

# Fast and Accurate Analysis of Fluorotelomer Alcohols and Acrylates using Triple Quadrupole GC-MS/MS

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## Introduction

Fluorotelomer-based polymers (FTPs) are utilised as oil and water repellents in consumer products [1]. However, its extensive use in products such as textiles has raised environmental concerns, as residual fluorotelomer alcohols and acrylates (FTOHs and FTAs) from FTPs are considered as probable precursors of bioaccumulative and potentially toxic perfluorocarboxylic acids [1,2,3]. Traditionally, the determination of FTOHs has been

performed using single quadrupole GC-MS in chemical ionization (CI) mode [4,5]. Although CI can achieve sensitive detection limits (less than 20 fg/ul for FTOHs), it is sometimes avoided due to higher upkeep and running cost than electron ionization (EI) systems [5]. Furthermore, EI is a more comprehensive analytical solution than CI in applications. This motivated the use of GC-MS/MS system in EI mode in this study.

## Methods and Materials

A mixture of four fluorotelomer alcohols (FTOHs) and three fluorotelomer acrylates (FTAs) was prepared from neat standards (see Table 1). FTAc 8:2 was purchased from Sigma Aldrich. The rest were purchased from Apollo Scientific. The internal standard compound, 2-Perfluorobutyl-[1,1,2,2-<sup>2</sup>H<sub>4</sub>]-ethanol (MFBET), was purchased from Wellington Laboratories. Calibration curve solutions were prepared in ethyl acetate (pesticide residue and PCB grade, from Kanto Kagaku). Textile samples were selected as test matrices for quantitation of

targeted analytes. Sample extraction was carried out in ethyl acetate and pre-concentrated before injection into the system. A triple quadrupole GC-MS/MS, GCMS-TQ8040 (Shimadzu Corporation, Japan) in EI mode by multiple reaction monitoring (MRM) acquisition was used in this work. Shimadzu AOC-20i/s autosampler was utilised as the autosampler. SH-Stabilwax column (30 m length, 0.25 mm ID, 0.25 µm df) was used for separation of the targeted fluorotelomers.

Table 1. List of FTOHs and FTAs Analysed in This Experiment

Compound	Acronym	CAS No.
1H,1H,2H,2H-Perfluorohexan-1-ol	FTOH 4:2	2043-47-2
1H,1H,2H,2H-Perfluorooctan-1-ol	FTOH 6:2	647-42-7
1H,1H,2H,2H-Perfluorodecan-1-ol	FTOH 8:2	678-39-7
1H,1H,2H,2H-Perfluorododecan-1-ol	FTOH 10:2	865-86-1
1H,1H,2H,2H-Perfluorooctyl acrylate	FTAc 6:2	17527-29-6
1H,1H,2H,2H-Perfluorodecyl acrylate	FTAc 8:2	27905-45-9
1H,1H,2H,2H-Perfluorododecyl acrylate	FTAc 10:2	17741-60-5

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### GC-MS/MS Analysis Condition

Autosampler	
# of rinses (pre-run)	: 3
# of rinses (post-run)	: 3
# of rinses with sample	: 1
Injection volume	: 1 µl
GC	
Injection temp	: 240°C
Injection mode	: Splitless
Flow control mode	: Linear velocity
Linear velocity	: 43.4 cm/s
High Pressure Inj	: 315 kPa for 1.5 min
Column temp. prog.	: 40°C (1 min) → 20°C/min → 150°C → 30°C/min → 240°C (2 min)
MS/MS	
Ion source temp.	: 200°C
Interface temp.	: 240°C
Acquisition mode	: MRM
MRM transitions	: See the table below



