

A Fast LC/MS/MS Method for High Sensitivity Determination of Twenty-Six Perfluorocompounds in Textiles

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Introduction

Perfluorocompounds (PFCs) are widely used in different consumer products including textile coatings for their excellent oil and water repellent property. However, researches in recent years have shown that PFCs can cause adverse effects to organisms and being persistent in both environment and organism. Hence, industries started to phase out the use of PFCs 2000 [1]. The European Union (EU) had announced a maximum level of

1 µg/m² for PFOS while for Norway, a maximum level of 1 µg/m² for PFOA. Hence, there is a need for quantitative analysis of extractable PFOS, PFOA and other PFCs in various skin-contact consumer products like textiles [2-3]. Here, we describe a fast LC/MS/MS method for high sensitivity screening and quantitation of 26 PFCs in textiles on Shimadzu LCMS-8050.

Experimental

A total of 26 PFCs and M-PFOA as internal standard (See Table 2) were obtained from Sigma Aldrich, Wellington Laboratories [4] and Apollo Scientific. For convenience, abbreviation names of the PFCs are used in reference of literature [4]. Textile samples obtained from stores was cut into smaller pieces and 1 gram of sample was weighed into a 50 mL polypropylene centrifuge tube. 20 mL of pure methanol was subsequently added. The samples were then left to sonicate at 50 °C for 2 hours, followed by 5 minutes of centrifugation at 10,000 rpm.

The supernatant was filtered using 0.22 µm Nylon filter. A calibration series was prepared mixing 490 µL of the filtrate with 5 µL of 26 PFC mix stock solution and 5 µL of internal standard. An LCMS-8050 triple quadrupole mass spectrometer coupled with a Nexera UHPLC system was used in this study. A Phenomenex, Kinetex UHPLC column (100 x 2.1 mm, 1.7 µm) was used and a gradient elution program was adopted for separation of the 26 PFCs and 1 internal standard. The detailed conditions are as shown in Table 1.

Table 1: Analytical conditions of 26 PFCs and 1 internal standard on LCMS-8050

Column	: Kinetex C18 100A (100 x 2.1mm, 1.7µm)
Flow Rate	: 0.4 mL/min
Mobile Phase	: A : 5mM Ammonium Formate in water B : Acetonitrile
Oven Temp.	: 40°C
Injection vol.	: 5 µL
Elution Mode	: Gradient elution, LC program 13.50 minutes 20%B (0.00mins to 0.50mins) → 80%B (9.00 mins to 12.00mins) → 20%B (12.01mins to 13.50mins)
Interface	: ESI
MS mode	: Negative
Block Temp.	: 400°C
DL Temp.	: 250°C
Interface Temp.	: 300°C
CID Gas	: Ar (270kPa)
Nebulizing Gas Flow	: N ₂ , 1.5 L/min
Drying Gas Flow	: N ₂ , 10 L/min
Heating Gas Flow	: 0 Air, 10 L/min

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Results and Discussion

Establishment of MRM method for detection and quantitation of 26 PFCs

The MRM optimisation of the 26 PFCs and IS was carried out using mixed standard sample. Two MRM transitions (if available) were used for each PFC, one as quantifier ion and the other for confirmation as shown in Table 2. A clothing sample free from the 26 PFCs was used as a blank matrix in preparing post-spiked calibrants for calibration curves construction. Each post-spiked calibrant was injected thrice to obtain the average area for reliable results. Calibration curves were built based on the internal standard with good linearity ($r^2 > 0.997$) for all 26 PFCs (Table 3). The calibration curves of PFOA and PFOS are displayed in Figure 2. As can be seen in Table 3, 22 out of the 26 PFCs exhibit excellent sensitivity with the LOQ at 4.1~50.2 pg/mL while the LOD at 1.4~16.6 pg/mL

in presence of matrix. The rest four PFCs, i.e., FOEA, H4PFUnA, N-MeFOSE and N-EtFOSE exhibit relatively lower sensitivity, with their LOQs at 97~476 pg/mL. The LOQs for PFOA and PFOS of the current method are 17.7 pg/mL and 16.1 pg/mL, respectively. The MRM peaks of PFOA and PFOS of 50 pg/mL (ppt) spiked in matrix are displayed in Figure 2, showing both the quantifier MRM and confirmation MRM of each compound. The repeatability of the method was evaluated using pre-spiked and post-spiked samples at two concentrations, 50 pg/mL & 1,000 pg/mL. The %RSD results of the post-spiked samples are tabulated in Table 3, indicating good repeatability of the method for all the 26 PFCs studied.

