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Fast and Accurate Quantitation of Perfluorinated Sources from Textiles using Gas Chromatography-Triple Quadrupole Mass Spectrometry

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Introduction

Polyfluorinated sulfon-amides and telomer alcohols are widely used in textiles as stain repellents. However, incomplete polymerization will produce residual precursors such as perfluorooctane sulfon-amides (FOSEs, FOSAs) and acrylates (FTAcrs), which may potentially degrade to perfluorooctane sulfonate (PFOS) and perflurooctanoic acid (PFOA), respectively. Due to strong C-F bonds, PFOS and PFOA are extremely stable and therefore bioaccumulative. Hence the presence of these perfluorinated substances and its precursors are environmental concerns.[1]
Previously, we presented the Gas Chromatography-Triple Quadrupole Mass Spectrometry (GC/TQMS) analysis method for fluorotelomer alcohols (FTOHs) and fluorotelomer acrylates (FTAcrs).[2] Our earlier results reflected the need to adopt a matrix-matched calibration and to improve sample extraction to reduce column deterioration. To resolve these issues, we herein present a GC/TQMS method for detection of PFOS and PFOA precursors, which are FOSEs, FOSAs; and FTAcrs, respectively. The PFOS and PFOA precursors covered in this study are also included in the list of substances surveyed and revised by OECD (Organisation for Economic Cooperation and Development) since 2007.[3]

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 targeted compounds are shown in Table 1. GCMS-TQ8050 (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

Table 2. GC/TQMS 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	: MRM
Ionization Type	: Electron Ionization

Results

Development of GC/TQMS Method

The quantitative and qualitative MRM transitions of each target are shown in Table 3. Four identification points were used for analyses of this set of perfluorocompounds (PFCs).
The four identification points are:
1. ±0.10 min deviation of absolute retention time
2. 1 quantitative/ target MRM transition
3. ≥ 2 product ions (i.e. at least 1 qualitative/ reference MRM transition)
4. Maximum tolerances for relative intensity% of reference MRM are shown below:

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

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Table 3. MRM transitions of targets and internal standard.

Compound	Quantitative MRM	CE (V)	Quantitative MRM	CE (V)	Quantitative MRM	CE (V)
FTAcr 6:2	418 > 99.20	10	418 > 71.00	24	418 > 137.10	24
Naphthalene-D_8 (ISTD)	136.10 > 108.10	20	134.10 > 82.00	20		
FTAcr 8:2	518 > 99.20	20	518 > 72.10	21	518 > 57.00	27
FTAcr 10:2	618 > 99.10	15	618 > 72.00	21	618 > 137.20	30
N-MeFOSA	448 > 428.10	9	448 > 378.00	21		
N-EtFOSA	512 > 447.90	9	448 > 428.10	9	448 > 378.00	21
N-MeFOSE	526 > 462.00	18	526 > 69.10	35	526 > 169.10	20
N-EtFOSE	540 > 447.80	24	540 > 57.20	25	540 > 168.90	25

Calibration Curve, Matrix Effects and Repeatability

Matrix effect was evaluated by comparing peak area ratios of standards in THF and of that in blank textile matrix (see Table 4). Calculations were based on six replicates at three concentration levels (low, mid and high). Generally, the matrix effects calculated are above 100%. In view of matrix enhancements, a matrix-matched calibration was adopted for more accurate quantitation of testing samples. FTAcr 6:2, N-MeFOSE and N-EtFOSE were calibrated from 2.00 to 200 ng/ml. The remaining compounds were calibrated from 5.00 to 200 ng/ml. ISTD was spiked at 50 ng/ml. Linear IS calibration curves (average $R^2 \geq 0.998$) are displayed in Figures 1-7.

