Application Note

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PFAS Quantitation from Food Contact Materials Using the Agilent 6495D Triple Quadrupole LC/MS System

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1290 Infinity III LC

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Abstract

There has been growing concern about per- and polyfluoroalkyl substances (PFAS) in food contact materials (FCMs) and their potential migration into food. This has necessitated the development of methods for accurate and reliable PFAS characterization. In this application note, 110 PFAS, comprised of 73 native and 37 labeled compounds, were quantified from paper straws using an Agilent 6495D triple quadrupole LC/MS system. The method detection limit was within 0.2 µg/kg for all 73 target analytes. For most analytes, R^2 values were greater than 0.99, confirming linearity. Matrix-spiked quality control (QC) recovery was 65 to 120% in 90% of analytes, with precision (%RSD) ≤ 20%. These performance attributes confirm the sensitivity and reliability of the 6495D LC/TQ system for PFAS screening in paper straws.

Introduction

PFAS are a large group of manufactured chemicals used in various industries worldwide due to their unique properties.[1,2] Since the 1950s, PFAS-containing materials have been used in food packaging as coatings to prevent the paper from absorbing fats and water, and to serve as barriers to printing inks and moisture.[3,4] However, there have been increasing concerns about the potential health impacts and environmental safety of specific critical PFAS such as perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), perfluorohexanesulfonic acid (PFHxS), perfluorononanoic acid (PFNA), their salts, and related compounds.

Regulatory bodies such as the Stockholm Convention, US Food and Drug Administration (FDA), European Union (EU), and the Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH), have introduced legislation to restrict the use of PFAS in many applications. For example, the Regulation EU No. 10/2011 limits the use of PFAS in plastic FCMs.[5] Additionally, in 2016, the FDA revoked regulations authorizing the use of long-chain PFAS, such as PFOS and PFOA, in food contact applications. In January 2023, Germany, Denmark, the Netherlands, Norway, and Sweden jointly proposed to the European Chemicals Agency (ECHA) that a broad ban be placed on PFAS in the EU market (REACH Appendix XV).[6] More regulations and voluntary actions are anticipated to monitor and mitigate PFAS contamination in food packaging and contact materials.

Therefore, it is critical to establish a sensitive and accurate quantitative analytical approach that ensures the safety of FCMs. Technologies such as liquid chromatography (LC) and gas chromatography (GC), combined with tandem mass spectrometry (MS/MS), are often used to analyze different PFAS groups based on their properties. Fluorotelomer alcohols (FTOHs), a type of fluorotelomer with an alcohol functional group, are volatile compounds suitable for GC/MS analysis. However, FTOHs may degrade into perfluorinated carboxylic acids (PFCAs) such as PFOA, PFDA, and PFNA, which are specific to LC/MS analysis.[4]

Special care must be taken during sample collection, handling, and laboratory analysis to reduce sources of contamination. However, analytical instrumentation, reagents, and consumables must also be selected carefully, as they can serve as a significant source of contamination by PFAS and lead to false positive results.

In this application note, a sensitive and reliable method using a 6495D triple quadrupole LC/MS system (LC/TQ) equipped with a PFAS-free flow path was developed for the quantitation of PFAS in a food contact material, specifically paper straws.

Experimental

A total of 110 PFAS, including 73 native and 37 labeled compounds (34 surrogates and three internal standards) were analyzed based on the solvent extraction principle, followed by a dilute-and-shoot method.

Chemicals and reagents

All chemicals and solvents used for this study were LC/MS grade and purchased from Sigma-Aldrich (St. Louis, MO, USA). Agilent InfinityLab Ultrapure LC/MS grade water (part number 5191-4498) was also used.

Consumables

Variability in consumable geometry and composition can greatly impact background levels as well as contribute to unplanned downtime and troubleshooting. Therefore, to remove uncertainty from measurements, it is important to source consumables that have strict quality control (QC) protocols in place during production and that are proven to deliver specific results. All consumables used in this work were from Agilent, and all were tested and verified for their suitability in PFAS analysis to deliver ultra-low PFAS background levels.[7] These consumables included:

- 15 mL Falcon tubes (part number 5610-2039)
- Agilent Captiva 5 mL polypropylene (PP) syringe (part number 9301-6476)
- Agilent Captiva Premium syringe filter, nylon membrane (part number 5190-5092)
- Agilent 2 mL polyfluorinated compound (PFC)-free PP vials (part number 5191-8150)
- Agilent 250 µL PP vials and caps (part numbers 5190-2242 and 5191-8151)

Standards and calibration preparation

Native and isotopically labeled PFAS standards were sourced from Wellington Laboratories Inc. (Guelph, ON, Canada) and Toronto Research Chemicals (Toronto, ON, Canada) as stock solutions, solution mixes, or powdered standards. Twelve calibration standards were prepared ranging from 1 to 50,000 ng/L (ppt) in methanol:water (80:20, v:v). Each calibration level included a constant amount of surrogate mix (used as an extracted internal standard, EIS) and isotope performance standard mix (EPA 533IS, used as a nonextracted internal standard, IPS).

