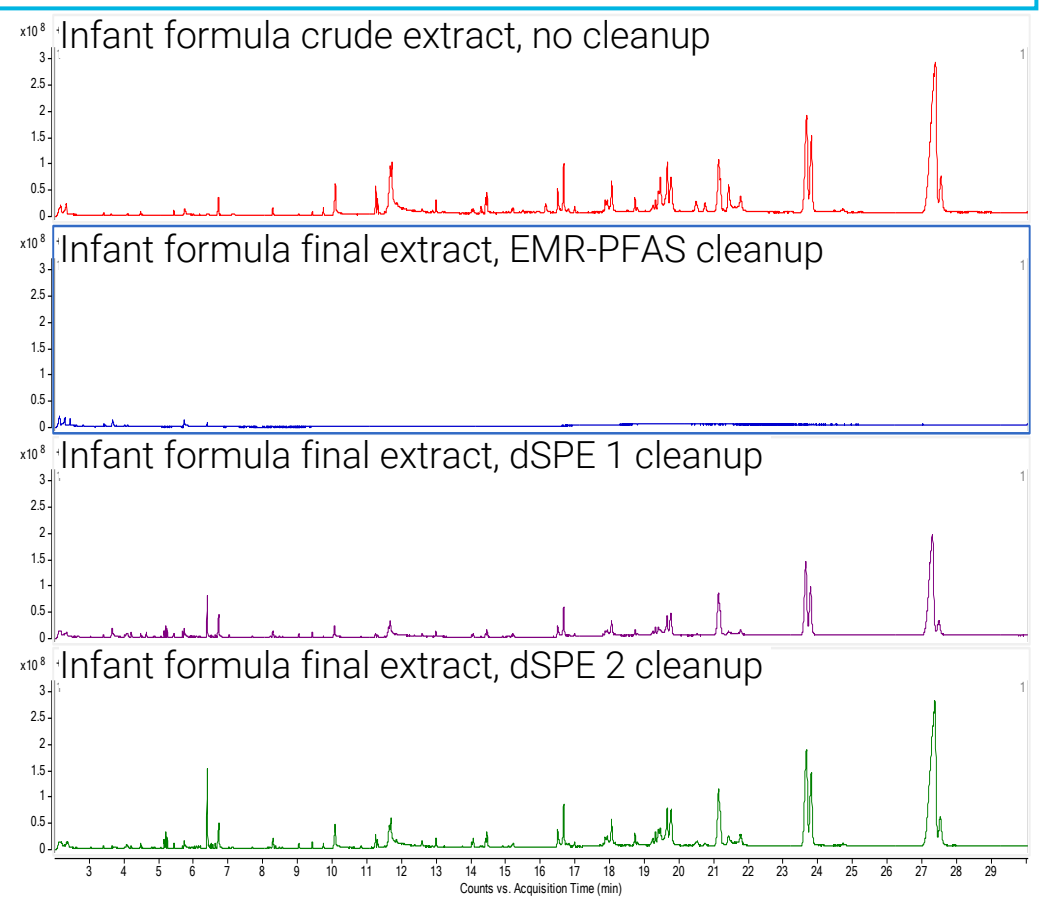


Figure 7. GC/MS full scan chromatograms for infant formula matrix background comparison.

Conclusions

- A novel sample preparation method was developed for PFAS in food analysis.
- Captiva EMR-PFAS passthrough cleanup demonstrated with improved PFAS recovery and high efficiency of matrix cleanup.
- Method delivered the reliable PFAS quantitation in food down to sub-ppt level.

References

[1] EURL POPs, Guidance Document on Analytical parameters for the Determination of Per- and Polyfluoroalkyl Substances (PFAS) in Food and Feed

https://www.agilent.com/en/promotions/asms

DE13020848

Published in USA, May 31,2023

Agilent
Trusted Answers