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Application News

No. AD-0201

Textile Analysis / LCMS-8050

Analysis of Perfluorooctane Sulfonamides (FOSEs) and Fluorotelomer Alcohols (FTOHs) in Textiles by LC/MS/MS

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1. Introduction

Perfluorinated compounds (PFCs) represent a large collective of chemicals, which have been used widely in textile, leather and other consumer products for their unique water and oil repellent properties. However, PFCs including PFAS (per- and polyfluoroalkyl substances) also become environmental and health concerns. Some components like perfluoro-octanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) are regulated as restricted substances in textiles by industrial standards and regulations[1]. LC/MS/MS and GC-MS have used in analyses of various PFCs or PFAS in various environmental samples and consumer products. A LC/MS/MS method was reported previously for simultaneously analysis of 24 PFCs in textiles[2]. Perfluorooctane sulfonamides (FOSEs) and fluorotelomer alcohols (FTOHs) belong to less-polar PFCs and may degrade to form PFOS and PFOA. Normally, they are analysed using GCMS with chemical ionisation (CI) due to their non-polar properties[3,4]. In this study, an alternative method using LC/MS/MS was developed for the analysis of four FTOHs and two FOSEs in textiles to respond the recent demands in testing analysis for textile and consumer products.

2. Experimental

Four FTOH standards, i.e., 2-perfluorobutyl ethanol (4:2 FTOH), 2-perfluorohexyl ethanol (6:2 FTOH), 2-perfluorooctyl ethanol (8:2 FTOH) and 2-perfluorodecyl ethanol (10:2 FTOH) were purchased from Apollo scientific, while two FOSE standards, 2-(N-methyl-perfluoro-1-octanesulfonamido)-ethanol (N-MeFOSE) and 2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol (N-EtFOSE) were purchased from Wellington Laboratories. Stock standard solutions were prepared individually in methanol. The six compounds studied were mixed together and a calibration series was prepared using acetonitrile and water as diluent. A white textile sample was cut into smaller pieces and 1 gram of the sample was weighed into a 50mL polypropylene centrifuge tube. 20mL of pure methanol was subsequently added. The samples were sonicated for 30 minutes, followed by centrifugation at 10,000 rpm for 5 min. The supernatant was filtered using 0.22µm Nylon filter. 2 mL of supernatant was blown to dryness under a gentle stream of nitrogen gas. The obtained sample was re-constituted with 1 mL of diluent (A CN : water (50/50)) and analysed on a Shimadzu LCMS-8050, a triple quadrupole system with heated ESI, and a Shim-Pack GIST C18 column.

Table 1. Analytical conditions of four PFOH and two FOSE on LCMS-8050 with ESI

Column	Shim-Pack GIST C18 2um, (2.1 mm I.D. x 100 mm L)
Flow	0.3 mL/min
Mobile phase	A : 5mM Ammonium Acetate in water B : Acetonitrile
Oven Temp	40 ºC
Injection vol	20 µL
Elution gradient	B% : 30% (0.0 min) ➡ 95% (15.0 to 18.5 min) ➡30% (18.6 to 22 min)

Interface	**ESI (heated)**
MS Mode	Negative mode
CID gas	Argon, 230 kPa
Block Temperature	100 ºC
DL Temperature	100 ºC
Interface Temp.	250 ºC
Nebulizing Gas Flow	Nitrogen, 3.0 L/min
Drying Gas Flow	Nitrogen, 3.0 L/min
Heating Gas Flow	Zero Air, 17.0 L/min

3. Results and Discussion

3.1 MRM transitions and optimization

The six very less-polar compounds (4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, N-MeFOSE and N-EtFOSE) are ionised effectively with ESI to form acetate adduct ion $[M+CH_3COO]^-$ in negative mode (Figure 1). The ions tend to fragment to form acetate