Sample extraction procedure

A commonly used paper straw, purchased from a local store, was chosen as the FCM for testing in this study. Prior to weighing, the paper straw was cut into pieces smaller than 5 × 5 mm^2 using a stainless-steel cutter. The cutter was precleaned using isopropanol (IPA) to avoid contamination.

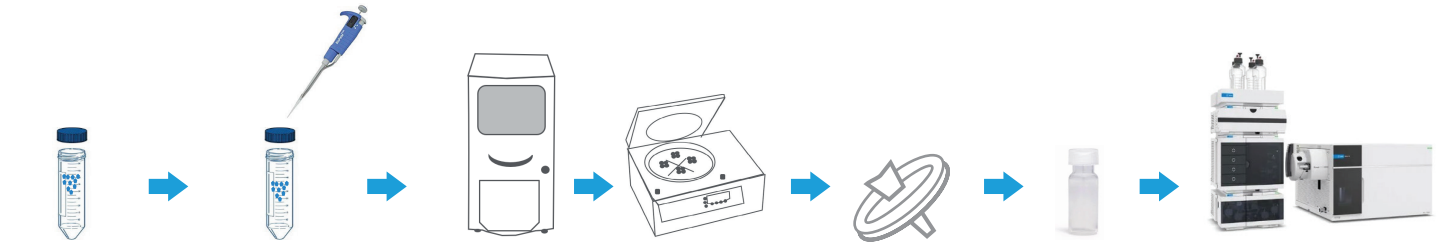
Solvent extraction is a common method used to analyze and test packaging materials, particularly for identifying compounds that can migrate from packaging materials into products or food.[5,8] In this study, a simple and fast solvent extraction method was developed for leaching PFAS from paper straw samples (Figure 1). A 1 ± 0.01 g sample was weighed into a 15 mL PP Falcon tube for extraction.

To prepare QC samples, an appropriate amount of native PFAS spike mix and surrogate spike (EIS) was added to the tube. QC samples were spiked to achieve low, middle, and high concentrations of 1.0 µg/kg (low spike quantity, LSQ), 10 µg/kg (middle spike quantity, MSQ), and 50 µg/kg (high spike quantity, HSQ), respectively. A matrix blank, which lacked the native PFAS standard mix, was also prepared.

Next, 10 mL of methanol was added into each sample tube. The samples were then mechanically shaken at 2,000 rpm for 30 minutes, followed by ultrasonic assisted extraction (UAE) at 60 °C for one hour. The mechanical shaking and UAE step was repeated twice. The samples were then centrifuged at 4,200 rpm for 15 minutes. After centrifugation, the supernatant extract was filtered into a PP vial. If not analyzed immediately, these extracts were stored at –20 °C. Prior to analysis, a final dilution was performed in which 800 µL of the filtered extract was transferred to a PP vial, with the addition of 150 µL of water and 50 µL of IPS mix (non-extracted internal standard). The solution was thoroughly vortexed and prepared for LC/TQ injection (Figure 1). Two technical preparations were performed for each QC sample concentration.

Instrumentation

An Agilent 1290 Infinity II UHPLC system was used for chromatographic separation. To minimize PFAS contamination, the standard LC system fluid path was replaced with an Agilent InfinityLab PFC-free HPLC conversion kit (part number 5004-0006), including bottle head assembly, pump head adapter assembly, inline filter, multiwash tubing kit, and a PFC delay column. An Agilent ZORBAX RRHD Eclipse Plus C18, 2.1 × 100 mm, 1.8 µm column (part number 959758-902) was installed on the multicolumn thermostat. A gradient method with less than 15 minutes elution time, as outlined in the Agilent PFAS eMethod (part number G5285AA), was used. This method used 5 mM ammonium acetate in water (mobile phase A) and 100% methanol (mobile phase B) at a flow rate of 0.4 mL/min. Targeted



Sample

Finely cut the paper straw. Weigh a 1 ± 0.01 g sample into a 15 mL polypropylene (PP) Falcon tube (p/n 5610-2039).

Spiking/solvent addition

For QC sample preparation, spike an appropriate amount of surrogate mix and PFAS analyte mix. Add 10 mL of methanol.

Extraction

Place the samples on a mechanical shaker at 2,000 rpm for 30 minutes, followed by ultrasonic assisted extraction (UAE) at 60 °C for 1 hour. Repeat this step twice. Centrifuge the tube at 4,200 rpm for 15 minutes.

Filtration

Filter the supernatant extract using a PP syringe (p/n 9301-6476) and nylon membrane syringe filter (p/n 5190-5092). If the analysis is not immediate, store the extract at –20 °C.

Final dilution

Transfer 800 µL of the filtered extract into a 2 mL PFC-free PP vial (p/n 5191-8150), then add 150 µL of H_2O and 50 µL of isotope performance standard. Vortex well.