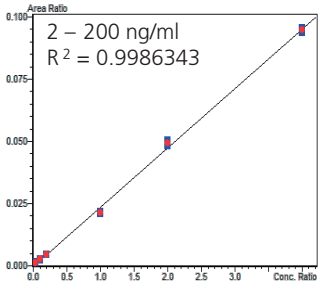

Figure 1. FTAcr 6:2

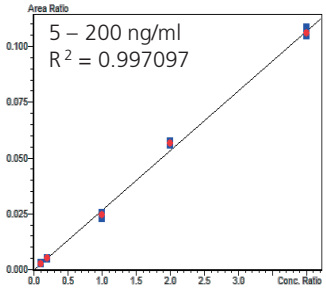

Figure 2. FTAcr 8:2

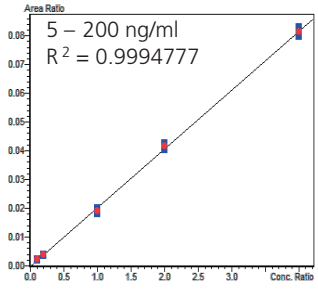

Figure 3. FTAcr 10:2

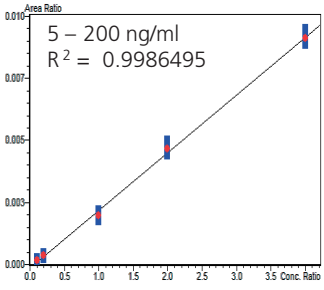

Figure 4. N-MeFOSA

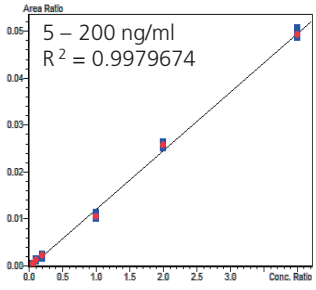

Figure 5. N-EtFOSA

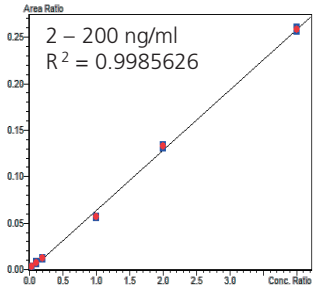

Figure 6. N-MeFOSE

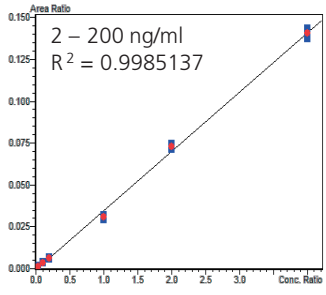

Figure 7. N-EtFOSE

Repeatability of the peak area ratios were evaluated at the lowest, mid and highest calibration levels from six replicates (see Table 4). The %RSD at the lowest calibration levels of all targets ranged from 2.39 to 14.72%.

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Table 4. Summary of matrix effects (%), %RSD of peak area ratios and the IDLs of targets.
[a]IDL based on three identification criteria. [b]IDL based on four identification criteria.

Compound	Conc. (ng/ml)	Matrix Effect (%) (n= 6)	%RSD (n = 6)	IDL (ng/ml)[a] S/N > 10	IDL (ng/ml)[b] S/N > 3
FTAcr 6:2	2.00		2.39	0.2	1.0
	5.00	129			
	50.0	114	1.56		
	200	115	0.98		
FTAcr 8:2	5.00	104	3.32	0.2	2.0
	50.0	112	3.58		
	200	110	1.23		
FTAcr 10:2	5.00	108	5.56	0.5	2.0
	50.0	106	3.01		
	200	105	1.38		
N-MeFOSA	5.00	139	7.58		ca. 3.5
	50.0	110	4.50		
	200	110	3.13		
N-EtFOSA	5.00	132	14.72	ca. 1.5	2.0
	50.0	105	4.38		
	200	109	1.72		
N-MeFOSE	2.00		7.07	0.2	0.5
	5.00	128			
	50.0	116	0.96		
	200	118	0.57		
N-EtFOSE	2.00		4.72	0.2	0.5
	5.00	118			
	50.0	116	3.00		
	200	120	1.93		

