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PFAS in Food Contact Materials (FCM) / LCMS-8050

Application News

Analysis of Per- and Polyfluoroalkyl Substances in Fast Food Packaging by LC-MS/MS Method

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User Benefits

- A direct LC-MS/MS method was established for quantitative determination of 15 targeted PFAS compounds in food contact materials (FCM) using LCMS-8050.
- The results show that 12 out of 15 targeted PFAS were present in seven fast food packaging samples. The concentrations of the PFAS were far below the limit set by the Danish Ministry of Environmental and Food Guideline in 2015.

■ Introduction

Per- and polyfluoroalkyl substances (PFAS) have been detected in waters, soils, sediments, fish, foods and human blood among others. Recently, PFAS were reported in disposable fast food packaging such as paper wrappers, paperboard clamshells and beverage cups [1,2]. In 2015, the Danish Ministry of Environmental and Food set a guideline to limit the maximum total organic fluorine to 0.35 ug/dm^2 for food contact materials (FCM) [3]. This value corresponds to 0.5 ug of PFOA/dm^2. However, the same organization has banned the use of all fluorinated substances in FCM since 2020 [4].

Targeted screening and quantitation of PFAS in drinking water by LC-MS/MS are well established with reference to the US EPA Method 537 [5]. Publications on PFAS analysis in FCM have become available in recent years. Laurel A. Schaider et al. [6] reported their results of PFAS analysis using PIGE and LC-HRMS methods on over 400 FCM samples. In this Application News, an LC-MS/MS method for the detection and quantitation of 15 PFAS, including PFOA and PFOS, in fast food packaging samples is presented. The same sample pre-treatment used by Schaider et al. [6] was adopted to extract PFAS from the samples.

■ Experimental

Reagents and PFAS Standards

Acetonitrile (LC-MS grade) and methanol (LC-MS grade) were obtained from commercial suppliers. Ammonium acetate (>99%) of LC-MS grade was used as additive in the mobile phase prepared with Milli-Q water. Fifteen PFAS standards (Table 2) were purchased from Wellington Laboratories and Apollo Scientific. M-PFOS (with $^{13}C_4$) and M-PFOA (with $^{13}C_4$) were used as internal standards during method development.

Sample preparation

Seven FCM samples including paper wrappers, paperboard clamshells and beverage cups were cut into 10 cm x 10 cm (100 cm^2) and weighed. Each sample was further cut into smaller pieces for extraction and immersed in 20 mL of MeOH in a polypropylene (PP) centrifuge tube. Approximately 4 mL of the extract was cleaned using Supelclean™ ENVI-Carb™ SPE (6 mL/500 mg). The collected extract was evaporated to dryness with N_2 on a TurboVap LV evaporator (Biotag). The dried sample was reconstituted with 0.8 mL of 5 mM ammonium acetate solution and transferred into a 1.5 mL glass vial for LC-MS analysis (Fig. 1)

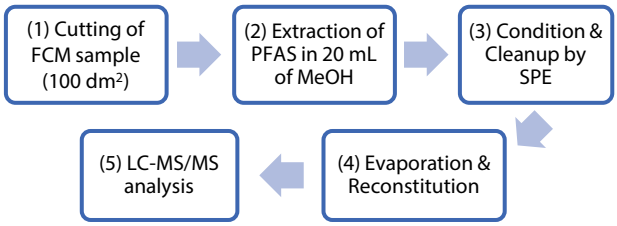

Figure 1 Flowchart of sample pre-treatment for PFAS in food contact materials (FCM).

LC-MS/MS analytical conditions

Details of the analytical conditions for PFAS using LCMS-8050 (Shimadzu Corporation, Japan) with a Shim-pack Velox C18 column are shown in Table 1.

