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Technical Report

Analyses of PFOS and PFOA Precursors in Textile Products Using EI-MRM and PCI-SIM Method

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Abstract:

Precursors of perfluoro compounds (PFCs) such as perfluorooctane sulfon-amides (FOSEs, FOSAs) and acrylates (FTAs), which may potentially degrade to perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), are analysed via an electron ionization-multiple reaction monitoring (EI-MRM) method and a positive chemical ionization-selective ion monitoring (PCI-SIM) method. For all targets, both acquisition methods report a limit of quantitation (LOQ) value of 5.0 ng/mL. The EI-MRM method provides a lower limit of detection (LOD) than the PCI-SIM method, LOD of the former is as low as 0.5 ng/mL whereas that of the latter is 4.0 ng/mL.

Keywords: PFCs, PFOS, PFOA, GC-MS/MS, textile, water repellent

1. Introduction

Perfluoro compounds (PFCs) refer to hydrocarbon compounds in which all hydrogen atoms on carbon atoms (except for carbons associated with functional groups) have been replaced by fluorine atoms. PFCs such as perfluorinated sulfon-amides and telomer alcohols are typically incorporated as fluorinated side-chains on a polymeric backbone, so as to impart water and stain repellent properties to textiles. However, incomplete polymerization will produce residual precursors such as perfluorooctane sulfon-amides (FOSEs, FOSAs) and acrylates (FTAs), which may potentially degrade to perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), respectively. Due to strong C-F bonds, PFOS and PFOA are extremely stable and therefore bioaccumulative. Since June 2017, PFOS is one of the 16 chemicals added to the Stockholm Convention on Persistent Organic Pollutants (POPs) [1].

Unlike most POPs, PFOS does not partition into fatty tissues, but instead it binds to proteins in the blood and the liver. PFOS has the capacity to undergo long-range transport and also fulfils the toxicity criteria of the Stockholm Convention. PFOA, its salts and esters are currently regulated in Norway and is proposed to be listed in the Stockholm Convention on POP [2]. The PFOS and PFOA precursors covered in this study are included in the list of substances surveyed and revised by OECD (Organization for Economic Cooperation and Development) in 2007 [3].

To address environmental concerns that may arise from PFOS and PFOA, two GC/MS methods were optimized for detection of PFOS and PFOA precursors, which are FOSEs, FOSAs; and FTAs, respectively. The acquisition methods are namely, a SIM analysis using positive chemical ionization method (PCI-SIM) and a MRM analysis using electron ionization mode (EI-MRM).

2. Experiment

2-1. Instruments Used and Analytical Conditions

For the PCI-SIM method, a single quadrupole GC/MS, GCMS-QP™ 2020 NX was used. A triple quadrupole GC-MS/MS system, GCMS-TQ™8050 NX, was used for the EI-MRM method. The same GC conditions were applied to both methods. The details of mass spectrometer conditions are shown in Table 1.

Table 1 Analytical Conditions

GC-MS	: GCMS-QP2020 NX and GCMS-TQ8050 NX
Auto-Injector	: AOC™-20i + 20s
Column	: SH-Rtx™-200 (length 30 m, 0.32 mm I.D., film thickness 0.5 µm)
[GC]	
Injection Temp.	: 250 °C
Column Oven Temp.	: 80 °C => (30 °C /min) => 260 °C (1 min)
Injection Mode	: Splitless
Carrier Gas	: He
Carrier Gas Control	: 48.7 cm/sec (Constant Velocity)
High Pressure Injection	: 150 kPa (1 min)
Injection Volume	: 2 µL
[MS]	
Ion Source Temp.	: 200 °C
Interface Temp.	: 250 °C
EI-MRM	
Ionization Mode	: EI
Acquisition Mode	: MRM
Event Time	: 0.3 sec
PCI-SIM	
Ionization Mode	: PCI
Acquisition Mode	: SIM
Reagent Gas	: Methane (200 kPa)
Event Time	: 0.1 sec

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2-2. Methods and Chemicals

A mixture of four perfluorooctane sulfonamides (FOSEs, FOSAs) and three acrylates (FTAs) was prepared from neat standards. Naphthalene-D_8 was used as an internal standard. The seven targets and internal standard (ISTD) were chromatographically separated within a short GC analysis time of 7 minutes (Fig. 1). A matrix-matched calibration was adopted and an analyte protectant (D-Sorbitol of 5 µg/mL vial concentration) was incorporated to counter matrix interferences. 50 µL of 20 µg/mL D-Sorbitol was added into each calibration standard. Details of the chemicals used are shown in Table 2.

