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Fast Screening and Quantitation of Perfluorinated Sources from Textiles using Chemical Ionization GC-MS

ASMS 2017 TP-295

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Introduction

Bioaccumulative and toxic perfluorooctane sulfonate (PFOS) and perflurooctanoic acid (PFOA) consist of fluorinated C8 backbones with a sulphonate and carboxylate group, respectively. Whilst strong C-F bonds deem PFOS biologically inert, its reactive sulphonate group can coordinate to different functional groups, which after polymerization, produces surface-active substances. For example, polyfluorinated sulfon-amides and telomer alcohols are widely used in textiles. However, incomplete polymerization will produce residual precursors such as perfluorooctane sulfon-amides (FOSEs, FOSAs) and acrylates (FTAcrs), which potentially degrade to PFOS and PFOA, respectively.[1]

Herein, we present a gas chromatography chemical ionization mass spectrometry (GC/CIMS) method capable of sensitive detection of four PFOS and three PFOA precursors. The PFOS and PFOA precursors covered in this study are included in the list of substances surveyed and revised by OECD (Organisation for Economic Cooperation and Development) since 2007.[2]

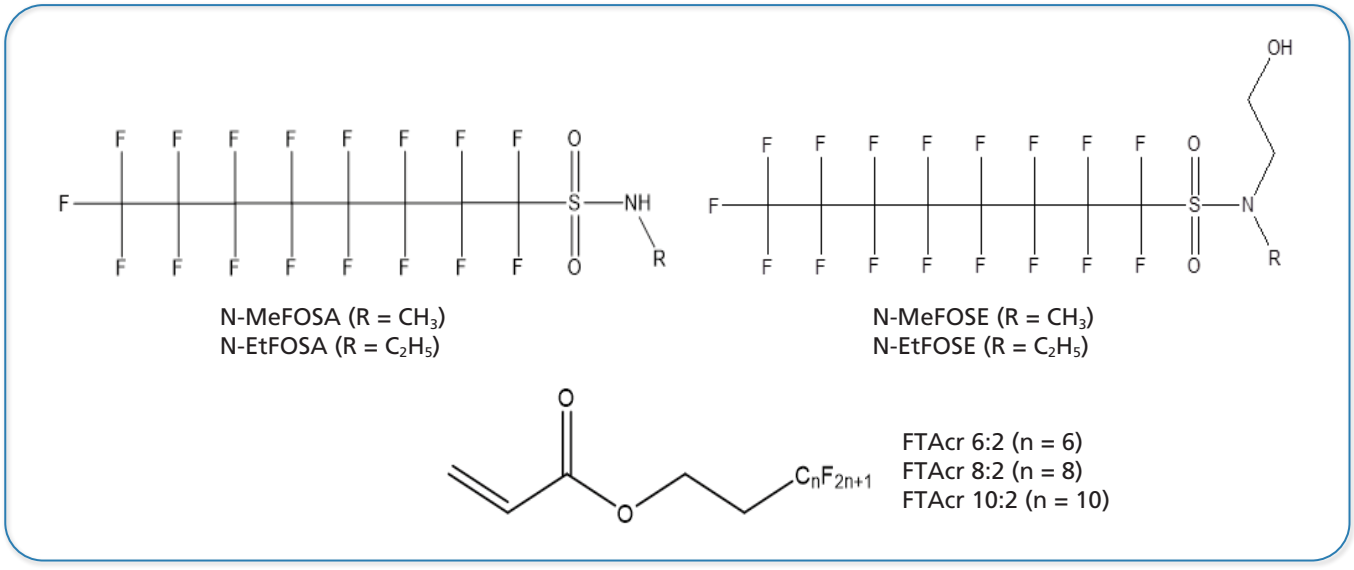

Figure 1. Molecular structures of FTAs, FOSEs and FOSAs.

Methods and Materials

A mixture of four perfluorooctane sulfon-amides (FOSEs, FOSAs) and three acrylates (FTAcrs) was prepared from neat standards. Napthalene-D_8 was used as internal standard. A matrix-matched calibration was adopted and an analyte protectant (D-Sorbitol) was incorporated to counter matrix interferences. Details of the chemicals used are shown in Table 1. GCMS-QP2020 (Shimadzu Corporation, Japan) was employed in this work. Shimadzu AOC-20i/s autosampler was utilised as the autosampler. Separation was achieved using a SH-Rtx-200 capillary column (30 m × 0.32 mm × 0.5 µm). The details of the analytical conditions are shown in Table 2.