Table 1 Analytical conditions of PFAS on LCMS-8050

LC Conditions	
Column	Shim-pack Velox™, C18 (2.1 X 100 mm, 2.7 µm)
Flow Rate	0.4 mL/min
Mobile Phase	A: 5 mM Ammonium acetate in water B: Acetonitrile
Elution mode	Gradient elution, 12 mins
Oven Temp.	40°C
Injection Vol.	10 µL
Interface Conditions	
Interface	Heated ESI
Interface Temp.	300°C
DL Temp.	250°C
Heat Block Temp.	400°C
Nebulizing Gas	2 L/min
Heating Gas Flow	10 L/min
Drying Gas Flow	10 L/min
MS mode	MRM, negative mode

■ Results and Discussion

MRM Method Setup

An LC-MS/MS method was developed for the detection and quantitation of 15 PFAS compounds in negative MRM mode (Table 2). A mixed standard was prepared from individual stock solutions to generate calibration curves. Approximately 40 µL of each PFAS stock solution (50 ppm) was transferred into a 1.5 mL LC sample vial and diluted with 400 µL of pure water, resulting in a 2 ppm mixed standard. Calibration series, with or without internal standards (M-PFOS and M-PFOA), were prepared from the mixed standard using pure water as the diluent.

Two MRM transitions were optimized for each compound except for PFBA and PFPeA with only one (Table 2).

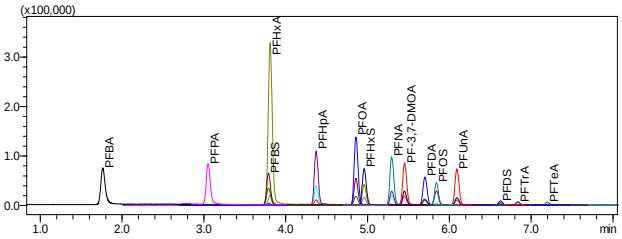

Figure 2 MRM peaks of 15 PFAS standards (1 ppb each).

With an optimized LC gradient elution, all 15 PFAS were eluted within 8 mins (Figure 2).

Table 2 MRM parameters, retention times and calibration curve ranges of 15 PFAS using LCMS-8050

Event #	PFAS (Abbr.)	Formula	CAS No.	Exact Mass	MRM (quantifier)	CE (V)	RT (min)	Range (ng/mL)	R^2
1	PFBA	C4HF7O2	375-22-4	214.0	212.9>169.1	10	1.76	0.1 ~ 10	0.999
2	PFPeA	C5HF9O2	2706-90-3	264.0	262.9>219.1	8	3.05	0.1 ~ 10	0.999
3	PFBS	C4F9SO3H	29420-49-3	300.0	298.9>79.9	31	3.79	0.1 ~ 10	0.993
4	PFHxA	C6HO2F11	307-24-4	314.0	313.0>269.1	9	3.81	0.1 ~ 10	0.998
5	PFHpA	C7HF13O2	375-85-9	364.0	362.9>319.1	10	4.37	0.1 ~ 10	0.999
7	PFOA	C8HF15O2	335-67-1	414.0	413.0>369.1	10	4.86	0.1 ~ 10	0.999
8	PFHxS	C6F13HO3S	82382-12-5	399.9	398.9>79.9	45	4.96	0.1 ~ 10	0.996
9	PFNA	C9HF17O2	375-95-1	464.0	463.0>419.0	10	5.30	0.1 ~ 10	0.998
10	PF-3,7-DMOA	C10HF19O2	172155-07-6	514.0	469.0>269.1	22	5.45	0.1 ~ 10	0.996
11	PFDA	C10HF19O2	335-76-2	514.0	513.0>469.1	11	5.70	0.1 ~ 10	0.987
13	PFOS	C8F17O3HS	4021-47-0	499.9	499.0>79.9	54	5.84	0.1 ~ 10	0.999
14	PFUnA	C11HF21O2	2058-94-8	564.0	563.0>519.1	11	6.09	0.1 ~ 10	0.952
15	PFDS	C10HF21SO3	2806-15-7	599.9	599.0>79.9	55	6.62	0.2 ~ 10	0.988
16	PFTrA	C13HO2F25	72629-94-8	664.0	663.0>619.0	13	6.84	0.5 ~ 10	0.996
17	PFTeA	C14HO2F27	376-06-7	714.0	712.9>668.9	13	7.20	1 ~ 10	0.988