The textile used for the blank matrix was cut into approximately 5 mm x 5 mm squares. 1 g of cut textiles was weighed into a 20 mL glass vial and 10 mL of tetrahydrofuran (THF) was added. The vials were then heated in a water bath at 60°C for 1 hour. After heating, the extract was subjected to a 0.45 µm nylon filter. The filtered extract was then concentrated 10 times before being used as diluent for matrix-matched calibration standards. Textile samples used for sample analyses were subjected to the same preparation method. Instrument detection limit (IDL), limit of quantitation (LOQ), matrix effect, method accuracy and repeatability were assessed.

Table 2 Details of targeted compounds

No.	Target	Acronym	CAS No.	Supplier
1	1H,1H,2H,2H-Perfluorooctyl acrylate	FTA 6:2	17527-29-6	Apollo Scientific
2	1H,1H,2H,2H-Perfluorodecyl acrylate	FTA 8:2	27905-45-9	Sigma Aldrich
3	1H,1H,2H,2H-Perfluorododecyl acrylate	FTA 10:2	17741-60-5	Apollo Scientific
4	N-methylperfluoro-1-octanesulfonamide	N-MeFOSA	31506-32-8	Wellington Laboratories
5	N-ethylperfluoro-1-octanesulfonamide	N-EtFOSA	4151-50-2	Wellington Laboratories
6	2-(N-methylperfluoro-1-octanesulfoamido)-ethanol	N-MeFOSE	24448-09-7	Wellington Laboratories
7	2-(N-ethylperfluoro-1-octanesulfoamido)-ethanol	N-EtFOSE	1691-99-2	Wellington Laboratories