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Table 1. List of targets in this study.

No.	Target Compound	Acronym	CAS No.	Supplier
1	1H,1H,2H,2H-Perfluorooctyl acrylate	FTAcr 6:2	17527-29-6	Apollo Scientific
2	1H,1H,2H,2H-Perfluorodecyl acrylate	FTAcr 8:2	27905-45-9	Sigma Aldrich
3	1H,1H,2H,2H-Perfluorododecyl acrylate	FTAcr 10:2	17741-60-5	Apollo Scientific
4	N-methylperfluoro-1-octanesulfoaminde	N-MeFOSA	31506-32-8	Wellington Laboratories
5	N-ethylperfluoro-1-octanesulfoaminde	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

GC/CIMS Analytical Conditions

Table 2. GC/CIMS analytical conditions

Gas Chromatography		
Injection Condition	:	250°C, splitless mode, high pressure injection at 150kPa
Injection Volume	:	2 µL
Gas Flow Condition	:	Constant linear velocity
(Helium carrier gas)		Linear velocity 48.7 cm/s
		Purge flow 3 mL/min
Oven Temperature Programming	:	80°C → 30°C/min to 260°C (hold 1 min)
Mass Spectrometer		
Ion Source Temperature	:	200°C
Interface Temperature	:	250°C
Acquisition Mode	:	SIM
Ionization Type	:	Positive Chemical Ionization
Reagent Gas	:	Methane

Sample Extraction

The matrix was prepared from a blank textile sample. The textile used was cut into approximately 5 mm ×5 mm squares. 1 g of cut textile was weighed into a 20 mL glass vial and 10 mL of tetrahydrofuran was added. The vial(s) were then heated in a water bath at 60°C for 1 hour. After which the extract was subjected to a 0.45 µm nylon filter. The filtered extract was then concentrated 10 times before use as a diluent for matrix-matched calibration standards. Textile samples used for testing were subjected to the same preparation method.

Results

Development of GC/CIMS Method

Seven targets and internal standard (ISTD) were chromatographically separated within a GC analysis time of 7 minutes. Four identification points were used for this study:

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 below:

Ref Ion Intensity % (area relative to base peak)	Maximum tolerance
> 50%	± 20%
> 20% to 50%	± 25%
> 10% to 20%	± 30%
≤ 10%	± 50%

Table 3. Monitoring ions of targets and internal standard.

Compound	Quantitative Ion	Qualitative Ion
FTAcr 6:2	419	447
Naphthalene-D_8 (ISTD)	136	165
FTAcr 8:2	519	547
FTAcr 10:2	619	647
N-MeFOSA	514	515
N-EtFOSA	528	529
N-MeFOSE	540	558
N-EtFOSE	554	572

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Calibration Curve, Matrix Effects and Repeatability

Matrix effect was evaluated by comparing peak area ratios of standards in THF and of that in blank matrix (see Table 4). ISTD was spiked at 50 ng/ml. Calculations were based on three replicates at the low and mid concentration levels.

FTAcrs and N-EtFOSA displayed an ion suppression effect, whereas the FOSE compounds displayed an ion enhancement effect. In order to achieve more accurate quantitation of testing samples, a matrix-matched calibration was adopted. Linear IS calibration curves (average $R^2 \geq 0.999$) are displayed in Figures 2-8.