Analysis

The sample is ready for LC/TQ injection (dilution factor: 12.5-fold).

Figure 1. Workflow for PFAS extraction from a paper straw.

quantification was performed using the 6495D LC/TQ system equipped with an Agilent Jet Stream (AJS) ion source operating in negative ionization mode. Autotuning was performed in standard quadrupole mode to optimize instrument parameters. Data processing was performed using Agilent MassHunter LC/MS Acquisition software version 12.1 Update 3 and Agilent MassHunter Quantitative Analysis software version 12.1. The acquisition method was based on the Agilent PFAS multiple reaction monitoring (MRM) database for 108 compounds (part number G1736AA) and two other analytes (PFUnDS and PFTrDS). This method covers the four regulated PFAS in EU 2023/915 and forty PFAS in EPA 1633, as well as the recommended targets under EURL POPs for PFAS in food and feed, AOAC SMPR 2023.003, US FDA C-010.03, and USDA CLG-PFAS 2.04 for PFAS in food. The full list of PFAS targets and CAS numbers is shown in Table 1.

Table 1. Analytical results summary.

Target Number	Compound Name	CAS Number	Surrogate	RT (min)	MDL (µg/kg)	LOQ (Validated) (µg/kg)	% Recovery LSQ (1 µg/kg)	% Recovery MSQ (10 µg/kg)	% Recovery HSQ (50 µg/kg)
1	PFBPA	52299-24-8	Cl-PFOPA	1.2	0.07	1	67	61	59
2	PFBA	375-22-4	$^{13}C_4$-PFBA	3.1	0.08	1	98	97	90
3	PFMPA	377-73-1	$^{13}C_4$-PFBA	3.2	0.07	1	81	88	85
4	PFPeA	2706-90-3	$^{13}C_5$-PFPeA	3.5	0.06	1	112	88	82
5	3:3 FTCA	356-02-5	$^{13}C_5$-PFPeA	3.5	0.10	1	89	94	91
6	PFBS	375-73-5	$^{13}C_3$-PFBS	3.5	0.04	1	82	86	83
7	PFHxPA	40143-76-8	Cl-PFOPA	3.6	0.09	1	110	101	89
8	PFMBA	863090-89-5	$^{13}C_5$-PFPeA	3.6	0.03	1	73	82	80
9	Cl-PFHxPA	N/A	Cl-PFOPA	3.7	0.11	1	98	94	86
10	PFEESA	113507-82-7	$^{13}C_3$-PFBS	3.7	0.03	1	80	87	84
11	NFDHA	151772-58-6	$^{13}C_5$-PFHxA	3.9	0.04	1	74	81	79
12	4:2 FTSA	757124-72-4	$^{13}C_2$-4:2 FTSA	3.9	0.06	1	87	93	76
13	PFHxA	307-24-4	$^{13}C_5$-PFHxA	4.0	0.03	1	94	82	79
14	PFPeS	2706-91-4	$^{13}C_3$-PFHxS	4.0	0.07	1	74	82	80
15	HFPO-DA	13252-13-6	$^{13}C_3$-HFPO-DA	4.1	0.04	1	99	99	97
16	FBSA	30334-69-1	$^{13}C_3$-PFHxS	4.2	0.04	1	80	88	86
17	P5MeODIOXOAc	1190931-41-9	$^{13}C_3$-HFPO-DA	4.4	0.17	1	100	93	91
18	PFHpA	375-85-9	$^{13}C_4$-PFHpA	4.6	0.06	1	120	81	78
19	PFHxS	355-46-4	$^{13}C_3$-PFHxS	4.7	0.07	1	77	84	83
20	DONA	919005-14-4	$^{13}C_4$-PFHpA	4.7	0.03	1	71	75	76
21	PFOPA	40143-78-0	Cl-PFOPA	4.8	0.11	1	80	100	100
22	5:3 FTCA	914637-49-3	$^{13}C_2$-6:2 FTUCA	4.8	0.08	1	78	84	82
23	6:2 FTUCA	70887-88-6	$^{13}C_2$-6:2 FTUCA	4.8	0.07	1	86	90	89
24	6:2 FTCA	53826-12-3	$^{13}C_2$-6:2 FTCA	5.0	0.09	1	111	111	114
25	4-PFecHS	646-83-3	$^{13}C_8$-PFOS	5.3	0.10	1	82	90	89
26	6:2 FTSA	27619-97-2	$^{13}C_2$-6:2 FTSA	5.4	0.06	1	89	92	71
27	PFOA	335-67-1	$^{13}C_8$-PFOA	5.4	0.02	1	82	78	79
28	PFHpS	375-92-8	$^{13}C_8$-PFOS	5.5	0.06	1	78	84	84
29	MeFBSA	68298-12-4	$^{13}C_8$-PFOSA	5.7	0.15	1	69	69	73
30	FHxSA	41997-13-1	$^{13}C_8$-PFOS	6.0	0.04	1	83	90	89
31	PFNA	375-95-1	$^{13}C_9$-PFNA	6.3	0.03	1	81	82	81
32	PFOS	1763-23-1	$^{13}C_8$-PFOS	6.4	0.05	1	76	82	81
33	8:2 FTUCA	70887-84-2	$^{13}C_2$-8:2 FTUCA	6.6	0.05	10	52	77	79
34	PFDPA	52299-26-0	Cl-PFOPA	6.6	0.14	1	79	112	108
35	7:3 FTCA	812-70-4	$^{13}C_2$-8:2 FTUCA	6.7	0.11	1	80	85	86