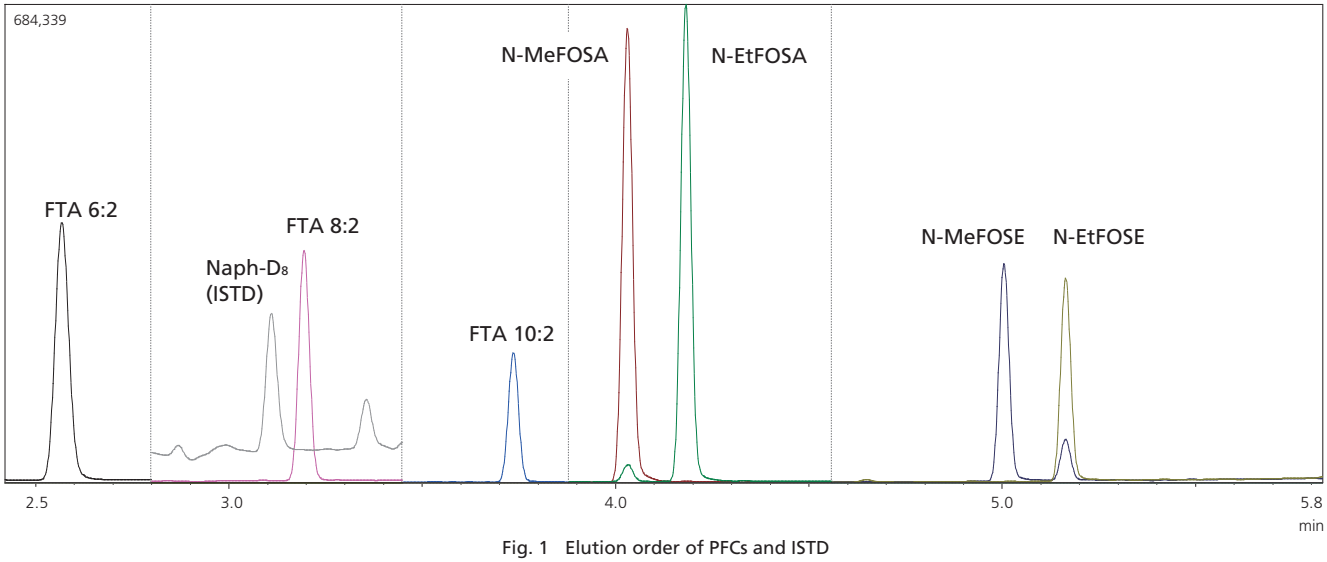

Fig. 1 Elution order of PFCs and ISTD

Table 3 MRM transitions and CEs of targets and ISTD

Compound	Quantitative MRM	CE (V)	Qualitative MRM (1)	CE (V)	Qualitative MRM (2)	CE (V)
FTA 6:2	418.0>99.0	10	418.0>71.0	24	418.0>137.0	24
Naphthalene-D_8 (ISTD)	136.0>108.0	20	134.1>82.0	20		
FTA 8:2	518.0>99.0	20	518.0>72.0	21	518.0>57.0	27
FTA 10:2	618.0>99.0	15	618.0>72.0	21	618.0>137.0	30
N-MeFOSA	430.0>111.0	9	448.0>378.0	21		
N-EtFOSA	512.0>448.0	9	448.0>428.0	9		
N-MeFOSE	526.0>462.0	18	526.0>169.0	20		
N-EtFOSE	540.0>448.0	24	540.0>169.0	25		

3. Results and Discussion

3-1. Identification Points of EI-MRM Method

The quantitative and qualitative MRM transitions of each target and their corresponding collision energies are shown in Table 3. Four identification points were applied.

The four identification points were:

(1) ±0.10 min deviation of absolute retention time
(2) 1 quantitative or target MRM transition
(3) ≥ 2 product ions (i.e. at least 1 qualitative or reference MRM transition)
(4) The maximum tolerances for relative intensity% of reference MRM are shown in Table 4.

Table 4 Tolerance range of reference MRM and ion

Ref MRM/Ion Intensity % (area relative to quantitative MRM/ion)	Maximum tolerance
> 50%	± 20%
> 20% to 50%	± 25%
> 10% to 20%	± 30%
≤ 10%	± 50%

3-2. Instrument Detection Limit (IDL) and Limit of Quantitation (LOQ) of EI-MRM Method

By injecting post-spiked samples of increasingly lower concentrations, the instrument detection limit (IDL) and limit of quantitation (LOQ) of compounds were determined. At IDL of the EI-MRM method, the S/N of quantitative MRM is greater than 5 and the relative intensity% of at least one qualitative MRM falls within the set tolerance range. S/N is calculated by the peak-to-peak method. Satisfying these two criteria, the IDL of N-MeFOSE and N-EtFOSE were determined to be 0.5 ng/mL (Fig. 2) and that of FTA 6:2 was 1.0 ng/mL. The IDL of the remaining targets were estimated to be 4.0 ng/mL. This is because results of 2.0 ng/mL and 3.0 ng/mL injections of these targets did not yield results which satisfy the criteria set for IDL. At LOQ, the S/N of quantitative MRM is greater than 10 and all qualitative MRM fall within the set tolerance range. LOQ of all compounds were determined to be 5.0 ng/mL.