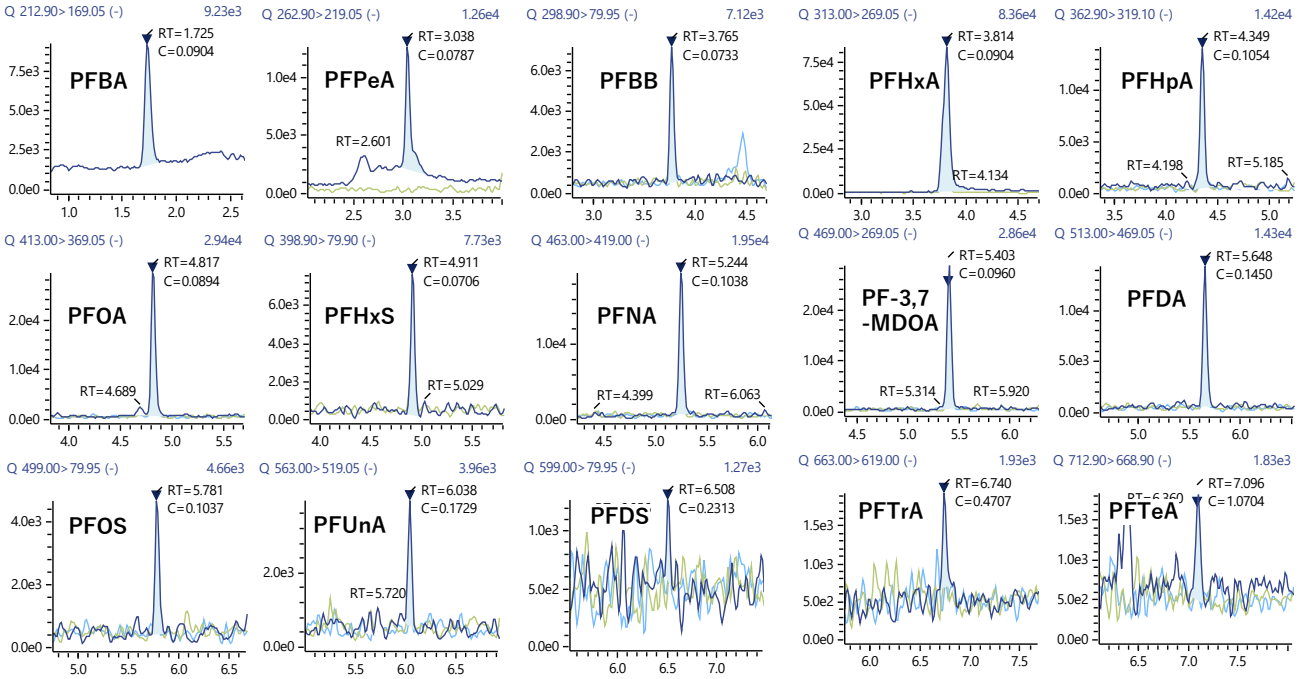

Figure 3 Individual MRM peaks of 15 PFAS compounds at the lowest calibration levels (refer to Table 2) using LCMS-8050

Calibration curves of 15 PFAS

Linear calibration curves were established with or without internal standards. Table 2 shows the R^2 values and ranges without the use of internal standards. The LODs of the method are lower than 0.1 ppb for most PFAS except for PFDS, PFTrA and PFTeA. The MRM peaks of the lowest calibration levels are shown in Figure 3.

Results of PFAS in fast food packaging

Seven fast food packaging samples (Table 3) were analysed using the validated LC-MS/MS method with external calibration. Sample pre-treatment described previously (Figure 1) was employed using MeOH for extraction and SPE for removal of pigments, dyes etc. The same pure water (Milli-Q) for preparing the standards was used as blank in the batch run of LC-MS/MS analysis.

Table 3 Fast food packaging samples for PFAS screening by LC-MS/MS method

S. No.	FCM Type	Description	Weight (mg /100 cm^2)
P1	paper	wrapping paper	302.4
P2	paper	pouch	551.3
P3	paper	wrapping paper	306.5
P4	paperboard	clamshell	2686.9
P5	paperboard	clamshell	2831.0
P6	paperboard	clamshell	2765.6
P7	paperboard	beverage cup	2406.2