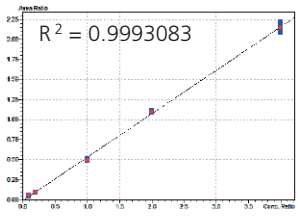

Figure 2. FTAcr 6:2

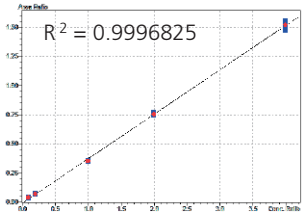

Figure 3. FTAcr 8:2

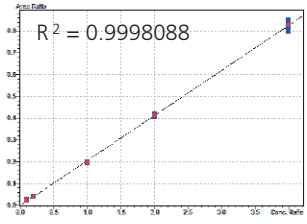

Figure 4. FTAcr 10:2

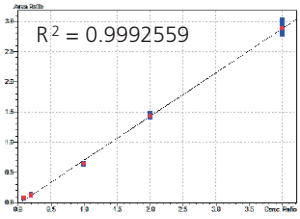

Figure 5. N-MeFOSA

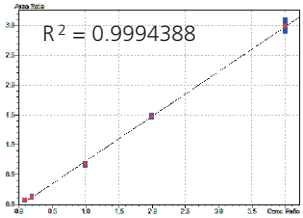

Figure 6. N-EtFOSA

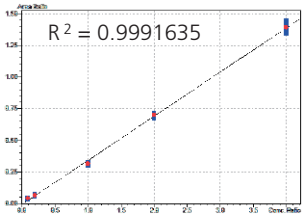

Figure 7. N-MeFOSE

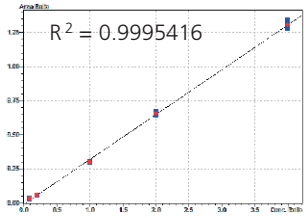

Figure 8. N-EtFOSE

Repeatability of the peak area ratios was evaluated at the lowest and mid concentration levels from three replicates (see Table 4). The %RSD at the lowest calibration levels of all targets ranged from to 5.94 to 9.55%

Table 4. Summary of matrix effects (%) and %RSD of peak area ratios.

Compound	Conc. (ng/ml)	Matrix Effect (%) (n=3)	%RSD (n=6)
FTAcr 6:2	5.00	91.8	6.31
	100	91.1	0.89
FTAcr 8:2	5.00	80.5	8.82
	100	89.3	1.23
FTAcr 10:2	5.00	96.4	6.08
	100	85.8	1.21
N-MeFOSA	5.00	108.6	5.94
	100	99.5	1.83
N-EtFOSA	5.00	94.1	7.09
	100	97.2	0.79
N-MeFOSE	5.00	130.3	8.80
	100	128.7	2.06
N-EtFOSE	5.00	105.5	9.55
	100	128.0	1.93

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IDL, LOQ and Accuracy

The instrument detection limit (IDL) of each compound was determined by injection of increasingly lower concentrated post-spiked samples. The IDL of acrylates is 3.0 ng/ml and that of FOSAs and FOSEs is 2.0 ng/ml. The target ion of targets at IDL have S/N > 5 (Figures 9-15). S/N was calculated via the Peak to Peak method. The limit of quantitation (LOQ) of each compound was determined based on the criteria in section 3.1, and the quantifier ion should have S/N > 10. The LOQ of all targets is 5.0 ng/ml.

Method accuracy was evaluated at the low, mid and high concentration levels with QC samples. QC samples were quantitated to be in the range of ±20% of the spiked concentrations. Summary of the results are shown in Table 5.

