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Application News

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Textile Analysis / LCMS-8050

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

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❑ 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 been used in analyses of various PFCs or PFAS in various environmental samples and consumer products. A LC/MS/MS method was reported previously for simultaneous analysis of 24 PFCs in textiles[2]. Perfluorooctane sulfonamidoethanols (FOSEs) and fluorotelomer alcohols (FTOHs) belong to less-polar PFCs and may degrade to form PFOS and PFOA. Normally, they are analysed using GC/MS 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 to the recent demands in testing analysis for textile and consumer products.

❑ 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, i.e. *N*-methyl perfluorooctane sulfonamidoethanol (*N*-MeFOSE) and *N*-ethyl perfluorooctane sulfonamidoethanol (*N*-EtFOSE), were purchased from Wellington Laboratories. Stock solutions were prepared individually in methanol. The six compounds were mixed together and a series of calibration standards 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 50 mL polypropylene centrifuge tube. 20 mL of pure methanol was subsequently added. The samples were sonicated for 30 min, followed by centrifugation at 10,000 rpm for 5 min. The supernatant was filtered using a 0.22 µm nylon filter. 2 mL of the supernatant was blown to dryness under a gentle stream of nitrogen gas. The obtained sample was re-constituted with 1 mL of diluent (ACN : Water, 50:50, *v/v*) and was 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 PFOHs and two FOSEs on LCMS-8050 with heated ESI

Column	Shim-pack GIST C18 2um, (2.1 mm I.D. x 100 mm L)
Flow	0.3 mL/min
Mobile Phase	A: 5 mM ammonium acetate in water B: Acetonitrile
Oven Temp	40 °C
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 °C
DL Temperature	100 °C
Interface Temp.	250 °C
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

❑ Results and Discussion

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

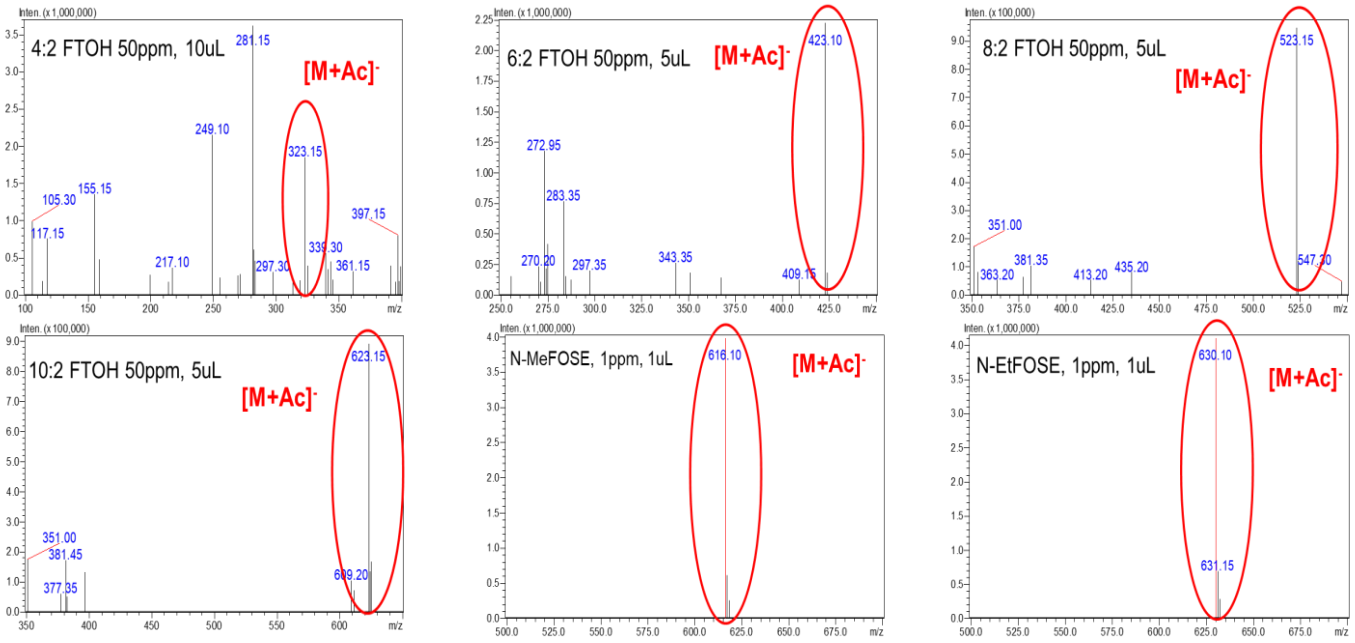

Figure 1. MS Spectra and precursors of individual FTOHs and FOSEs in negative ESI mode on LCMS-8050