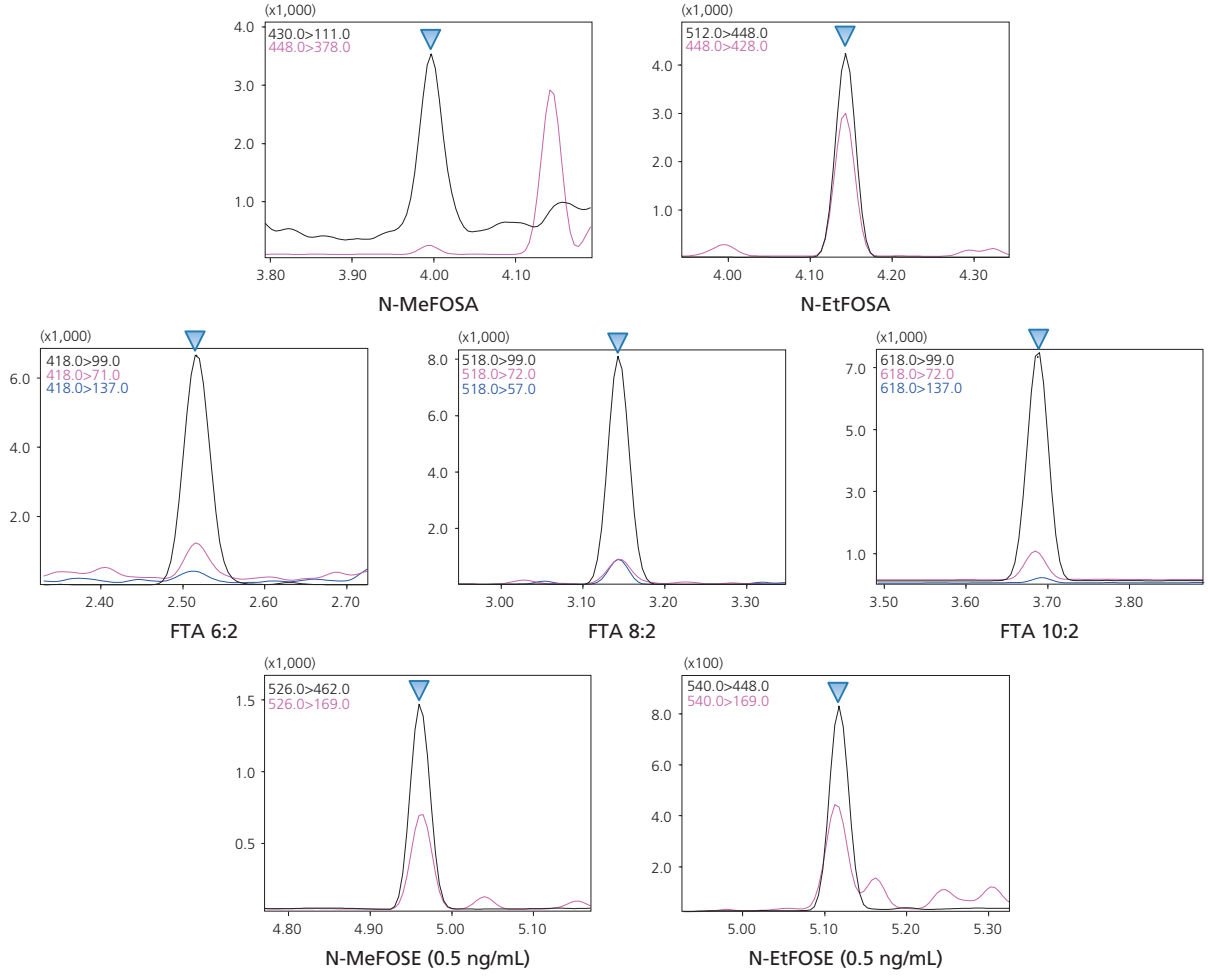

Fig. 2 EI-MRM chromatograms of PFCs at 5.0 ng/mL (Except for N-MeFOSE and N-EtFOSE)

3-3. Matrix Effects, Calibration Curve and Accuracy of EI-MRM Method

Matrix effects were evaluated by comparing peak area ratios of standards in the blank textile matrix and of that in THF (Table 5). Calculations were based on three replicates at three concentration levels (low, mid and high). Generally, the matrix effects calculated are above 100% or nearly insignificant. In view of matrix enhancements, a matrix-matched calibration was adopted for more accurate quantitation of testing samples.

All targets were calibrated from 5.0 ng/mL to 200 ng/mL. Linear IS calibration curves with average $R^2 \geq 0.998$ were obtained. Repeatability of the peak area ratios were evaluated at the lowest, mid and highest calibration levels from six replicates (Table 5). The %RSD at the lowest calibration levels of all targets ranged from 3.54 to 17.2%.

Method accuracy was also evaluated at the low, mid and high concentration levels with post-spiked Quality Control (QC) samples. On average, the QC samples were quantitated to be in the range of approx. ±30% of the spiked concentrations. A summary of the results is shown in Table 6.

Table 5 Summary of matrix effects (%) and %RSD of peak area ratios

Compound	Conc. (ng/mL)	Matrix Effect (%) (n= 3)	%RSD (n = 6)
FTA 6:2	5.00	123	3.54
	50.0	117	1.65
	200	114	1.63
FTA 8:2	5.00	98.1	6.78
	50.0	108	4.14
	200	110	1.48
FTA 10:2	5.00	113	6.39
	50.0	107	3.07
	200	104	1.66
N-MeFOSA	5.00	110	16.9
	50.0	100	7.81
	200	108	3.49
N-EtFOSA	5.00	115	17.2
	50.0	98.9	4.47
	200	110	1.59
N-MeFOSE	5.00	114	7.26
	50.0	115	0.96
	200	119	0.57
N-EtFOSE	5.00	142	14.1
	50.0	120	3.00
	200	119	1.98