Target Number	Compound Name	CAS Number	Surrogate	RT (min)	MDL (µg/kg)	LOQ (Validated) (µg/kg)	% Recovery LSQ (1 µg/kg)	% Recovery MSQ (10 µg/kg)	% Recovery HSQ (50 µg/kg)
36	HFPO-TA	13252-14-7	$^{13}C_9$-PFNA	6.7	0.07	1	75	81	80
37	8:2 FTCA	27854-31-5	$^{13}C_2$-8:2 FTCA	6.7	0.09	1	94	90	80
38	9Cl-PF3ONS	756426-58-1	$^{13}C_8$-PFOS	6.9	0.09	1	68	74	74
39	FOSAA	2806-24-8	$^{2}H_3$-N-MeFOSAA	7.1	0.09	1	83	89	86
40	8:2 FTSA	39108-34-4	$^{13}C_2$-8:2 FTSA	7.2	0.06	1	88	92	75
41	PFNS	68259-12-1	$^{13}C_8$-PFOS	7.2	0.08	1	83	91	91
42	PFDA	335-76-2	$^{13}C_6$-PFDA	7.2	0.09	1	74	79	79
43	8:3 FTCA	34598-33-9	$^{13}C_6$-PFDA	7.6	0.07	1	97	100	98
44	N-MeFOSAA	2355-31-9	$^{2}H_3$-N-MeFOSAA	7.6	0.08	1	82	89	87
45	MeFHxSA	68259-15-4	$^{13}C_8$-PFOSA	7.8	0.10	1	71	74	75
46	PFDS	335-77-3	$^{13}C_8$-PFOS	7.9	0.09	1	80	90	89
47	PFUnDA	2058-94-8	$^{13}C_7$-PFUnDA	8.0	0.11	1	67	73	75
48	N-EtFOSAA	2991-50-6	$^{2}H_5$-N-EtFOSAA	8.0	0.04	1	76	86	84
49	PFOSA	754-91-6	$^{13}C_8$-PFOSA	8.0	0.03	1	77	82	81
50	10:2 FTUCA	70887-94-4	$^{13}C_2$-10:2 FTUCA	8.2	0.07	1	77	82	82
51	11Cl-PF3OUdS	763051-92-9	$^{13}C_8$-PFOS	8.3	0.06	1	65	72	71
52	PFUnDS	749786-16-1	$^{13}C_7$-PFUnDA	8.5	0.07	10	64	72	76
53	PFDoDA	307-55-1	$^{13}C_2$-PFDoDA	8.5	0.08	1	72	73	71
54	10:2 FTSA	120226-60-0	$^{13}C_2$-8:2 FTSA	8.5	0.07	1	107	115	96
55	10:2 FTCA	53826-13-4	$^{13}C_2$-10:2 FTCA	8.5	0.08	10	N.A.	98	99
56	6:6 PFPi	40143-77-9	$^{13}C_2$-PFDoDA	8.7	0.09	1	77	82	82
57	PFDoS	79780-39-5	$^{13}C_8$-PFOS	8.9	0.06	1	83	78	78
58	PFTrDA	72629-94-8	$^{13}C_2$-PFDoDA	8.9	0.11	1	66	74	76
59	N-MeFOSA	31506-32-8	$^{2}H_3$-N-MeFOSA	9.2	0.12	1	93	97	96
60	FDSA	N/A	$^{13}C_8$-PFOSA	9.2	0.04	1	66	72	70
61	MeFOSE	24448-09-7	$^{2}H_7$-MeFOSE	9.2	0.08	1	79	82	85
62	PFTrDS	791563-89-8	$^{13}C_2$-PFTDA	9.3	0.08	10	57	75	74
63	6:2 diPAP	57677-95-9	$(^{13}C_2)_2$-6:2 diPAP	9.3	0.07	1	84	87	86
64	PFTDA	376-06-7	$^{13}C_2$-PFTDA	9.3	0.11	1	67	72	72
65	6:8 PFPi	610800-34-5	$(^{13}C_2)_2$-6:2 diPAP	9.4	0.07	N.D.*	24	26	27
66	N-EtFOSA	4151-50-2	$^{2}H_5$-N-EtFOSA	9.6	0.10	1	74	79	79
67	EtFOSE	1691-99-2	$^{2}H_9$-EtFOSE	9.6	0.08	1	93	90	92
68	6:2/8:2 diPAP	943913-15-3	$(^{13}C_2)_2$-6:2 diPAP	9.9	0.06	10	61	65	67
69	8:8 PFPi	40143-79-1	$(^{13}C_2)_2$-6:2 diPAP	10.0	0.05	N.D.*	24	25	28
70	PFHxDA	67905-19-5	$^{13}C_2$-PFHxDA	10.1	0.05	1	84	83	80
71	8:2 diPAP	678-41-1	$(^{13}C_2)_2$-8:2 diPAP	10.4	0.04	1	75	77	77
72	PFODA	16517-11-6	$^{13}C_2$-PFHxDA	10.7	0.08	1	76	85	83
73	diSAmPAP	2965-52-8	$(^{13}C_2)_2$-8:2 diPAP	11.0	0.04	N.D.*	54	58	59