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

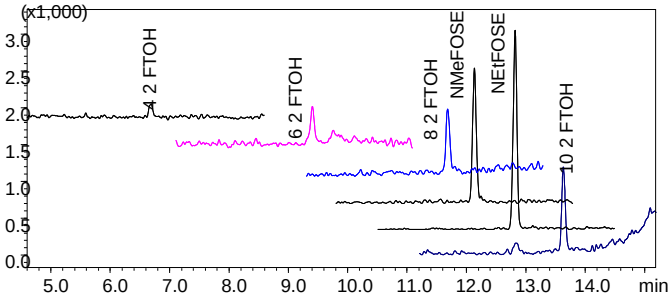

Figure 2. MRM chromatograms of four FTOHs (1 ng/mL each) and two FOSEs (0.02 ng/mL each) in a mixed standard solution on LCMS-8050.

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

Fig.2 shows MRM chromatograms of the six PFCs, which are well separated and eluted as sharp peaks

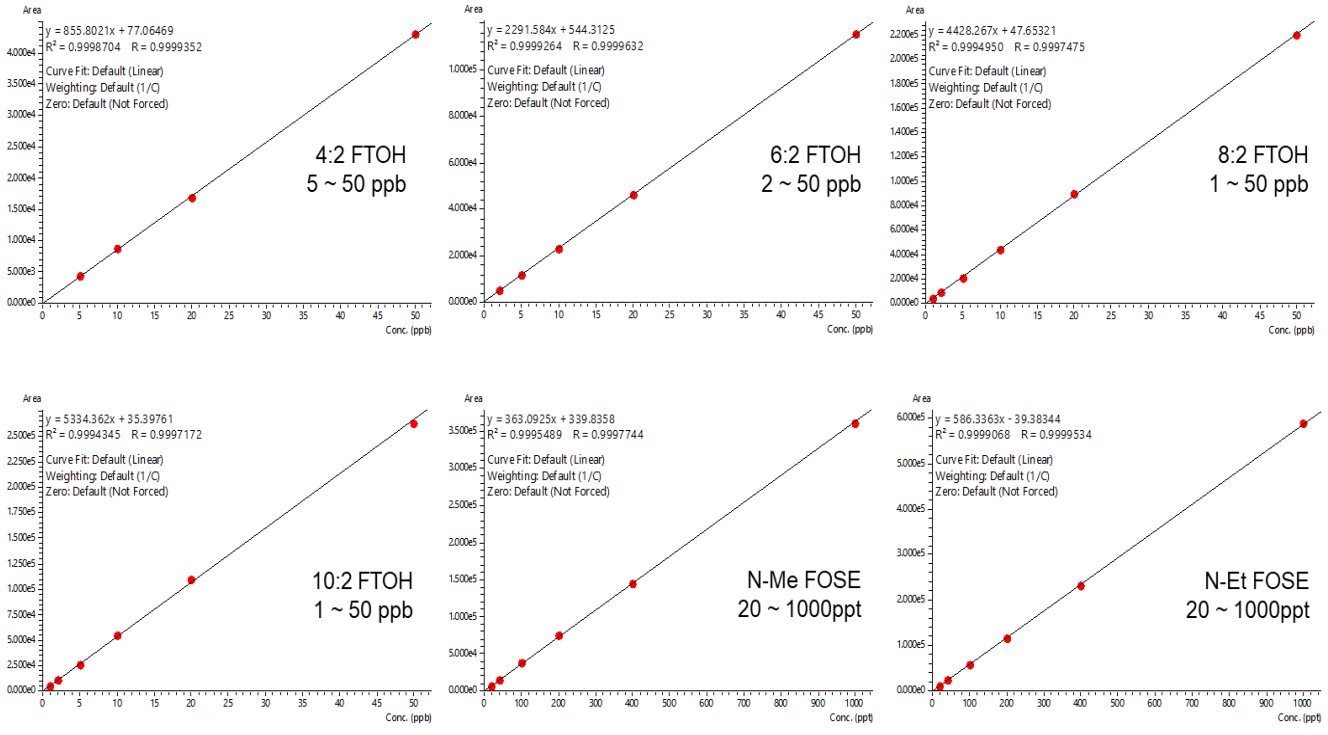

Figure 3: MRM calibration curves of four FTOHs and two FOSEs in pure solvent on LCMS-8050

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

No	Compound Abbr.	Formula	CAS No	RT (min)	Quantifier MRM	Qualifier 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	*N*-MeFOSE	$C_{11}H_8F_{17}NO_3S$	24448-09-7	12.13	616.1>59.1	616.1>616.1	0.9995	0.02~1	0.005	0.002
6	*N*-EtFOSE	$C_{12}H_{10}F_{17}NO_3S$	1691-99-2	12.81	630.1>59.1	630.1>630.1	0.9999	0.02~1	0.002	0.001

with a C18 column and a gradient program (Table 1). Calibration curves of the six PFCs were constructed in different ranges of concentrations due to their distinct differences in sensitivity. The FOSEs exhibited higher sensitivities than the