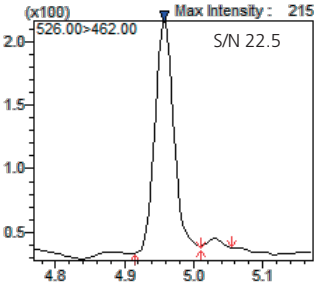

Figure 8. 0.2 ng/ml N-MeFOSE

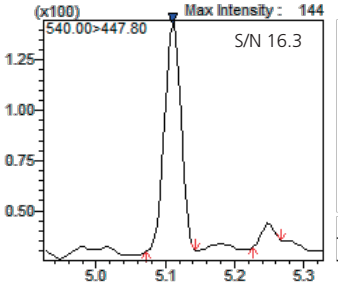

Figure 9. 0.2 ng/ml N-EtFOSE

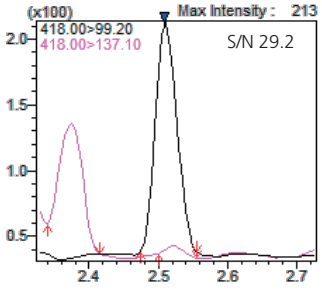

Figure 10. 1.0 ng/ml FTAcr 6:2

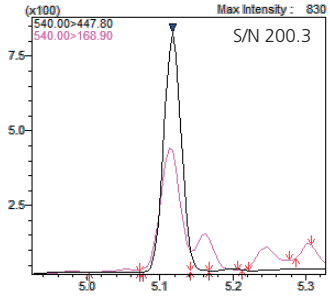

Figure 11. 0.5 ng/ml N-EtFOSE

IDL, LOQ and Accuracy

The instrument detection limit (IDL) of each compound was determined by injecting post-spiked standards of increasingly lower concentrations. Satisfying three identification criteria, where deviation of absolute retention time is ±0.10 min, detection of target MRM transition with S/N > 10, the IDL of targets were determined to be in the range of 0.2 ng/ml to ca. 1.5 ng/ml (Table 4 & Figures 8-9). In consideration of the above-mentioned identification criteria, the IDL of N-EtFOSA is estimated to be approximately 1.5 ng/ml. This is because the average S/N of N-EtFOSA target MRM is > 200 at 2.0 ng/ml, but the peak detection at 1.0 ng/ml is unstable due to low intensity. On the basis of four identification criteria, whereby deviation of absolute retention time is ±0.10 min, detection of target and one reference MRM transition, the S/N of target MRM transition is > 3 and relative intensity% of one reference MRM transition is within the set maximum tolerance, the IDL of targets were determined to be in the range of 0.5 ng/ml to 3.5 ng/ml (Figures 10 & 11). The IDL of N-MeFOSA is estimated to be approximately 3.5 ng/ml. This is because of poor repeatability for concentrations of 3.0 ng/ml and below. The limit of quantitation (LOQ) of each compound was determined based on the criteria in section 3.1, with S/N of target MRM > 10. The LOQ of targets are set to be its lowest calibration point. S/N was calculated via the Peak to Peak method.

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. Summary of the results are shown in Table 5.

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

Compound	Accuracy% (n=3)			
	3.0 ng/ml	7.5 ng/ml	30 ng/ml	150 ng/ml
FTAcr 6:2	97.7		77.4	82.9
FTAcr 8:2		84.3	80.1	81.5
FTAcr 10:2		70.0	83.6	75.9
N-MeFOSA		106.7	87.5	82.5
N-EtFOSA		74.0	74.2	79.9
N-MeFOSE	108.0		78.5	77.5
N-EtFOSE	121.8		73.7	78.6

Sample Analysis

The developed MRM method was applied to textiles of regular- and sports-wear. There was positive detection and quantitation of N-EtFOSE (2.47 ng/ml) in the sample of 100% polyester sportswear (Figure 12). There was positive detection of N-MeFOSE in the cotton and spandex textile blend (Figure 13). However, N-MeFOSE was not quantitated in this sample because the deduced concentration of 0.84 ng/ml is below its determined LOQ of 2 ng/ml.

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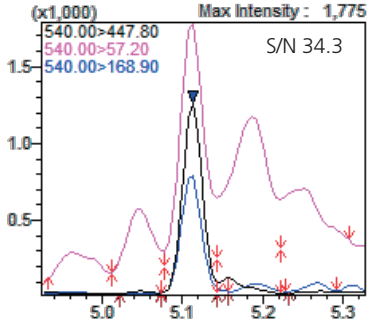

Figure 12. N-EtFOSE in 100% polyester sportswear

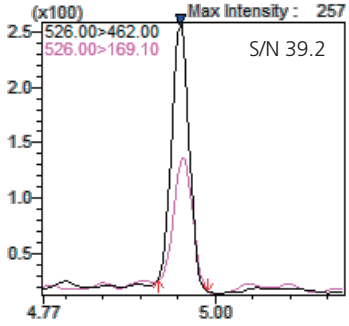

Figure 13. N-MeFOSE in cotton & spandex blend

Conclusion

An optimized GC/TQMS method was developed for analyses of FTAcrs, FOSEs and FOSAs. Good calibration linearity and sensitivity were obtained in this study. Additionally, a matrix-matched calibration has been adopted and applied for quantitation of testing samples.

References

[1] Renner, R. Perfluorinated Sources Outside and Inside. *Environ. Sci. Technol*. **2004**, 38 (5), 80A.
[2] Lahey, C. M.; Ting, G. W. E.; Yeong, H. X. C.; Jackie, J.; Chong, C. M.; Loo, L. C. *Fast and Accurate Analysis of Fluorotelomer Alcohols and Acrylates using Triple Quadrupole GC-MS/MS*. ASMS poster session. **2016**, ThP156.
[3] Lists of PFOS, PFAS, PFOA, PFCA, related Compounds and Chemicals that may Degrade to PFCA. ENV/JM/MONO(**2006**)15.

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