* N.D.: Not determined. The LOQ for three compounds were not determined due to lower recovery.

Results and discussion

Method sensitivity and linearity

By implementing the described LC/TQ acquisition method setup and data processing steps, the 6495D LC/TQ system demonstrated excellent sensitivity for 73 native PFAS across 14 target groups (Figure 2). The abbreviations for these 14 target groups are defined in Table 2. The MRM overlay of 15 PFCA targets in the LSQ illustrates the symmetric separation and superior sensitivity of the 6495D LC/TQ system for the determination of PFAS in FCMs (Figure 3). Despite the close elution of two pairs of PFCAs (PFUnDS with PFDoA, and PFTrDS with PFTDA), the unique MRMs of these targets enable unambiguous compound quantitation and superior accuracy.

Method detection limit (MDL) and the limit of quantification (LOQ) assessments were performed to evaluate the sensitivity of the entire workflow. The MDL was calculated using MassHunter Quantitative Analysis software version 12.1, based on nine continuous injections derived from two technical replicates of LSQ samples.[9] A similar procedure is described in 40 CFR Part 136 Appendix Revision 2, US EPA.[10] The MDL values (based on sample weight) for each target are summarized in Table 1.

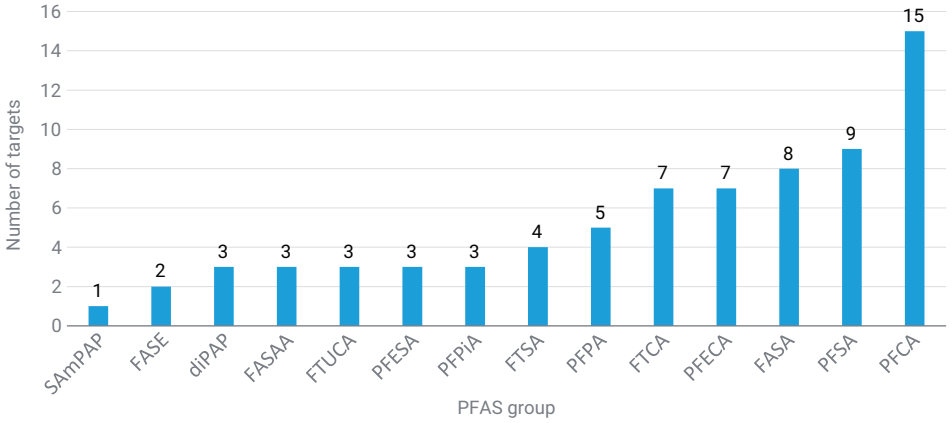


Figure 2. Distribution of 73 native PFAS across different groups.

Table 2. Abbreviations for 14 PFAS groups.

Abbreviation	Description
diPAP	Polyfluoroalkyl phosphoric diester
SAmPAP	Perfluorooctane sulfonamido-ethanol-based phosphate diester
FASA	Perfluoroalkane sulfonamides
FASAA	Perfluoroalkane sulfonamido acetic acid
FASE	Perfluoroalkane sulfonamido ethanol
FTCA	Fluorotelomer carboxylic acid
FTSA	Fluorotelomer sulfonic acid
FTUCA	Fluorotelomer unsaturated carboxylic acid
PFCA	Perfluoroalkyl carboxylic acid
PFECA	Perfluoroether carboxylic acid
PFESA	Perfluoroether sulfonic acid
PFPA	Perfluoroalkyl phosphonic acid
PFPiA	Perfluoroalkyl phosphinic acid
PFSA	Perfluoroalkyl sulfonic acid