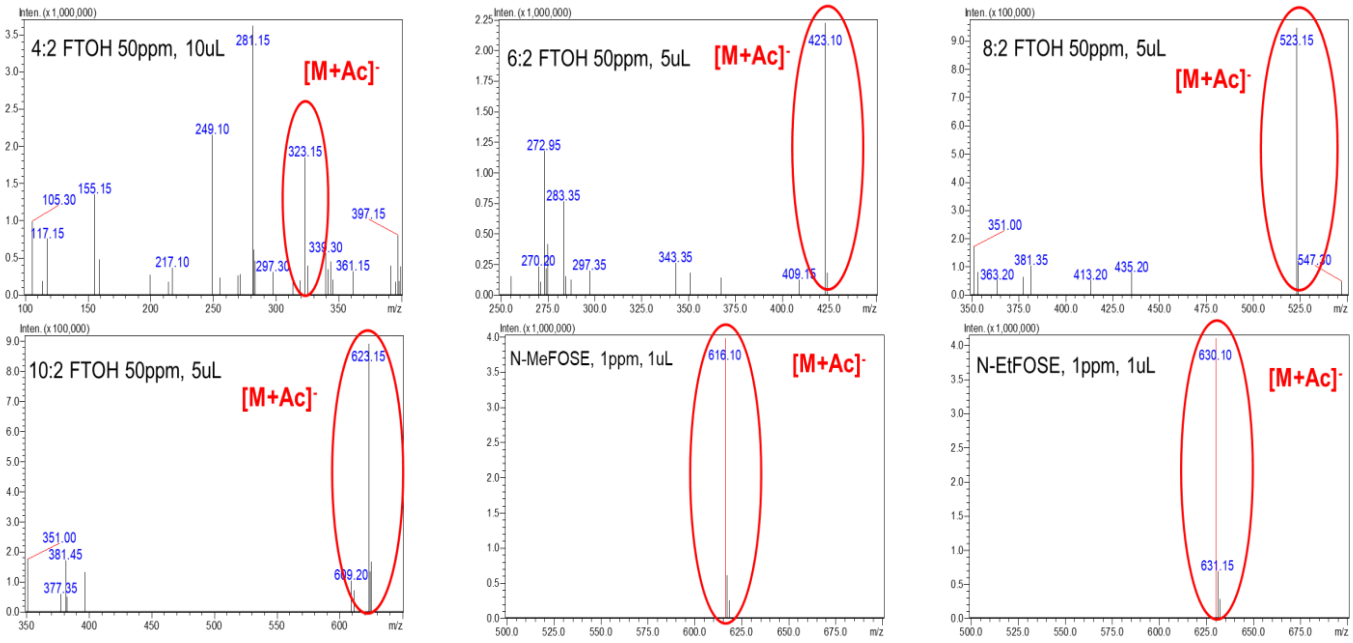

Figure 1: MS Spectra and precursors of individual FTOHs and FOSEs in negative ESI mode on LCMS-8050

ion or remain intact due to the extreme stability of the structures. With an automated MRM optimisation program in LabSolutions, MRM transitions and respective CE were obtained for two transitions, $[M+CH_3COO]^-$ > $[CH_3COO]^-$ and [precursor] > [precursor]. These two MRMs for each compound were used, the former for quantitation and the latter for confirmation to set up an LC/MS/MS method.

3.2 Establishment of LC/MS/MS method for detection and quantification

Fig.2 shows the MRM chromatograms of the six compounds, which are well separated elute as sharp

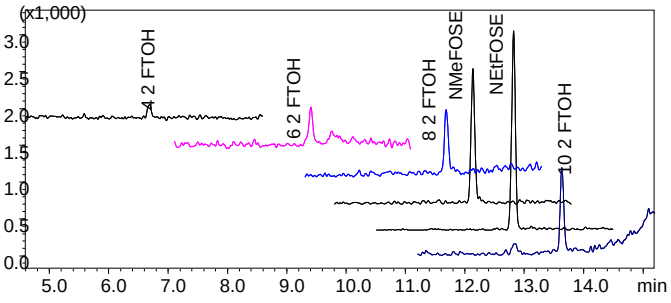

Figure 2: MRM chromatograms of four FTOHs (1 ng/mL each) and two FOSEs (0.02 ng/mL each) in a mixed standard solution on LCMS-8050.