Each sample was analysed in triplicate using LC-MS/MS to ensure repeatability of results (RSD < 10%). The average results of the seven fast food packaging samples are shown in Table 4, while PFAS profiles of P1, P3 and P6 are shown in Figure 4. Multiple PFAS were found in every sample. PFOA, a PFAS banned under the POPs regulation in 2020, was detected in every sample ranging from 0.19 ng/dm^2 to 1.69 ng/dm^2. In contrast, PFOS was not detected in all the samples. The highest amount PFAS found is PF-3,7-DMOA (up to 53.03 ng/dm^2). It is worth to note that the total amounts of the 15 PFAS measured range from 6.07 ng/dm^2 (P3) to 95.9 ng/dm^2 (P1), which levels are far below the limit set by the Danish Ministry of Environment and Food in 2015 for total organic fluorine (0.35 ug/dm^2) in food contact materials (FCM). Laurel A. Schaider et al. [6] reported various fluorinated compounds, including known PFAS, in 20 FCM samples by LC-HRMS, with 70% having a total fluorine level greater than 200 nmol/cm^2.

■ Conclusion

An LC-MS/MS method was established for quantitative determination of 15 PFAS compounds in food contact materials using LCMS-8050. Twelve (12) out of the 15 PFAS compounds studied were present in seven fast food packaging samples. The total amounts of PFAS (6.07-95.9 ng/dm^2) were far below the limit set by Danish Ministry of Environment and Food in 2015.

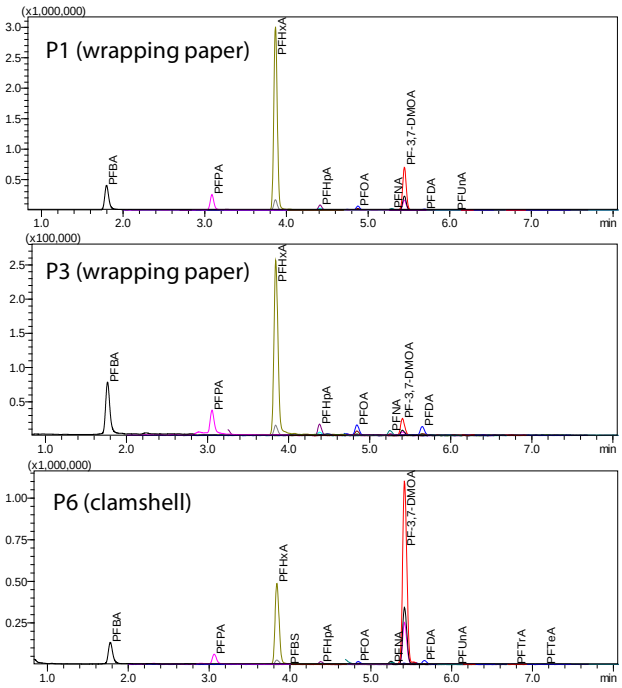

Figure 4 PFAS detected in P1, P3 and P 6 samples.

Table 4 Types and amounts of PFAS in seven fast food packaging samples

PFAS (Abbr.)	PFAS Content (ng/dm^2)						
	P1	P2	P3	P4	P5	P6	P7
PFBA	19.89	2.59	2.59	4.43	6.32	7.02	3.93
PFPeA	10.93	1.46	1.47	1.87	2.48	3.20	2.1
PFBS	-	-	-	-	-	0.32	-
PFHxA	30.47	1.68	1.15	2.91	3.66	5.33	2.42
PFHpA	2.58	0.44	0.21	0.62	0.46	0.59	0.53
PFOA	1.69	0.23	0.17	0.73	0.19	0.33	0.24
PFHxS	-	-	-	-	-	-	-
PFNA	0.32	0.11	0.09	0.44	0.17	0.41	0.17
PF-3,7-DMOA	28.98	0.36	0.2	2.14	1.41	53.03	0.56
PFDA	0.92	0.36	0.2	2.1	0.59	1.73	0.51
PFOS	-	-	-	-	-	-	-
PFUnA	0.12	-	-	-	-	0.07	-
PFDS	-	-	-	-	-	-	-
PFTrA	-	-	-	0.92	1.23	0.91	-
PFTeA	-	-	-	1.73	1.96	2.24	-
Total	**95.9**	**7.23**	**6.07**	**17.88**	**18.47**	**75.17**	**10.45**

■ References

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5. Brahm P. et al., "Analysis of PFAS Specified in EPA Method 537 using Shimadzu UFMS", Shimadzu Application News C184A (2019).
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