FTOHs. Linear calibration curves were established in ranges of 1~50 ng/mL for the FTOHs (except for 4:2 FTOH and 6:2 FTOH) and 0.02~1 ng/mL for the FOSEs, respectively. Excellent linearity was obtained for all the PFCs (R2 > 0.999) as shown in Fig. 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 calibration standard using LabSolutions, with S/N values of 3 and 10, respectively. The S/N values of the PFCs were calculated according to the ASTM method with an interval of 0.5 min for the whole time range. For the four FTOHs, LOQs and LODs are 0.5~3.7 ng/mL and 0.2~1.2 ng/mL, respectively. Much higher sensitivities were achieved for the two FOSEs compared to the FTOHs, with LOQs and LODs of 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 the FTOHs and 0.04 ng/mL for the FOSEs and (ii) 5 ng/mL for the FTOHs and 0.1 ng/mL for the FOSEs. The results are tabulated into Table 3. Good repeatability was obtained for all the six PFCs with peak area RSD < 10% at both of the levels.

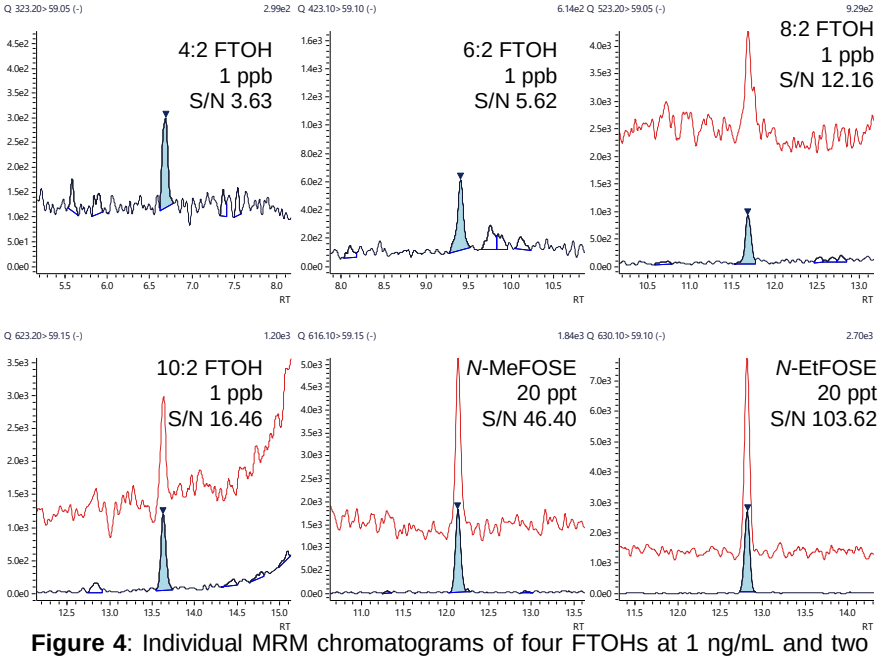

Figure 4: Individual MRM chromatograms of four FTOHs at 1 ng/mL and two FOSEs at 0.02 ng/mL in mixed standards