Table 6 Summary of accuracy% at low, mid and high concentration levels

Compound	Accuracy%		
	7.50 ng/mL	30.0 ng/mL	150 ng/mL
FTA 6:2	74.7	78.7	81.3
FTA 8:2	71.4	81.2	80.4
FTA 10:2	69.1	78.9	76.5
N-MeFOSA	101	81.5	82.0
N-EtFOSA	93.4	90.2	78.7
N-MeFOSE	91.6	78.8	75.8
N-EtFOSE	89.7	78.5	77.4

3-4. Identification Points of PCI-SIM Method

The quantitative and qualitative monitoring ions of each target are shown in Table 7. Four identification points were applied.

Four identification points were:

(1) ±0.10 min deviation of absolute retention time
(2) 1 quantitative/ target monitoring ion
(3) 1 qualitative/ reference monitoring ion
(4) Maximum tolerances for relative intensity% of reference ion are shown in Table 4.

Table 7 Quantitative and qualitative ions of targets and ISTD

Compound	Quantitative ion	Qualitative ion
FTA 6:2	419.0	447.0
Naphthalene-D_8 (ISTD)	136.0	165.0
FTA 8:2	519.0	547.0
FTA 10:2	619.0	647.0
N-MeFOSA	514.0	515.0
N-EtFOSA	528.0	529.0
N-MeFOSE	540.0	558.0
N-EtFOSE	554.0	572.0

3-5. Instrument Detection Limit (IDL) and Limit of Quantitation (LOQ) of PCI-SIM Method

By injecting post-spiked samples of increasingly lower concentrations, the instrument detection limit (IDL) and limit of quantitation (LOQ) of compounds were determined. At IDL of the PCI-SIM method, the S/N of quantitative monitoring ion is greater than 5 and the relative intensity% of the qualitative ion falls within the set tolerance range. S/N is calculated by the peak-to-peak method. Satisfying these two criteria, the IDL of all compounds was determined to be 4.0 ng/mL (Fig. 3).

At LOQ, the S/N of the quantitative ion is greater than 10 and the relative intensity% of the qualitative ion falls within the set tolerance range. LOQ of all compounds was determined to be 5.0 ng/mL.