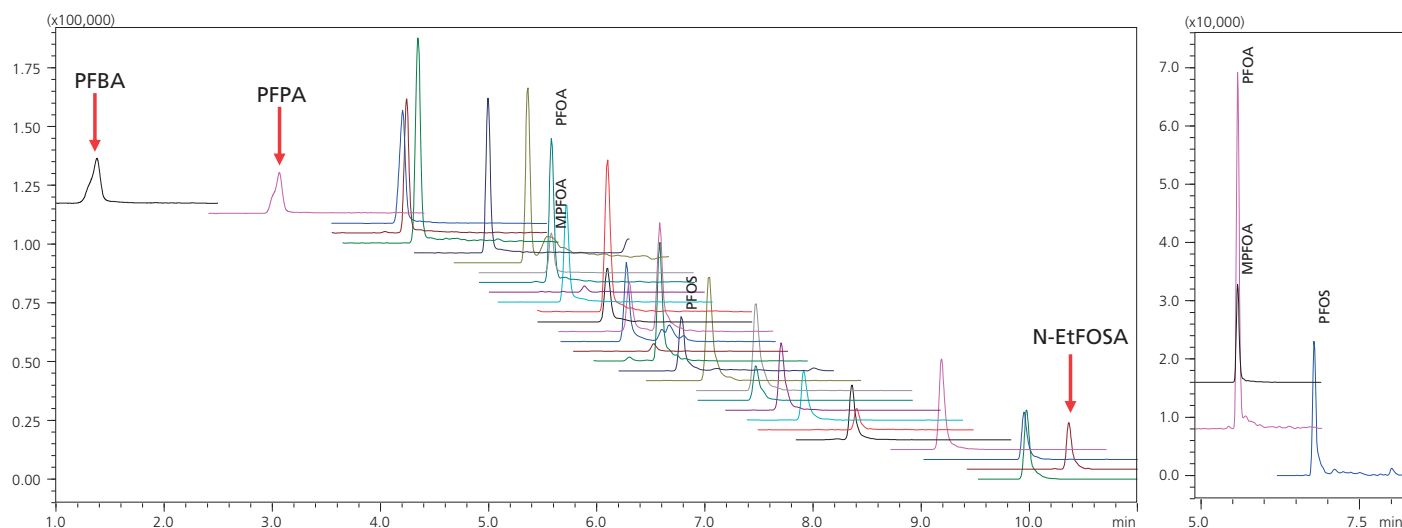


Figure 1: MRM chromatograms of 26 PFC mixed standards with ^{13}C -PFOA (IS) spiked in textile blank matrix, 1,000 pg/mL for each compound (left). Separate display of MRM peaks of PFOA, M-PFOA (IS, 500 pg/mL) and PFOS (Right).

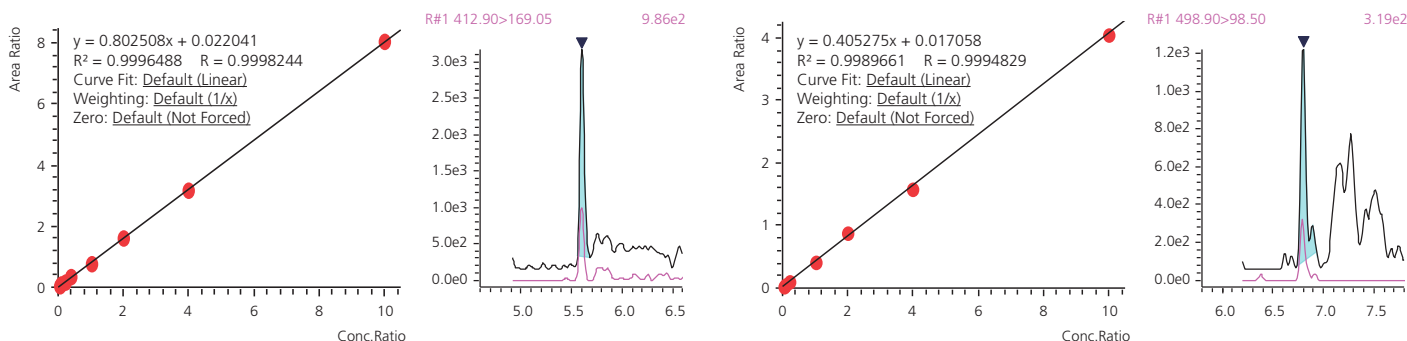


Figure 2: Calibration curves and MRM peaks (50 pg/mL or ppt) of PFOA (Left) and PFOS (Right) in blank matrix

