# Negative electrospray ionisation of fluorotelomer alcohols (FTOH) and FTOH-derived acrylate surfactants by liquid chromatography coupled to accurate (tandem) mass spectrometry

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*Publication date:*
2013

*Document Version*
Publisher's PDF, also known as Version of record

DTU Food
National Food Institute

# Negative electrospray ionisation of fluorotelomer alcohols (FTOH) and FTOH-derived acrylate surfactants by liquid chromatography coupled to accurate (tandem) mass spectrometry

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## Abstract:

**Fluorotelomer alcohols (FTOHs) are used to synthesize fluorinated surfactants, which form bioaccumulative perfluorinated degradation products, which are toxic to humans and the environment. To facilitate screening for FTOH-derived surfactants by LC-ESI$^-$-MS, we identified product ions of FTOHs, and propose FTOH fragmentation pathways on two MS instruments. By extraction of FTOH basepeak ions from accurate mass spectra, homologues series of peaks showed up in an industrial blend of FTOH-derived fluoroacrylates used in food paper packaging.**

## Background

Fluorotelomer alcohols are used to produce fluorinated surfactants rendering surfaces of e.g. textiles or food paper packaging repellent towards oil and water. They and their perfluorinated degradation products have however adverse health effects, such as cancer, endocrine disruption and immunotoxicity *in-vitro* and humans. It is therefore of interest to develop methods that can screen for FTOH-derived substances in materials and matrices.

## Aims

1. To elucidate the fragmentation paths of FTOHs by LC-ESI$^-$ MS, based on determination of the elemental composition of product ions and fragments
2. To identify significant FTOH product ions useful for screening of FTOH derived substances.

## Results

Two major ionisation series from $[M-H]^-$ and $[M-H+CO_2]^-$ were observed in MS spectra (Fig. 2) and MSMS spectra (Fig. 3) of 4:2, 10:2, ($^{13}$C)-6:2 and ($^{13}$C)-8:2 FTOHs. FTOHs were separated on a $C_{18}$ UHPLC column with methanol /water as eluent and $NH_3$ as additive (Fig. 3A). Elemental compositions of product ions and neutral losses were assigned considering their accurate mass, DBE and loss of $^{13}$C isotopes, with a mass accuracy of 1-10 ppm. The proposed fragmentation paths (Fig. 1) show neutral losses of HF, CO, $CH_2O$ and $F_2$. Base peak ions were typically

- $[M-H-3HF]^-$ e.g. *m/z* 403 product ion
- $[M-H-4HF-CO]^-$ e.g. *m/z* 355 product ion
- $[M-H-CH_2O]^-$ e.g. *m/z* 333 product ion
- $[M-H+CO_2]^-$ e.g. *m/z* 507 adduct ion

depending on the instrument and the fluorocarbon chain length (Fig. 2). Other minor series were observed including the $[F(CF_2)_x]^-$, typical for perfluorinated acids. Extracted ion chromatograms (EIC) of the *m/z* ion series x03 and x55 from an industrial blend of fluoroacrylates (Zonyl TM) showed homologues series of fluoroacrylates also forming FTOH ions (Fig. 3B)