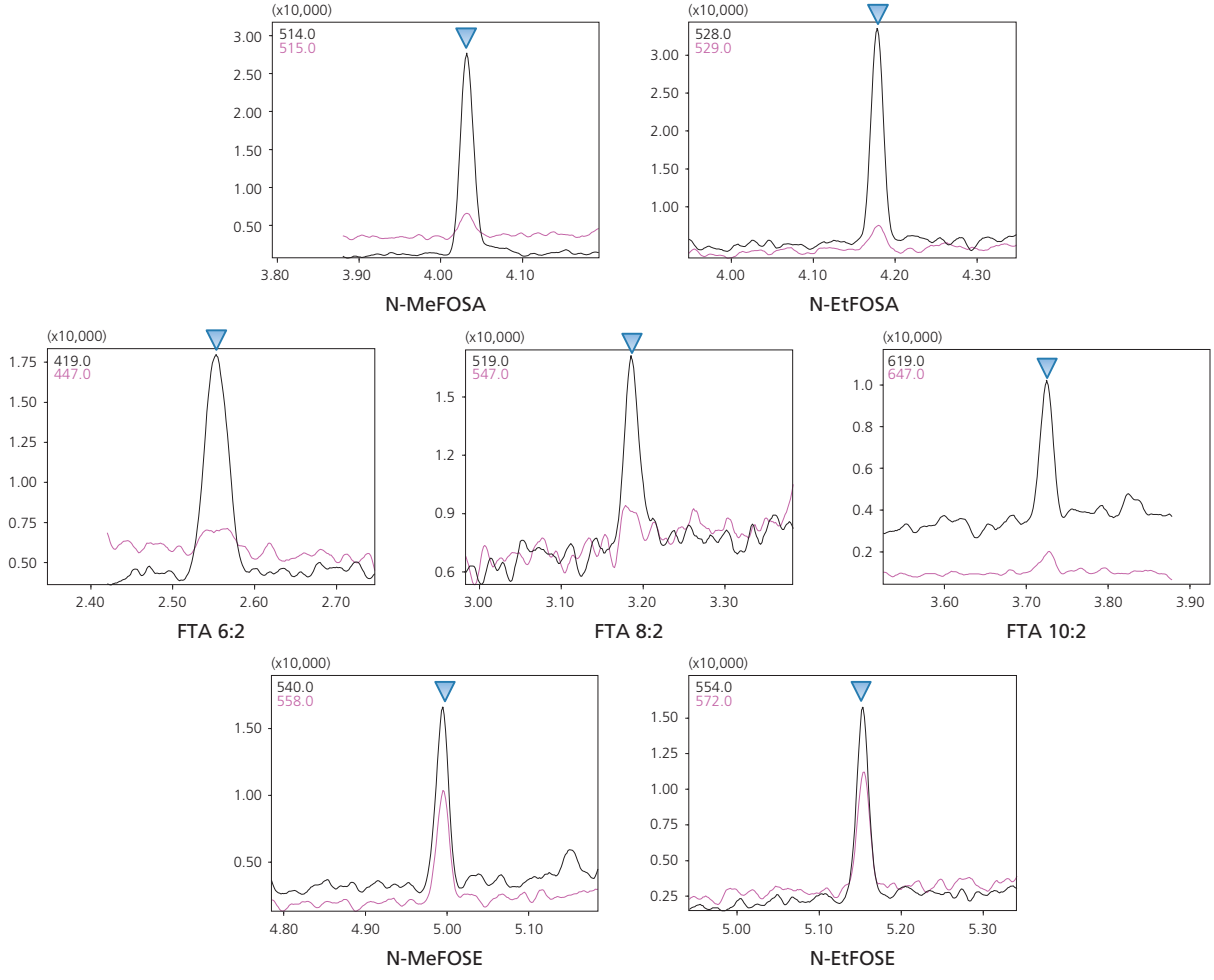

Fig. 3 PCI-SIM chromatograms of PFCs at 4.0 ng/mL

3-6. Matrix Effects, Calibration Curve and Accuracy of PCI-SIM Method

Matrix effects were evaluated by comparing peak area ratios of standards in blank textile matrix and of that in THF (Table 8). Calculations were based on three replicates at three concentration levels (low, mid and high). The matrix effects of FOSEs and FOSAs were above 100%, whereas the matrix suppression of FTA 8:2 and FTA 10:2 were more significant at 5.0 ng/mL (88.3% and 88.7%, respectively). In view of matrix enhancements, a matrix-matched calibration was adopted for more accurate quantitation of testing samples.

All targets were calibrated from 5.0 ng/mL to 200 ng/mL. Linear IS calibration curves with average R^2 = 0.999 were obtained. Repeatability of the peak area ratios were evaluated at the lowest, mid and highest calibration levels from six replicates (Table 8). The %RSD at the lowest calibration levels of all targets ranged from 5.15 to 12.64%.

Method accuracy was evaluated at the low, mid and high concentration levels with post-spiked QC samples. The QC samples were quantitated to be in the range of ±30% of the spiked concentrations. A summary of the results is shown in Table 9.

Table 8 Summary of matrix effects (%) and %RSD of peak area ratios

Compound	Conc. (ng/mL)	Matrix Effect (%) (n= 3)	%RSD (n = 6)
FTA 6:2	5.00	99.7	7.94
	50.0	102	1.52
	200	97.3	2.54
FTA 8:2	5.00	88.3	12.6
	50.0	101	1.25
	200	95.6	2.87
FTA 10:2	5.00	88.7	8.28
	50.0	94.2	1.74
	200	93.0	2.94
N-MeFOSA	5.00	107	9.21
	50.0	107	1.46
	200	101	2.93
N-EtFOSA	5.00	109	7.01
	50.0	106	2.14
	200	102	2.97
N-MeFOSE	5.00	137	9.64
	50.0	137	2.84
	200	136	3.33
N-EtFOSE	5.00	134	5.15
	50.0	130	2.38
	200	133	2.96

Table 9 Summary of accuracy% at low, mid and high concentration levels

Compound	Accuracy%		
	7.50 ng/mL	30.0 ng/mL	150 ng/mL
FTA 6:2	104	88.6	88.1
FTA 8:2	76.6	83.7	83.1
FTA 10:2	95.8	87.4	82.1
N-MeFOSA	89.8	78.8	79.7
N-EtFOSA	97.7	80.0	82.7
N-MeFOSE	84.5	81.0	85.9
N-EtFOSE	92.1	83.4	86.2

3-7. Analyses of Textiles using EI-MRM and PCI-SIM Methods

The EI-MRM and PCI-SIM methods were applied to textile analyses of commercially sold products. Using the EI-MRM method, N-MeFOSE was detected in a sample of cotton and spandex blend and N-EtFOSE was detected in a sample of 100% polyester sportswear.