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Table 2: Names and MRM transitions of 26 PFCs & M-PFOA (IS) on LCMS-8050

No.	Abbr. Name	Quantified MRM		Reference MRM	
		MRM (m/z)	CE (V)	MRM (m/z)	CE (V)
1	PFBA	213.00>169.05	10	Not Available	
2	PFPeA	262.90>219.10	8	Not Available	
3	PFBS	298.80>79.90	32	298.80>98.80	27
4	PFHxA	312.90>269.05	9	312.90>119.00	21
5	HPFHpA	345.10>281.00	11	345.10>131.15	23
6	PFHpA	362.90>319.10	9	362.90>168.95	17
7	1H,1H,2H,2H-PFOS9	462.90>407.05	23	426.90>81.00	33
8	PFOA	412.90>369.00	10	412.90>169.05	17
9	PFHxS	398.90>79.90	44	398.90>99.00	33
10	FOEA	477.00>392.90	12	477.00>243.05	23
11	PFNA	462.90>418.95	10	462.90>219.10	17
12	PFHpS	448.90>99.05	40	448.90>79.85	51
13	PF-3,7-DMOA	469.00>269.00	22	469.00>219.10	23
14	PFDA	513.00>469.05	10	513.00>218.90	18
15	PFOS	498.90>79.90	53	498.90>98.50	42
16	H4PFUnA	491.10>367.00	20	491.10>387.00	12
17	PFUdA	563.00>519.00	13	563.00>319.05	19
18	PFDoA	612.90>568.90	12	612.90>169.00	25
19	PFDS	598.80>80.00	55	598.80>98.80	48
20	PFTTrDA	663.00>619.00	14	663.00>169.10	32
21	PFTeDA	712.90>668.95	13	712.90>168.90	35
22	FOSA	497.90>77.90	40	Not Available	
23	PFDHxA	812.90>768.80	15	812.90>169.10	34
24	N-MeFOSA	512.00>169.10	30	512.00>218.9	26
25	PFODA	912.90>868.7	18	912.90>268.95	35
26	N-EtFOSA	526.00>169.00	30	526.00>219.15	26
IS	M-PFOA	416.90>372.00	10	416.90>168.90	17

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Table 3: Calibration curves and key performance values of the MRM method with M-PFOA as IS for quantitative determination of 26 PFCs on LCMS-8050 with heated ESI interface