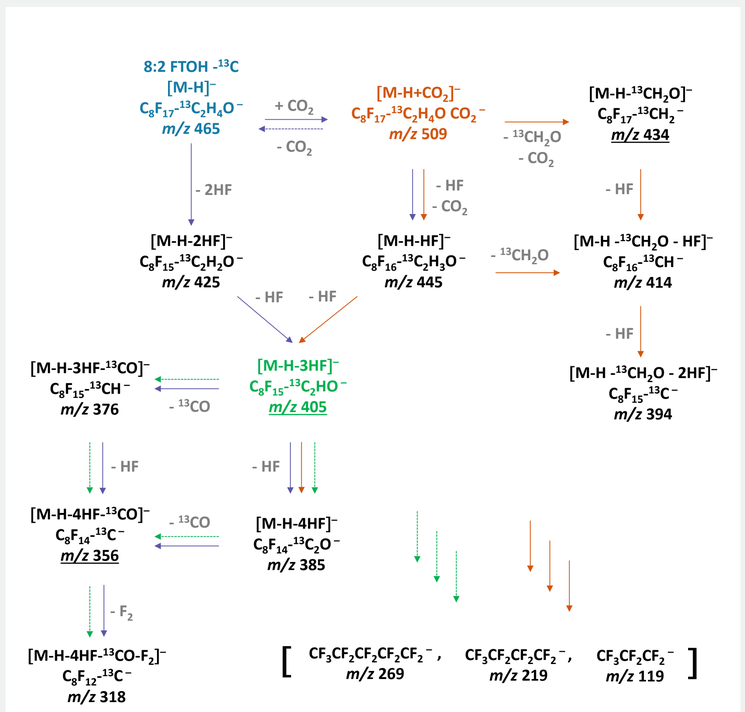


**Figure 1.** Suggested fragmentation path for fluorotelomer alcohols FTOH, shown for $^{13}$C- 8:2 FTOH. MSMS spectra were recorded for *m/z* 509 (marked in orange), *m/z* 465 (marked in blue) and *m/z* 405(marked in green). Base peaks are underlined, but vary with the FTOH chain length and the type of instrument.

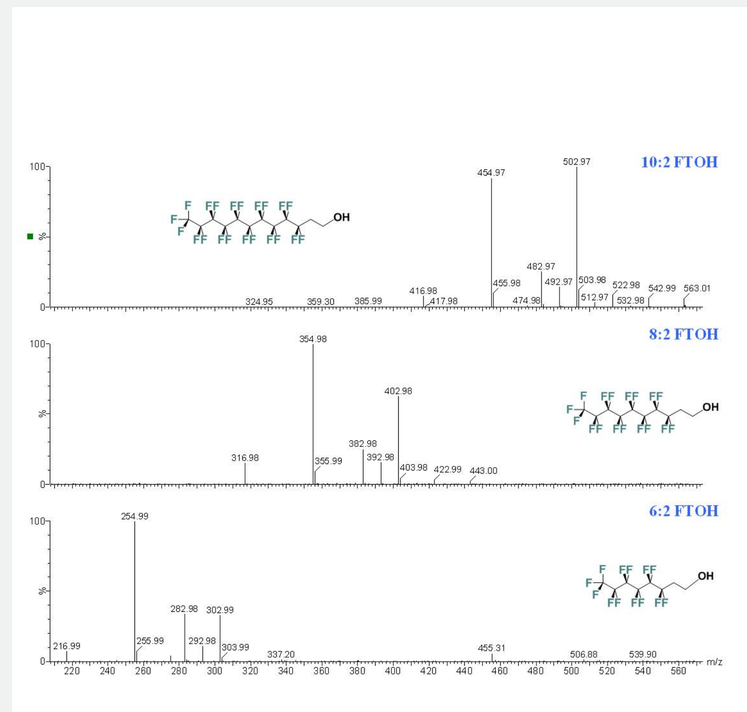


**Figure 2.** As the fluorocarbon chain length increases, the intensities increase of product ions with higher *m/z*. As a consequence the base peak shifts from $[M-H-4HF-CO]^-$ (e.g. *m/z* 255) to $[M-H-3HF]^-$ (e.g. *m/z* 503).

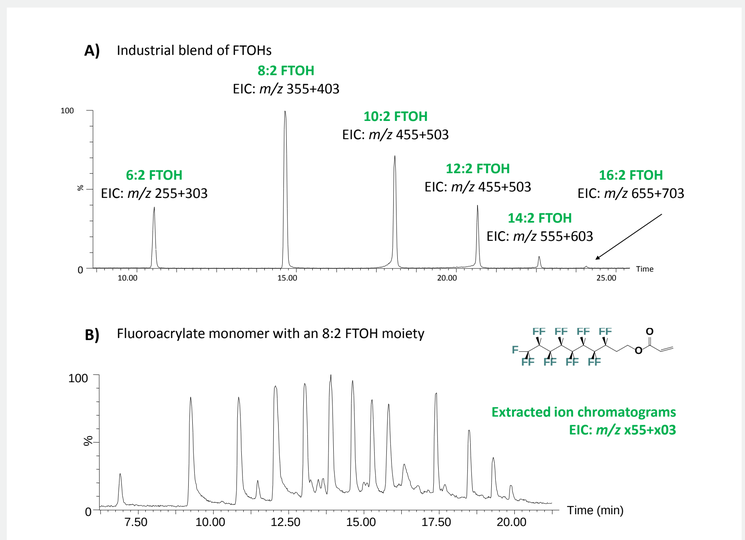


Figure 3. Extracted ion chromatograms of FTOH basepeak ion series (*m/z* x03, x55) showing homologues series in industrial blends of A) FTOHs in Zonyl BA-L and B) FTOH-derived fluoroacrylates in Zonyl TM.