The detected and quantitated concentrations of N-MeFOSE was 1.74 ng/g and that of N-EtFOSE was 2.91 ng/g (Fig. 4 & 5), which were above the determined IDL (0.5 ng/mL) of FOSEs.

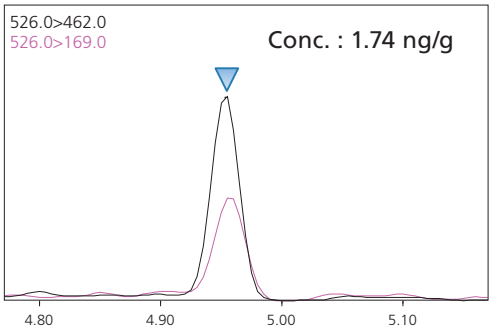

Fig. 4 Detection of N-MeFOSE in cotton and spandex blend

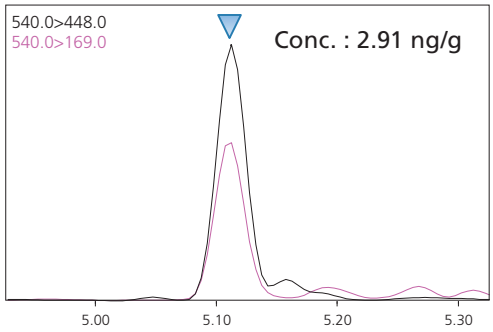

Fig. 5 Detection of N-EtFOSE in 100% polyester sportswear

The above-mentioned samples were not analysed using the PCI-SIM method as the detected concentration of FOSEs were below the determined IDL of the single-quadrupole method, which was 4.0 ng/mL. The PCI-SIM method was used to analyse the waterproof material of an umbrella.

FTA 8:2 and FTA 10:2 were quantitated to be 89.8 ng/g and 41.0 ng/g, respectively (Fig. 6). It is noteworthy that quantitation of the same sample using EI-MRM yielded the similar concentrations of FTA 8:2 and FTA 10:2 (83.1 ng/g and 38.7 ng/g, respectively; Fig. 7).