No.	Name	RT (min)	Range (pg/mL)	R ²	LOD (pg/mL)	LOQ (pg/mL)	RSD (%), n=6	
							(50 pg/mL)	(1,000 pg/mL)
1	PFBA	1.379	50~5,000	1.000	15.6	47.3	3.5	3.7
2	PFPA	3.063	50~5,000	0.9993	11.5	34.8	6.9	1.0
3	PFBS	4.211	20~5,000	0.9991	6.1	18.5	3.5	3.4
4	PFHxA	4.245	50~5,000	0.9995	16.6	50.2	5.7	3.6
5	HPFHpA	4.353	20~5,000	0.9993	2.8	8.5	4.5	2.2
6	PFHpA	5.004	50~5,000	0.9992	13.8	41.8	9.1	3.9
7	1H,1H,2H,2H-PFOS	5.373	50~5,000	0.9992	14.9	45.3	9.3	5.7
8	PFOA	5.594	20~5,000	0.9996	5.8	17.7	5.9	1.3
9	PFHxS	5.733	50~5,000	0.9992	11.8	35.6	10.7	2.1
10	FOEA	5.896	1,000~5,000	0.9988	246.3	746.3	N.A.	12.6
11	PFNA	6.112	50~5,000	0.9996	13.3	40.2	6.3	6.7
12	PFHpS	6.285	50~5,000	0.9991	8.7	26.3	9.6	3.5
13	PF-3,7-DMOA	6.308	50~5,000	0.9996	15.3	46.5	14.4	4.1
14	PFDA	6.592	50~5,000	0.9998	9.6	29.0	7.8	7.2
15	PFOS	6.793	20~5,000	0.9990	5.3	16.1	12.8	6.1
16	H4PFUnA	6.541	500~5,000	0.9973	82.3	249.3	N.A.	12.4
17	PFUdA	7.045	20~5,000	0.9995	5.3	16.0	11.1	4.8
18	PFDoA	7.484	50~5,000	0.9990	11.5	35.0	10.4	3.4
19	PFDS	7.721	50~5,000	0.9991	15.3	46.2	8.0	3.6
20	PFTrDA	7.928	50~5,000	0.9991	15.2	46.0	13.5	8.3
21	PFTeDA	8.372	50~5,000	0.9991	13.4	40.6	7.6	8.8
22	FOSA	8.42	50~5,000	0.9995	11.6	35.0	14	8.2
23	PFDHxA	9.198	20~5,000	0.9985	1.4	4.1	14.7	2.5
24	N-MeFOSA	9.955	200~5,000	0.9986	60.8	184.1	NA	6.2
25	PFODA	9.98	20~5,000	0.9982	5.0	15.1	11	1.7
26	N-EtFOSA	10.369	100~5,000	0.9984	32.1	97.2	N.A.	6.0
IS	M-PFOA	5.556	500				Not Available	

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Matrix effect and recovery

The matrix effect and recovery of the method for the 26 PFCs were evaluated at two concentrations, 50 pg/mL and 1,000 pg/mL. The results are shown in Table 4. Most PFCs exhibited matrix effect at 60.8 %~143.9 % for 50 pg/mL and 74.0 %~ 142.3 % for 1,000 ng/mL. However, two PFCs, namely FOSA and N-MeFOSE, exhibited strong ion enhancement effect (measured matrix effect at 193.3 %~247.9 % for both concentration). The recovery of the method was determined from pre-spiked and post-spiked

samples at two concentrations, 50 pg/mL and 1,000 pg/mL. As shown in Table 4, the recoveries of the 22 PFCs which were detectable at 50 pg/mL level were determined to be 95.8 %~130.4 %. For 1,000 pg/mL level, good recoveries of all the PFCs except H4PFUnA were obtained at 96.7 %~125.5 %, respectively. The overly high recovery of H4PFUnA (143.8 %) may be from interferences due to its relatively low sensitivity.

Table 4: Matrix effect and recovery of the 26 PFCs compounds spiked in matrix, MeOH extract of blank textile (n=3)

Peak No.	Name	Matrix effect (%)		Recovery (%)	
		(50 pg/mL)	(1,000 pg/mL)	(50 pg/mL)	(1,000 pg/mL)
1	PFBA	143.9	90.1	121.6	102.2
2	PFFA	118.2	95.3	128.6	108.4
3	PFBS	86.2	85.1	124.5	109.5
4	PFHxA	103.6	89.7	128.1	109
5	HPFHpA	105.2	82.8	125.4	114.4
6	PFHpA	92.6	89.8	125.5	113.9
7	1H,1H,2H,2H-PFOS	60.8	99.3	102	120.8
8	PFOA	110.9	87.5	127.5	112.0
9	PFHxS	124.8	80	95.8	107.6
10	FOEA	NA	105.3	NA	108.8
11	PFNA	110.9	91.4	105	108.5
12	PFHpS	105.6	80.3	98.2	108.5
13	PF-3,7-DMOA	118.3	86.8	124.3	112.2
14	PFDA	107.8	91.3	98.4	106.7
15	PFOS	135.4	83.1	98.9	105.7
16	H4PFUnA	NA	80.2	NA	143.8
17	PFUdA	86.2	88.5	98.2	105.6
18	PFDoA	75.7	75.7	113.1	112.2
19	PFDS	105.7	88.8	120.6	111.6
20	PFTrDA	74.1	74	128.5	111.8
21	PFTeDA	97.2	98.3	130.4	109.7
22	FOSA	247.9	193.3	106.6	125.5
23	PFDHxA	108.4	97.9	115.6	103.3
24	N-MeFOSA-M	NA	209.7	NA	102.8
25	PFODA	91.4	99.8	122.6	103.2
26	N-EtFOSA-M	NA	142.3	NA	96.7