Compound name	MRM (Target)	CE (V)	MRM (Ref 1)	CE (V)	MRM (Ref 2)	CE (V)
MF BET (IS)	199.00>130.10	9	248.00>97.10	15	248.00>130.10	9
FTOH 4:2	196.00>127.10	9	244.00>196.00	3	-	-
FTAc 6:2	418.00>99.10	9	99.00>57.10	12	-	-
FTOH 6:2	344.00>127.10	9	95.00>69.00	15	127.00>77.00	15
FTAc 8:2	518.00>99.10	12	99.00>57.10	12	-	-
FTOH 8:2	396.00>127.10	9	127.00>77.00	15	95.00>69.00	15
FTAc 10:2	618.00>99.10	15	99.00>57.10	12	-	-
FTOH 10:2	95.00>69.00	15	131.00>69.00	18	127.00>77.00	15

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## Sample Preparation

Individual neat standard was mixed and diluted in ethyl acetate to prepare calibration standard mixtures of 1, 2, 5, 10, 20, 50, 100, and 200 ng/ml. Calibration curves were in the range of 1- 100 ng/ml, except those of FTOH 6:2 and FTOH 8:2 (1 – 200 ng/ml). The peak shape of FTOH 4:2 was poorer at low concentration, than that of the other compounds. Hence, the calibration curve of FTOH 4:2 was generated in the range of 5 – 200 ng/ml. Internal standard (MFBET) was spiked to all standard mixtures at the

concentration of 100 ng/ml.

Each textile sample was cut into dimensions of 2 mm x 2 mm, after which 1 g of the sample was placed into a vial. Subsequently, 10 ml of ethyl acetate was added into the vial and capped. The sample vial was heated at 60 °C for 2 hours. The extract was subjected to a 0.22 µm nylon filter after heating. Finally, the filtered extract was concentrated 10 times and spiked with 100 ng/ml MFBET (Internal Standard), before injection to the GC-MS/MS.

## Results

### Calibration Curves

Linearity ( $R^2$ ) of the internal standard calibration curve of each compound is greater than 0.999 (refer to Figure 1).