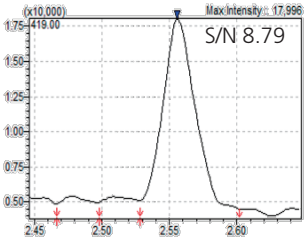

Figure 9. 3.0 ng/ml FTAcr 6:2

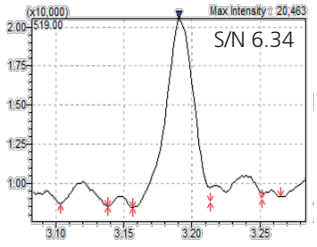

Figure 10. 3.0 ng/ml FTAcr 8:2

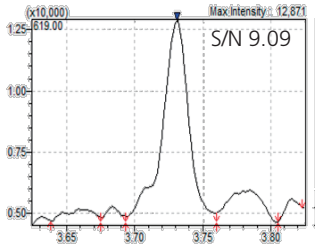

Figure 11. 3.0 ng/ml FTAcr 10:2

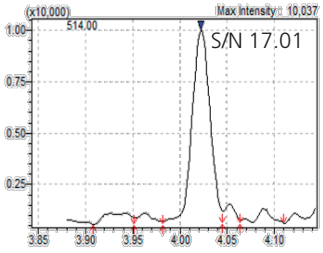

Figure 12. 2.0 ng/ml N-MeFOSA

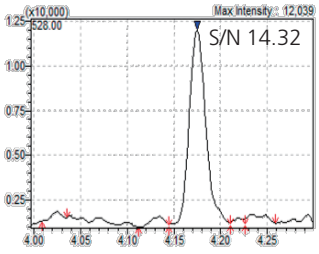

Figure 13. 2.0 ng/ml N-EtFOSA

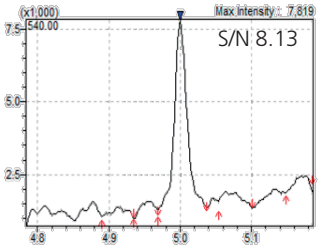

Figure 14. 2.0 ng/ml N-MeFOSE

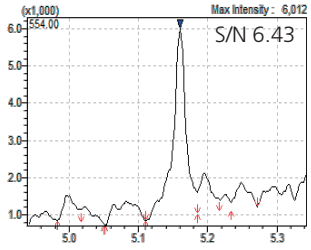

Figure 15. 2.0 ng/ml N-EtFOSE

Table 5. Summary of accuracy% at low, mid and high concentration levels.

Compound	Accuracy%		
	7.5 ng/ml	30 ng/ml	150 ng/ml
FTAcr 6:2	97.0	89.6	90.2
FTAcr 8:2	94.3	87.1	83.4
FTAcr 10:2	86.9	88.3	82.7
N-MeFOSA	93.3	84.2	80.9
N-EtFOSA	96.1	82.2	83.9
N-MeFOSE	94.4	87.3	88.2
N-EtFOSE	92.1	81.0	86.2

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Sample Analysis

A sportswear made of 100% polyester was shown to have N-EtFOSE in concentration of 2.54 ng/ml (Figure 16). As this concentration is below the LOQ herein, the sample was quantitated using an optimized EI MRM method,[3] where the LOQ of N-EtFOSE was 2.0 ng/ml. It is noteworthy that analysis of the sportwear sample via MRM displayed a close quantitation value of 2.45 ng/ml. A waterproof material from an umbrella displayed presence of FTAcr 8:2 and FTAcr 10:2 (Figures 17 & 18). The amount of FTAcr 8:2 was quantitated to be 76.3 ng/ml and that of FTAcr 10:2 was quantitated to be 36.8 ng/ml.

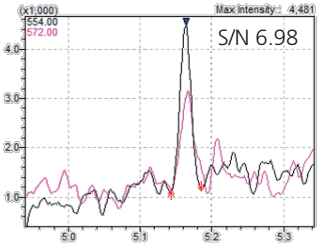

Figure 16. N-EtFOSE in 100% polyester sportswear

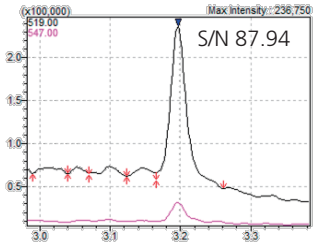

Figure 17. FTAcr 8:2 in waterproof material of umbrella

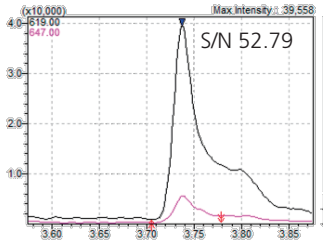

Figure 18. FTAcr 10:2 in waterproof material of umbrella

Conclusion

An optimized GC/CIMS method was developed for analyses of FTAcrs, FOSEs and FOSAs. Good calibration linearity and repeatability were obtained in this study. Additionally, the method has been applied to testing of real samples.

References

[1] Renner, R. *Perfluorinated Sources Outside and Inside. Environ. Sci. Technol.*, **2004**, 38 (5), 80A.
[2] Lists of PFOS, PFAS, PFOA, PFCA, related Compounds and Chemicals that may Degrade to PFCA. ENV/JM/MONO(**2006**)15.
[3] Yeong, H. X.; Olivia, S.; Lahey, C. M.; Ting, G. W. E.; Loo, L. C. *Fast and Accurate Quantitation of Perfluorinated Sources from Textiles using Gas Chromatography-Triple Quadrupole Mass Spectrometry*. ASMS poster session. **2017**, TP296.

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First Edition: June, 2017

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