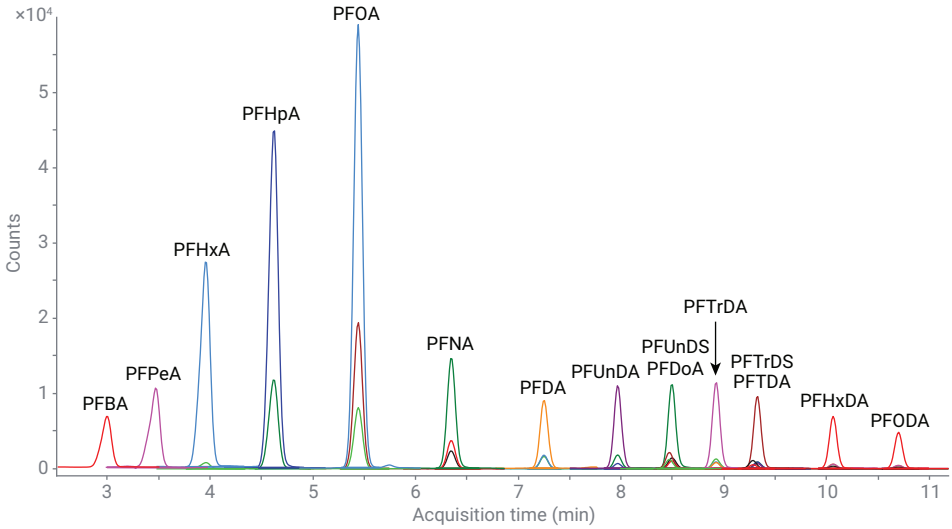


Figure 3. Overlaid MRM chromatogram of 15 PFCA targets in the paper straw LSQ at a spiking level of 1.0 µg/kg (target concentration in ready-to-inject sample vial is 80 ng/L).

Figure 4 illustrates the MDL distribution for all targets. Notably, all 73 analytes had an MDL of ≤ 0.2 µg/kg. Among these, 20 analytes exhibited an MDL of ≤ 0.05 µg/kg, while 43 targets fell within an MDL range of 0.05 to 0.1 µg/kg. Furthermore, the MDLs for PFOA (0.02 µg/kg), PFOS (0.05 µg/kg), PFDA (0.09 µg/kg), PFNA (0.03 µg/kg), and PFHxS (0.07 µg/kg) were < 0.1 µg/kg. These values are significantly lower than the typical regulatory requirements in similar food market spaces. These results underscore the exceptional sensitivity of PFAS analysis from FCMs using the 6495D LC/TQ system equipped with the dedicated PFC-free conversion kit. This provides assurance that the compounds of interest can be quantified accurately without false positives.

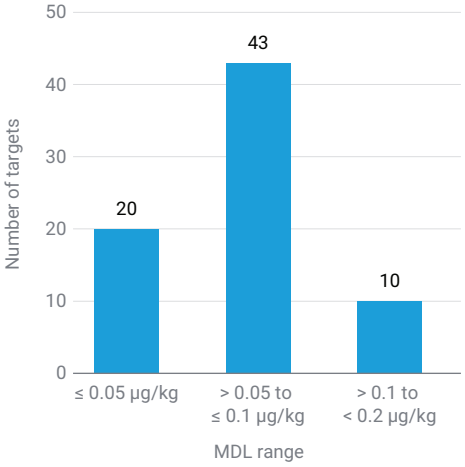


Figure 4. MDL distribution of all 73 targets.

LOQ is the lowest concentration of the analyte in the test material that has been validated with acceptable recovery and repeatability, using the entire workflow and identification criteria.[11] In this work, prespiked sample QCs (LSQ, MSQ, and HSQ) were used to establish the method LOQ following these identification criteria:

- Recovery between 65 and 135% with percent relative standard deviation (%RSD) ≤ 20%
- Intrabatch retention time (RT) tolerance 1%
- Signal-to-noise ratio (S/N) ≥ 3:1
- Ion ratio of quantifier and qualifier within ± 30%

The LOQ values for each analyte are summarized in Table 1. Notably, 65 out of 73 analytes (89%), including PFOA, PFOS, PFNA, and PFHxS, achieved an LOQ of 1 µg/kg, demonstrating the outstanding performance of this workflow for quantifying PFAS in FCM samples.

The method linearity range for each of the targets was established using linear regression with 1/x weighting for most of the 73 analytes and a minimum of five calibration levels. All target analytes exhibited excellent R^2 values, exceeding 0.99 (except for 8:2 FTCA). Additionally, the accuracy of each calibration standard fell within the commonly accepted limits of 70 to 130%.

Method recovery and precision

Matrix-spiked QC recovery was employed to evaluate the accuracy of this PFAS analysis workflow. The method was set up for the analysis of 73 native PFAS analytes and 34 labeled compounds (surrogates), which served as EIS for isotope dilution or internal standard quantification of the native PFAS. This isotope dilution method effectively corrects matrix effects and reduces target loss, significantly boosting the accuracy of analytical performance.[11-13] The EPA 533 isotope performance standard mix includes three labeled PFAS compounds ($^{13}C_3$-PFBA, $^{13}C_2$-PFOA, and $^{13}C_4$-PFOS), which are used as nonextracted internal standards (NIS) for calculating the surrogate recoveries. To correct for native PFAS levels, the measured concentration of each analyte in the spiked QC sample was adjusted by subtracting its presence in the unspiked FCM matrix blank sample.