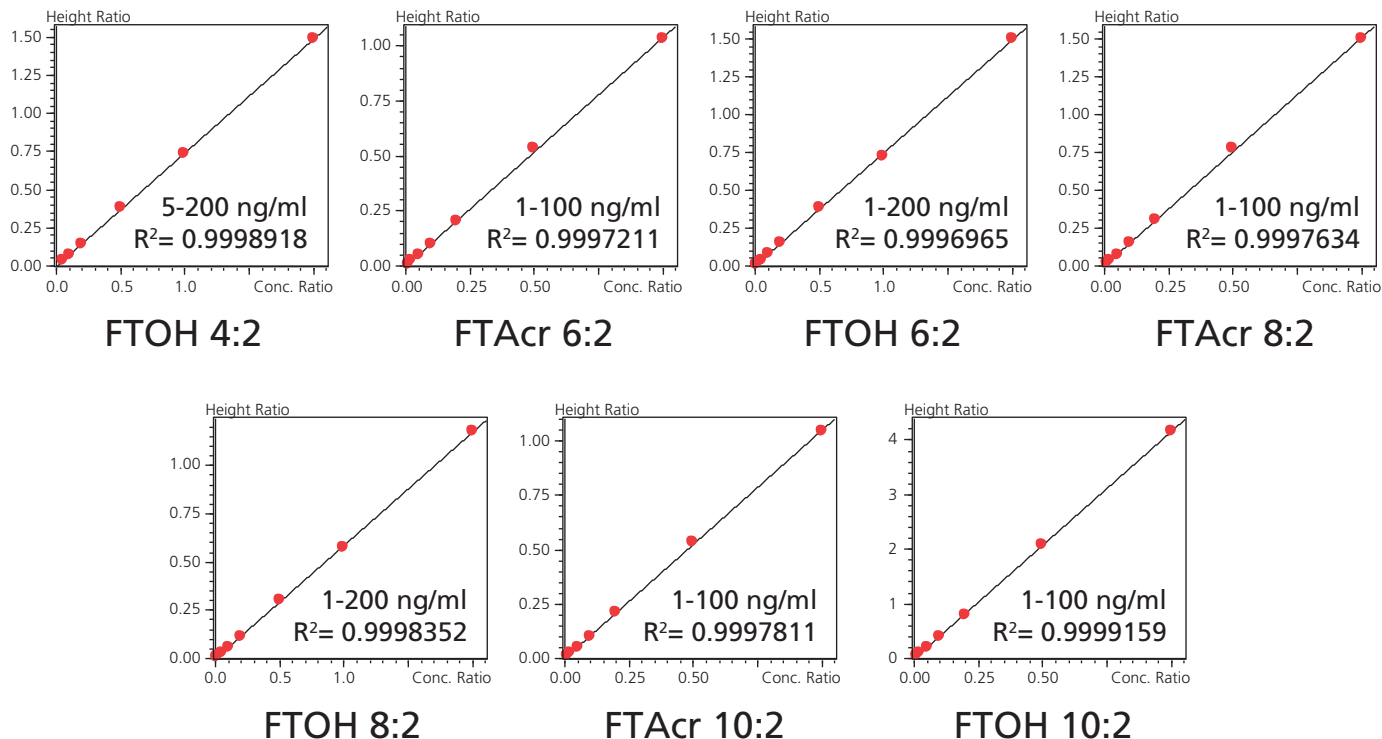


Figure 1: Calibration Curves

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## Mass Chromatograms

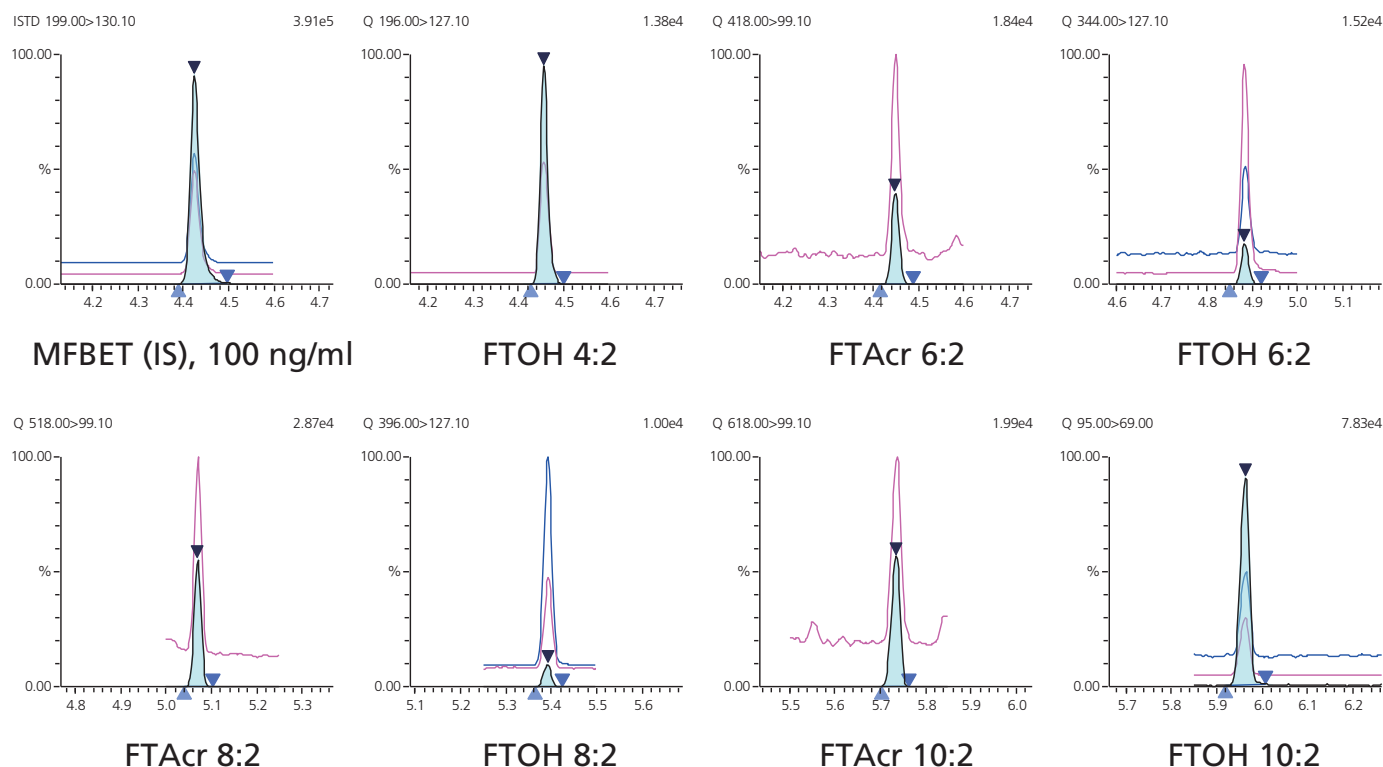


Figure 2: Mass Chromatograms of 5 ng/ml Calibration Standard

## Instrument Detection Limit and Method Precision

The Instrument detection limit (IDL) of each compound was determined by injecting 0.5 ng/ml standard mixture. IDLs were estimated to be between 0.1 – 0.5 ng/ml, whereby the S/N ratio is  $\geq 3$ . However, due to the poor peak shape of FTOH 4:2 at low concentration, its IDL was estimated to be 2 ng/ml.

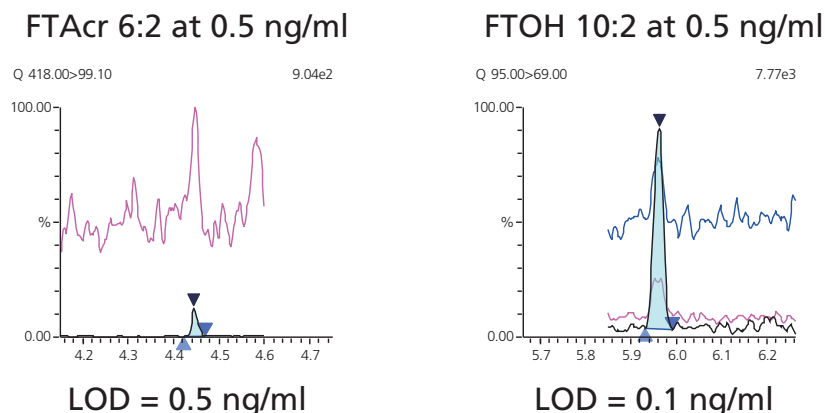


Figure 3: FTAc 6:2 and FTOH 10:2 at 0.5 ng/ml for Calculation of IDLs

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Method precision was evaluated by calculating the repeatability at the low and mid-calibration levels by injecting seven replicates of standard mixtures at 1 ng/ml (except FTOH 4:2, 5 ng/ml) and 20 ng/ml, as displayed in Table 2. All RSD were below 10%.

Table 2. Repeatability of Area Ratio (n=7) at Low and Mid-Calibration Levels

Compound name	Repeatability of Area Ratio (n=7)	
	% RSD of low calibration level (1 ng/ml)*	% RSD of mid calibration level (20 ng/ml)
FTOH 4:2	4.7	3.2
FTAc 6:2	5.5	2.4
FTOH 6:2	6.1	0.8
FTAc 8:2	3.2	0.5
FTOH 8:2	8.0	2.7
FTAc 10:2	5.6	1.6
FTOH 10:2	3.4	1.4

\*Except FTOH 4:2, which was 5 ng/ml spike

## Matrix Effect

Matrix effect (ME %) of the MRM method was calculated by comparing the peak area ratios of post-spiked standards in the sample extracts to those in the diluent. The results are shown in Table 3. This was performed in three

replicates. Most of the matrix effects calculated are more than 100 %, and especially greater for low concentration spikes. Hence, a matrix-match calibration method for more accurate quantification needs to be considered.