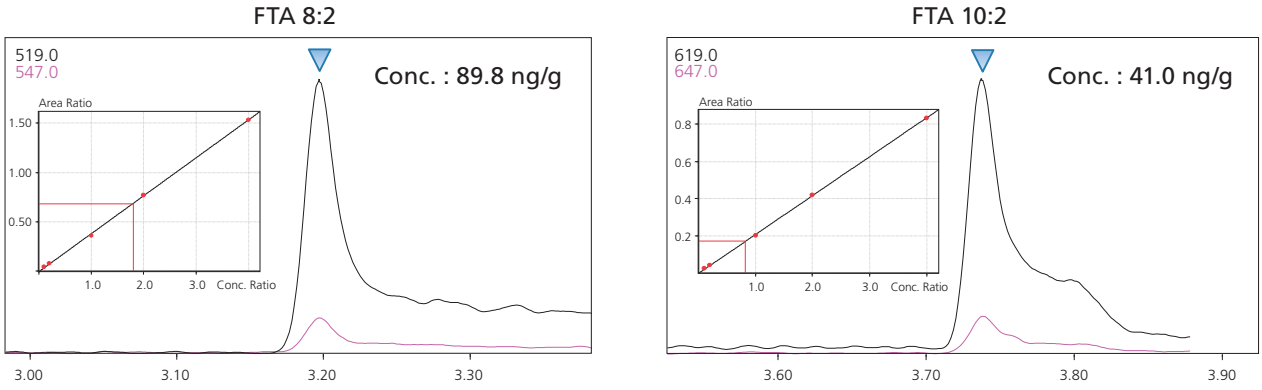

Fig. 6 Analysis results of waterproof material of umbrella in PCI-SIM method

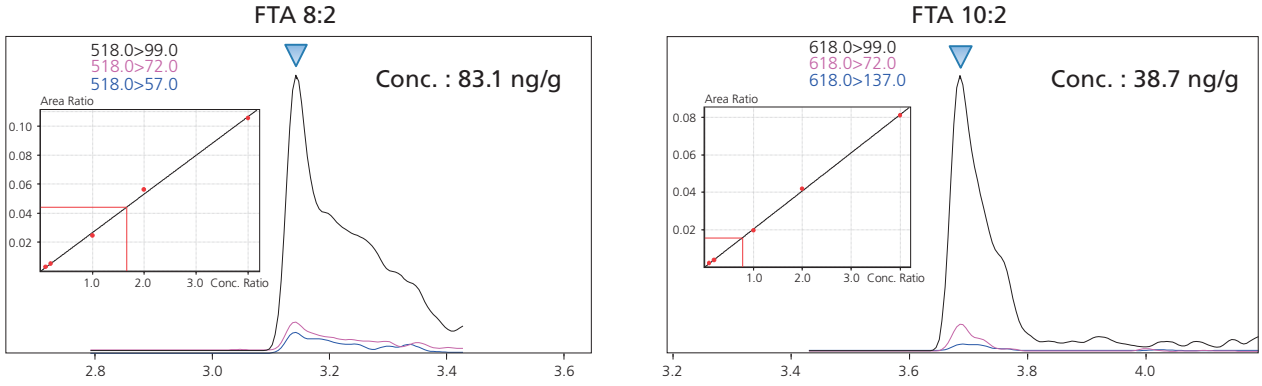

Fig. 7 Analysis results of waterproof material of umbrella in EI-MRM method

4. Conclusion

Due to the higher sensitivity of the EI-MRM method, it will be useful for detecting trace amounts of PFOA and PFOS precursors in high-performance outdoor products, which usually display oil, stain and water repellent properties. On the other hand, PCI-SIM method can be applied for fast screening of PFOA and PFOS precursors in textile articles. The LOQ of 5.0 ng/mL of both methods well covers the proposed EU regulation which states that PFOA, its salts and PFOA-related substances shall not be used in the production of, or placed on the market, in an article, in a concentration equal to or above 25 ppb (ng/g) of PFOA (including its salts) [4].

5. References

[1] The 16 New POPs. An Introduction to the chemicals added to the Stockholm Convention as Persistent Organic Pollutants by the Conference of the Parties (2017, June).

[2] PFOA-Restriction in Norway (Product regulation FOR 2004-06-01 Nr. 922, Section 2-32).

[3] Lists of PFOS, PFAS, PFOA, PFCA, related Compounds and Chemicals that may Degrade to PFCA. ENV/JM/MONO(2006)15.

[4] COMMISSION REGULATION (EU) 2017/1000 of 13 June 2017 amending Annex XVII to Regulation (EC) No 1907/2006 of the European Parliament and of the Council concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) as regards perfluorooctanoic acid (PFOA), its salts and PFOA-related substances.

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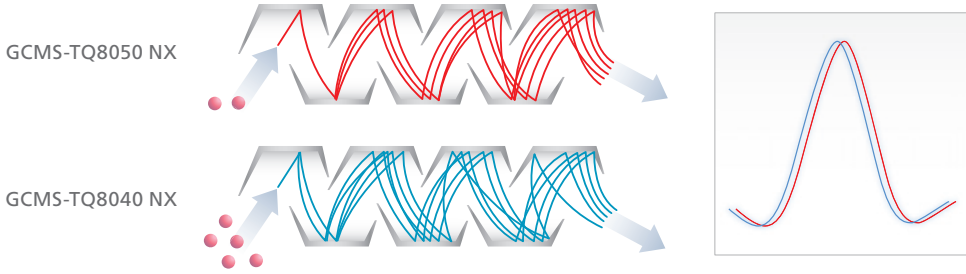

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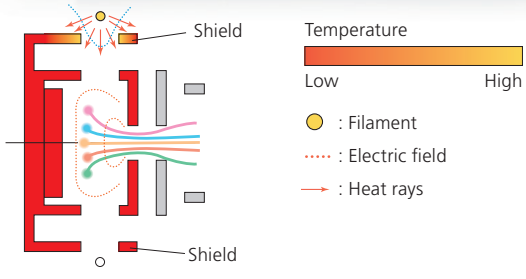

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