The method recovery was calculated based on the mean percent recovery. Method precision was assessed using the %RSD of recoveries, calculated from replicate injections of duplicate technical preparations (n = 6). Table 1 lists recovery values of each analyte. For LSQ, MSQ, and HSQ samples, approximately 90% of analytes achieved recovery within a range of 65 to 120%, meeting the commonly accepted range for food matrices (Figure 5).[11] Among these,

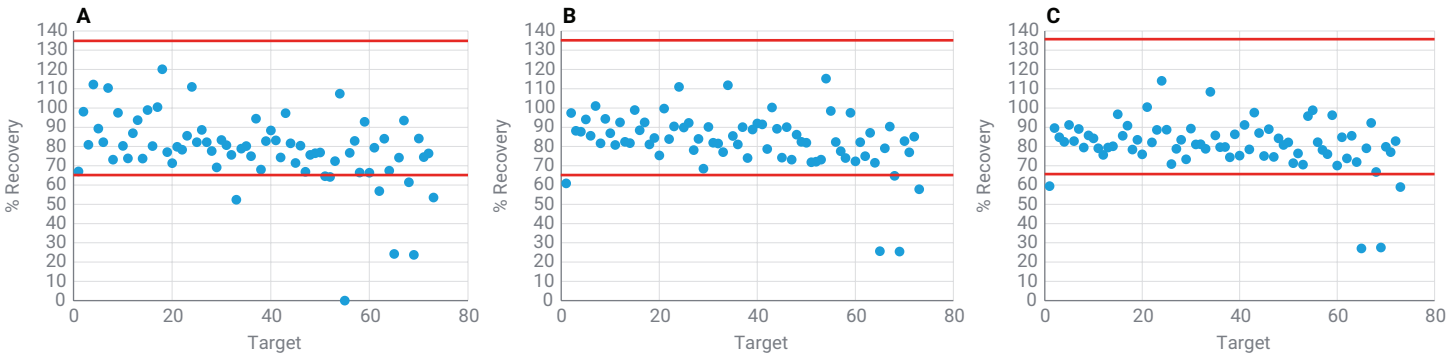


Figure 5. Mean recovery (n = 6) distribution of all 73 targets, (A) LSQ, (B) MSQ, and (C) HSQ. The recovery limit of 65 to 135% is marked using a red line.

PFNA, PFOS, PFOA, and PFHxS achieved recovery > 75% across all three QC levels.

Recovery analysis of 10:2 FTCA in the LSQ sample was impacted by matrix interference. Poor recovery was observed for two targets, 8:8 PFPi and 6:8 PFPi, in all three QC samples. The recovery repeatability for all targets was ≤ 20% RSD for all spiked QC samples. Notably, 96% of the samples were below 10% RSD, except for three outliers in LSQ and one outlier in MSQ (Figure 6). The repeatability of measures for 8:8 PFPi and 6:8 PFPi was within 10%, despite the poor recovery. However, these targets are currently not listed in any of the regulatory guidelines discussed here. These results confirm the excellent extraction efficiency of PFAS compounds from FCM and the reproducibility of measurements using these methods.

In various regulatory guidelines, PFAS compounds from the PFCA and PFSA groups, such as PFOA, PFDA, and PFOS, are consistently highlighted as critical concerns. Special evaluation of these three targets was performed. MRM overlays of duplicate LSQs demonstrate consistency between the two technical preparations (Figure 7). The response reproducibility of the targets confirms the reliability of this workflow for routine PFAS analysis in FCM samples.

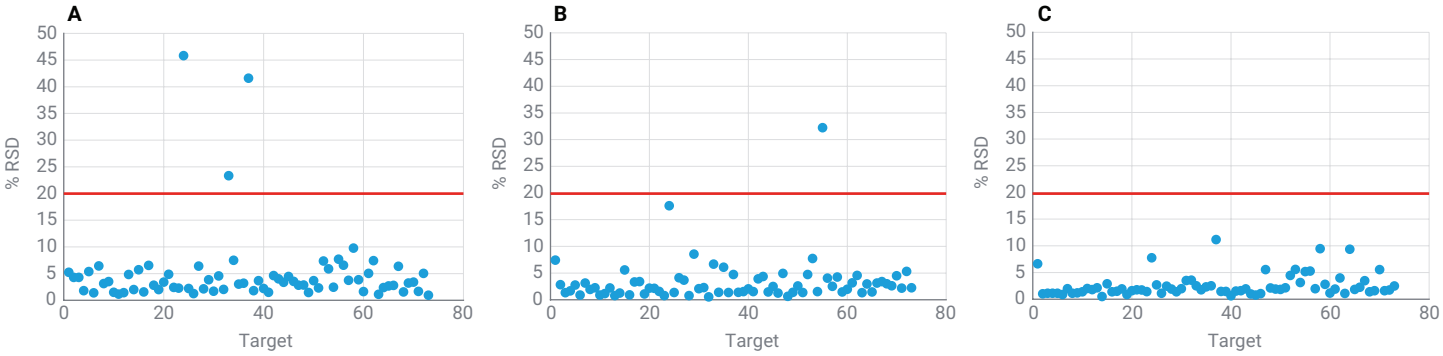


Figure 6. Recovery %RSD summary of all 73 targets calculated from replicate injections of duplicate spiked samples (n = 6), (A) LSQ, (B) MSQ, and (C) HSQ. The 20% RSD limit is marked using a red line.