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

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	*N*-MeFOSE	0.04	3.8	0.1	2.1
6	*N*-EtFOSE		4.2		1.1

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

No	Compound	Conc. (i)		Conc. (ii)		Conc. (iii)	
		ME	Rec.	ME	Rec.	ME	Rec
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

Matrix effects and recoveries of FTOHs and FOSEs in textiles

A simple extraction procedure of textile sample with ultrasonication at room temperature was employed. The matrix effect (ME) and recovery (Rec.) of the method for the six PFCs were evaluated at three concentrations: (i) 10 ng/mL for the FTOHs and 0.2 ng/mL for the FOSEs, (ii) 20 ng/mL for the FTOHs and 0.4 ng/mL for the FOSEs, and (iii) 50 ng/mL for the FTOHs and 1 ng/mL for the FOSEs. The results are shown in Table 4.

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

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

❑ Conclusions

An 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 from acetate adduct ion to acetate ion in ESI negative mode. High sensitivities were achieved with mixed standards. LOQs and LODs of the four FTOHs were 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 was present, resulting in matrix effects of 30.5~95.7%. Good recoveries for the sample preparation were 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.

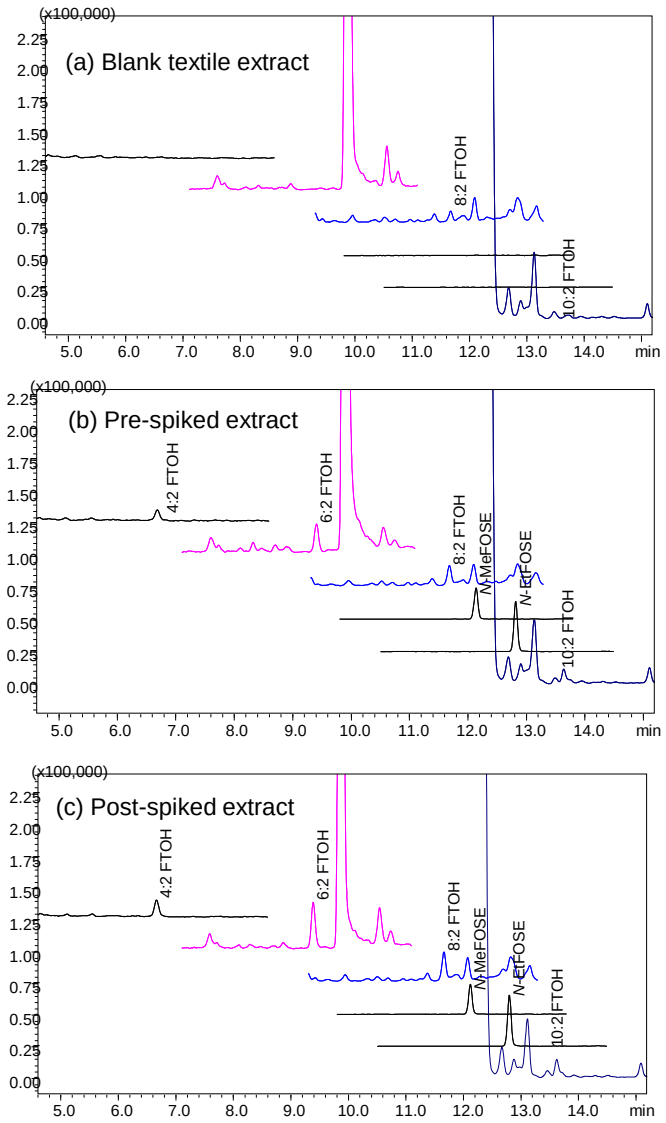

Figure 5. MRM chromatograms of spiked samples (ii); (a) blank textile extract; (b) pre-spiked textile extract of 20 ng/mL for each FTOH and 0.4 ng/mL for each FOSE; (c) post-spiked textile extract of 20 ng/mL for each FTOH and 0.4 ng/mL for each FOSE.

❑ References

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