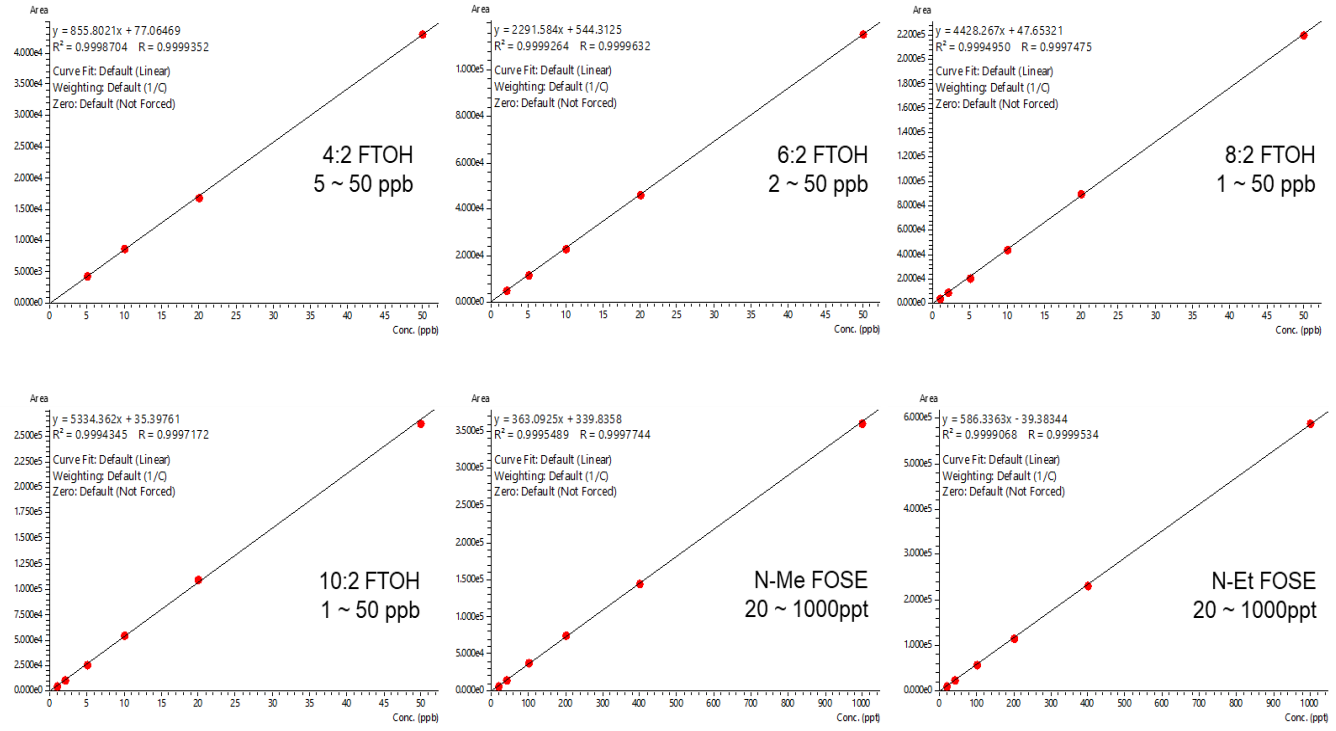

Figure 3: MRM calibration curves of four FTOHs and two FOSEs in pure solvent on LCMS-8050

Table 2. MRM-based calibration curves and sensitivity of four FTOHs and two FOSEs on LCMS-8050

No	Compound Abbr.	Formula	CAS No	RT (min)	Quantifier MRM	Reference MRM	R^2	Range (ng/mL)	LOQ (ng/mL)	LOD (ng/mL)
1	4:2 FTOH	$C_6H_5F_9O$	2043-47-2	6.67	323.2>59.0	323.2>323.2	0.9999	5~50	3.7	1.2
2	6:2 FTOH	$C_8H_5F_{13}O$	647-42-7	9.37	423.1>59.1	423.1>423.1	0.9999	2~50	1.7	0.6
3	8:2 FTOH	$C_{10}H_5F_{17}O$	678-39-7	11.57	523.2>59.0	523.0>523.0	0.9997	1~50	0.8	0.3
4	10:2 FTOH	$C_{12}H_5F_{21}O$	865-86-1	13.60	623.2>59.1	623.2>623.2	0.9994	1~50	0.5	0.2
5	NMeFOSE	$C_{11}H_8F_{17}NO_3S$	24448-09-7	12.13	616.1>59.1	616.1>616.1	0.9995	0.02~1	0.005	0.002
6	NEtFOSE	$C_{12}H_{10}F_{17}NO_3S$	1691-99-2	12.81	630.1>59.1	630.1>630.1	0.9999	0.02 ~ 1	0.002	0.001

peaks with a C18 column and gradient elution program (Table 1). Calibration curves of the six compounds were constructed in different concentration ranges due to their significant differences in sensitivity. FOSEs exhibited higher sensitivities than FTOHs. Linear calibration curves were established in ranges of 1~50 ng/mL for FTOHs (except for 4:2 FTOH) and 0.02~1 ng/mL for FOSEs, respectively. Excellent linearity was obtained for all compounds (R2 > 0.999) as shown in Figure 3.