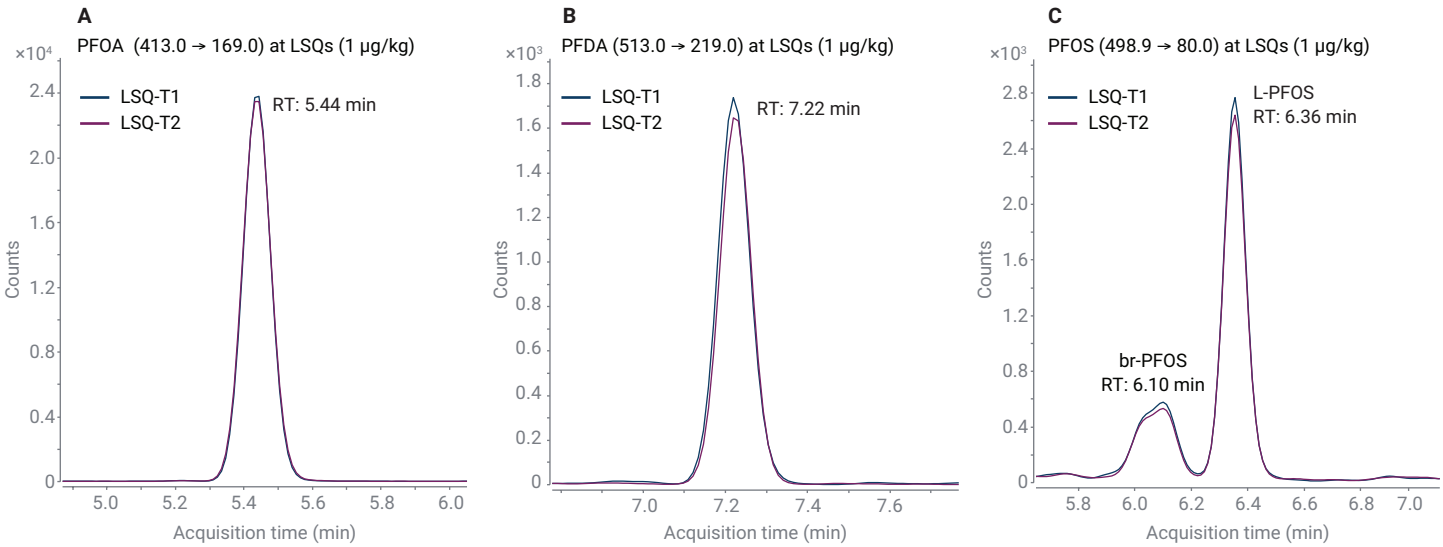


Figure 7. Overlay of MRM traces of critical targets: PFOA (A), PFDA (B), and PFOS (C) from two LSQ technical preparations (T1: techinical preparation 1, T2: techinical preparation 2). **Note:** The ready-to-injection concentration of targets at the LSQ level is 80 ng/L.

Quantitation of PFAS from blank food contact material matrix

The native concentration of PFAS in FCM samples was investigated to validate the reliability of this newly developed analytical method. Reagent blank (procedural blank without sample addition) and unspiked FCM samples (matrix blanks) were extracted in triplicate using the same preparation procedure and then analyzed by LC/TQ. The data revealed no contamination in the reagent blank, while approximately 10 native PFAS compounds at trace levels were observed in the matrix blank. Noteworthy compounds with residue concentrations greater than the MDL were PFHxA, PFHpA, PFOA, PFNA, and 10:2 FTCA.

Conclusion

This study successfully demonstrated an end-to-end workflow for the quantitative analysis of 73 native PFAS from food contact material (FCM) samples. A simple and rapid solvent extraction procedure was used to leach PFAS compounds from the matrix. This was followed by a dilute-and-shoot approach to LC/TQ without the need for drying and reconstitution. Superior chromatographic separation was achieved for all 110 PFAS compounds in the initial 12 minutes. This demonstrates the performance efficiency of the Agilent 1290 Infinity II LC for routine laboratory use and enhanced lab productivity. The Agilent 6495D triple quadrupole LC/MS equipped with the PFC-free conversion kit offered excellent background contamination removal and ppt-level sensitivity for precise PFAS quantitation from the FCM matrix.

The method verification results, including sensitivity and recovery, confirm the applicability of this workflow for PFAS measurements at lower concentrations. These high-quality analytical outcomes enable FCM manufacturers to make informed decisions during production, ensuring compliance with upcoming regulatory standards and enhancing consumer safety. Additionally, the use of the dedicated PFAS MRM database provided ease of method creation while helping to reduce the MS parameter optimization time.

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