Table 3. Matrix Effect (ME %) from Different Textile Samples (n=3)

Compound name	Blue Cloth Matrix Effect (ME %)		Black Cloth Matrix Effect (ME %)		Red Cloth Matrix Effect (ME %)	
	Post -spiked with 1 ng/ml*	Post-spiked with 20 ng/ml	Post -spiked with 1 ng/ml*	Post-spiked with 20 ng/ml	Post -spiked with 1 ng/ml*	Post-spiked with 20 ng/ml
FTOH 4:2	121	98	124	119	142	125
FTAc 6:2	180	107	162	171	207	171
FTOH 6:2	390	113	286	152	182	156
FTAc 8:2	172	118	204	195	189	192
FTOH 8:2	388	124	428	177	373	179
FTAc 10:2	187	130	201	221	203	218
FTOH 10:2	195	118	199	174	204	182

\*Except FTOH 4:2, which was 5 ng/ml spike

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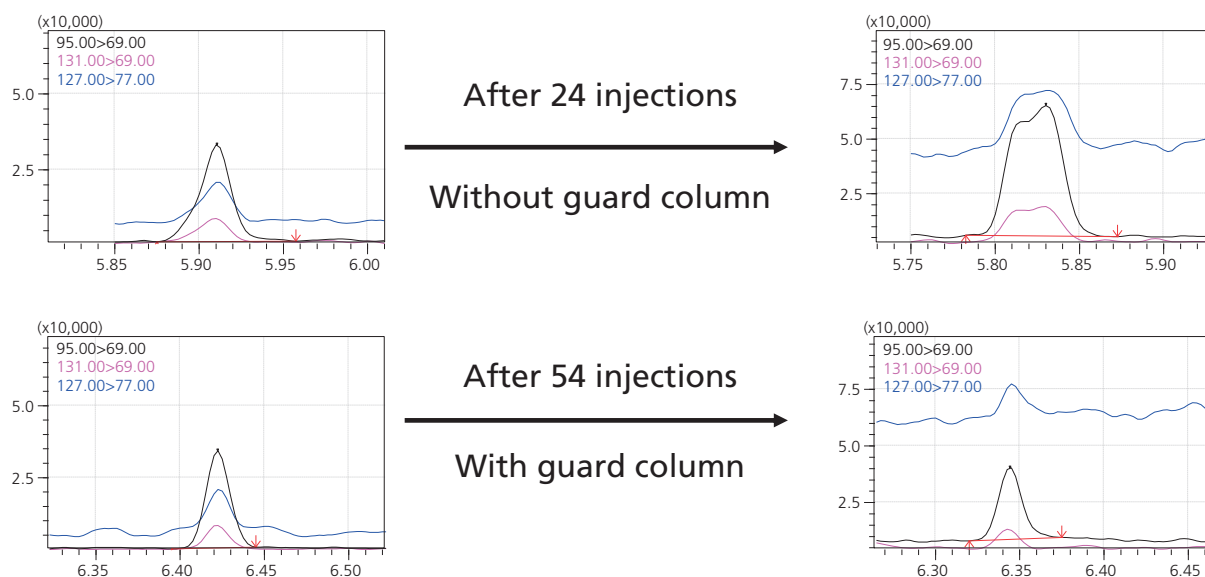


Figure 4: FTOH 10:2 in Spiked Textile Samples (1 ng/ml)

After injecting the sample extracts, retention times of the analytes gradually shifted and the peak shapes of FTAc 10:2 and FTOH 10:2 deteriorated. This phenomena did not occur with the calibration standards (prepared in diluent), before the sample extracts were analysed. As such, the sample matrix might be the cause of column deterioration.

It was observed that the use of a 5 m guard column in front of the analytical column helped to prevent the peak shape deterioration, as displayed in Figure 4. Better sample extraction method should be explored to extend the column lifetime.

## Conclusion

Analysis of FTOHs and FTAs was developed using triple quadrupole GC-MS/MS within 7 minutes. Excellent calibration curve linearity and repeatability were obtained from this experiment. The sample extracts in general gave high matrix effect (ME %) and deterioration to the column,

therefore the use of guard column is recommended. Future study might include quantification by matrix-match calibration and improvement of sample extraction method to reduce column deterioration.

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