The details of the quantitation method including sensitivity are summarized in Table 2. Refer to Fig.3, LOD and LOQ values were determined with the lowest level standard using LabSolutions, with S/N >/= 3 and 10, respectively. The S/N of each compound was calculated according to ASTM method with an interval of 0.5 min for the whole time range. For the four FTOHs, quantitation limit (LOQ) and detection limit (LOD) are at 0.5~3.7 ng/mL and 0.2~1.2 ng/mL, respectively. Much higher sensitivities were achieved for the two FOSEs as compared to FTOHs, with LOQ and LOD at 0.002~0.005 ng/mL and 0.001~0.002 ng/mL, respectively.

Repeatability of the method was evaluated at two concentrations, (i) 2 ng/mL for FTOHs and 0.04 ng/mL for FOSEs and (ii) 5 ng/mL for FTOHs and 0.1 ng/mL for FOSEs. The results were tabulated into Table 3. Good repeatability was obtained for all the six compounds with peak area RSD < 10% at both levels.

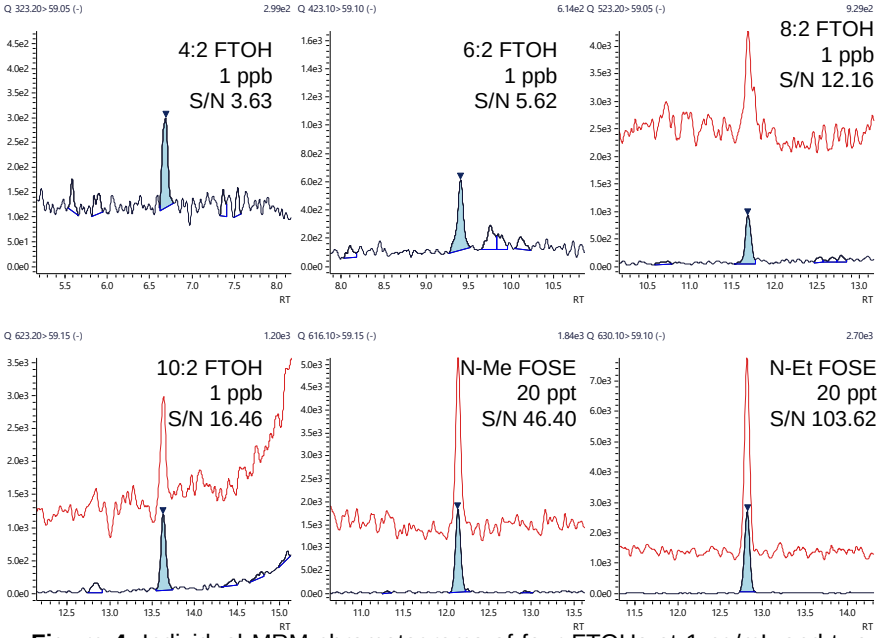

Figure 4: Individual MRM chromatograms of four FTOHs at 1 ng/mL and two FOSEs at 0.02 ng/mL in mixed standards

Table 3. Repeatability for FTOHs and FOSEs (n=6) of standards

No	Compound	Conc. (ng/mL)	Area RSD (%)	Conc. (ng/mL)	Area RSD (%)
1	4:2 FTOH	2.0	ND	5.0	6.7
2	6:2 FTOH		6.1		1.7
3	8:2 FTOH		7.5		3.1
4	10:2 FTOH		4.4		9.6
5	NMeFOSE	0.04	3.8	0.1	2.1
6	NEtFOSE		4.2		1.1

Table 4. Matrix effect and recovery of FTOHs and FOSEs spiked in white textile with MeOH extraction (n=3)

No	Compound	Conc. (i)		Conc. (ii)		Conc. (iii)	
		M.E	R.E	M.E	R.E	M.E	R.E
1	4:2 FTOH	71.1	107.6	95.7	68.7	83.8	68.7
2	6:2 FTOH	59.0	97.0	75.9	62.8	70.8	67.2
3	8:2 FTOH	46.2	91.0	70.1	70.9	67.8	74.5
4	10:2 FTOH	30.5	104.1	45.1	69.0	56.2	71.7
5	N-MeFOSE	56.8	142.9	73.5	106.9	67.9	110.5
6	N-EtFOSE	59.4	135.3	75.0	98.2	70.6	107.7

3.3 Matrix effect and recovery of FTOHs and FOSEs in textiles

A simple extraction procedure of textile sample with ultrasonication at RT was employed. The matrix effect (M.E.) and recovery (R.E.) of the method of the six compounds were evaluated at three concentrations: 10 ng/mL for FTOHs and 0.2 ng/mL for FOSEs, 20 ng/mL for FTOHs and 0.4 ng/mL for FOSEs and 50 ng/mL ppb for FTOHs and 1 ng/mL for FOSEs. The results are shown in Table 4.