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Screening and quantitation of targeted 26 PFCs in textile samples

Five clothing samples were obtained from local stores and labelled as BS, GS, YS, WS and BR. Using the method established, the samples were analysed for screening and quantitation of the targeted 26 PFCs. Following the sample extraction method described in experimental section, the IS (M-PFOA, equivalent 500 pg/mL in final extract) was spiked into the samples at the beginning of the MeOH extraction step before pre-treatment. For effective extraction of PFCs which may be present in the coating layer on the textile

surface, the extraction was carried out by sonication at 50 °C for 2 hours [2-3]. Duplicates of every sample were prepared and analysed for accurate and reliable results. The analysis results of the five samples reveal that only sample GS showed presence of PFOA of 650 pg/g (0.65 ppb). The targeted 26 PFCs were not detected in the other four samples. The MS chromatogram and the detected PFOA peak with IS peak of Sample GS are displayed in Figure 3.

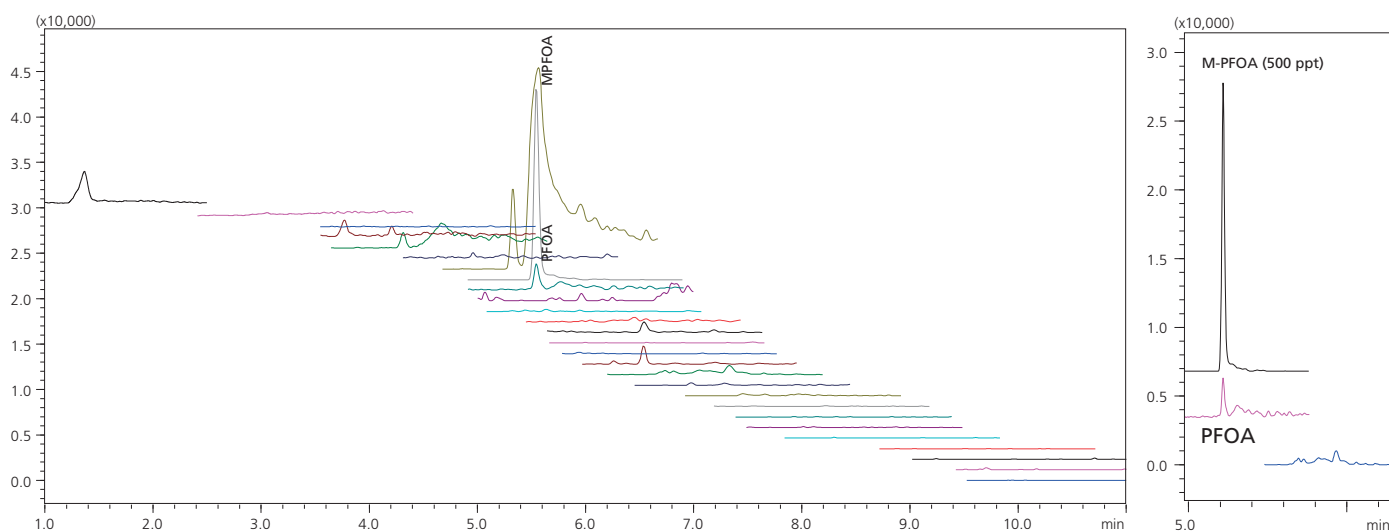


Figure 3: MRM chromatograms of textile sample GS with spiked internal standard (M-PFOA, 500 pg/mL) of the MeOH extract for screening and quantitation of 26 targeted PFCs. Trace level of PFOA was found in the sample.

Conclusions

A sensitive and reliable LC/MS/MS method has been developed for screening and quantitation of 26 PFCs including PFOA and PFOS on Shimadzu LCMS-8050 UFMS system. The method adopted M-PFOA (¹³C-PFOA) as internal standard to enhance the reliability for screening analysis of unknown sample. The LOQs of the MRM method achieve extremely low level, e.g., 17.7 and 16.1

ng/mL for PFOA and PFOS in textile matrix, respectively. The method performance which includes sensitivity, linearity, repeatability, matrix effect and recovery were evaluated. The results indicate that the method is feasible and reliable for determination of 26 targeted PFCs, especially PFOA and PFOS in different textile samples.

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