Across all three concentrations, it was observed that the textile extracts resulted in ion suppression for all the six PFCs. Most PFCs displayed matrix effect ranging from 46.2% to 95.7%.10:2 FTOH was more significantly affected by the interferences, resulting in matrix effect of 30.5% ~ 56.2% across. As shown in Figure 5, significant interference peaks appeared for every compound. This indicates that further clean up step may be needed for the MeOH extract before analysis to quantitate trace levels of FTOHs and FOSEs by ESI-LC/MS/MS method.

Recovery of the sample preparation was also evaluated. Overall, good recovery was obtained for all targets across the three spiked concentrations. The four FTOHs achieved a recovery of 62.8~107.6%, while the two FOSEs achieved a recovery of 98.2~142.9%.

4. Conclusions

A MRM based LC/MS/MS method for quantitation of very less-polar PFCs, i.e., two FOSEs and four FTOHs in textiles was developed on LCMS-8050. Linear calibration curves were established with MRM transition of acetate adduct ion to acetate ion in ESI negative mode. High sensitivity were achieved with mixed standards. The LOQs and LODs of the four FTOHs are in the range of 0.5~3.7 ng/mL and 0.2~1.2 ng/mL, respectively. While much lower LOQs and LODs for the two FOSEs were obtained at 0.002~0.005 ng/mL and 0.001~0.002 ng/mL, respectively. Ion suppression due to interferences in textile MeOH extract are present, resulting in matrix effect of 30.5~95.7%. Good recovery for the sample preparation was obtained with 62.8~142.9%. However, further study is needed in sample clean-up method to reduce interferences and ion suppression of the method.

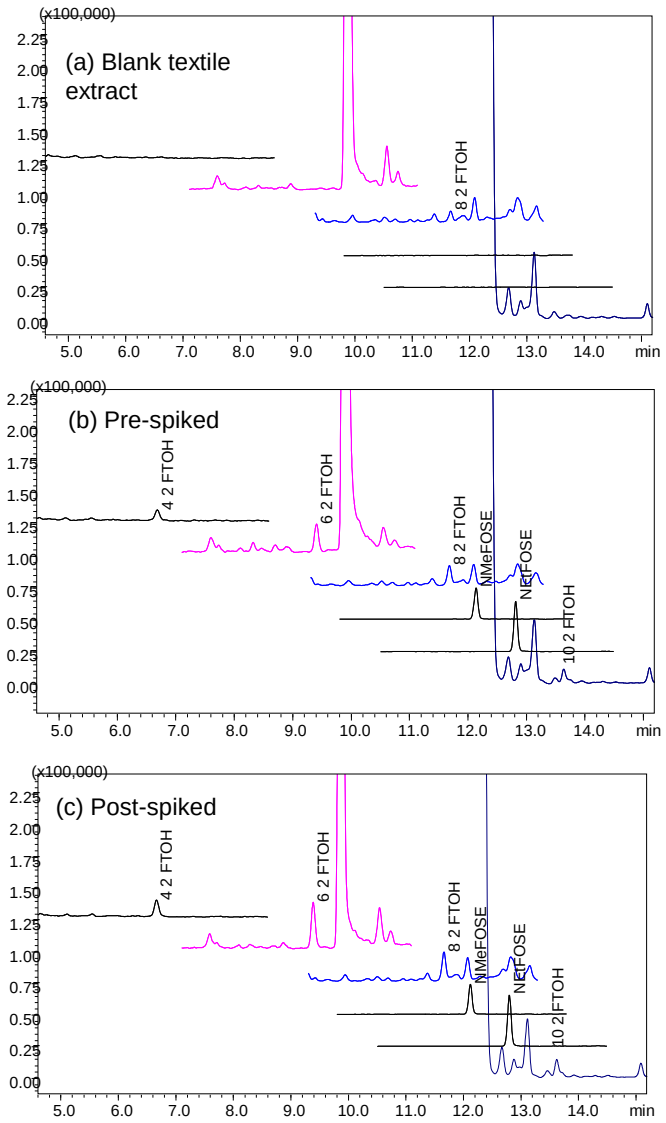

Figure 5: MRM chromatograms of spiked sample (ii); (a) Blank textile extract; (b) Pre-spiked textile extract of 20 ng/mL each FTOH, 0.4 ng/mL each FOSE; (c) Post-spiked textile extract of 20 ng/mL each FTOH, 0.4 ng/mL each FOSE.

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