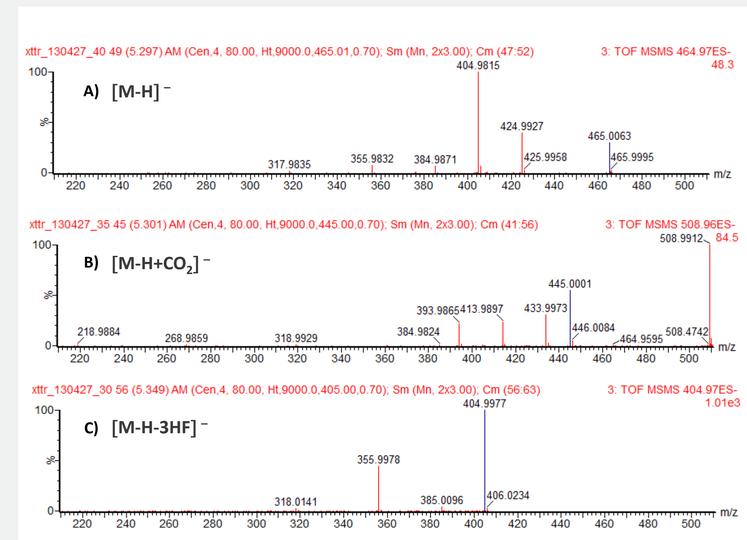


Figure 4. MSMS spectra are shown for $^{13}$C- 8:2 FTOH. of A) *m/z* 465 $[M-H]^-$, B: *m/z* 509 $[M-H+CO_2]^-$, C: *m/z* 405 $[M-H-3HF]^-$. Lock mass corrections using theoretical *m/z*'s has been done for peaks marked in blue.

## Instruments and methods

| | |
|---|---|
| MS 1: | Micromass QTOF Global, in ESI$^-$ mode (- 3 kV), V-mode, Resolution 9000<br>Calibration w NaF (*m/z* 118-1472), $N_p$ = 0.7 |
| MS 2: | Bruker Maxis QTOF, in ESI$^-$ mode (- 4 kV) |
| UHPLC: | Waters Acquity |
| Column: | Waters Acquity $C_{18}$, 1.7 µm*2.1 mm*150 mm (pH 1-12) |
| Eluent: | A: 95% water/5% MeOH + 0.001% $NH_3$, B: MeOH + 0.01% $NH_3$ |
| Gradient: | 5 to 98% B, 35 min, 0.28 to 0.4 mL/min |
| Vinj: | 2,4,5,7.5 µL |
| Standards: | 0.1-1 µg/mL FTOH standards (Wellington) in methanol<br>2.5 µg/mL industrial blends (Sigma Aldrich) of<br>DuPont Zonyl BA-L (FTOHs) and Zonyl TM (fluoroacrylates) |

Further condition s are given in :
Trier X.et al. (2011) *Environmental Science and Pollution Research.*

## Discussion

The Micromass QTOF MS produced a major ion series of $[M-H]^-$ (*m/z* 463) and a minor series of $[M-H+CO_2]^-$ (*m/z* 507), while the Bruker Maxis QTOF MS only produced the $[M-H+CO_2]^-$series. Reductive electrochemical reactions taking place inside the charged steel capillary needle in Micromass instruments, could thus be involved in the formation of the $[M-H]^-$series. In contrast capillaries in Bruker (and Agilent) instruments are grounded (zero charge). The $[M-H+CO_2]^-$ ion series might be formed by gas phase abstraction of hydrogen from the OH group by ammonia, which has a high gas phase basicity, or $CO_2$ might under pressure react with the FTOH to form an acid. Mechanistically the formation of HF will require charge migration, possibly via a cyclic intermediate.

## Conclusion

FTOHs were shown to fragment by two pathways in ESI$^-$-MS, from $[M-H]^-$ and $[M-H+CO_2]^-$. Significant base peak product and adduct ions were identified, and depended on the type of instrument and the fluorocarbon chain length. Basepeak ions of *m/z* x03 and x55 were successfully used to extract ion chromatograms (EICs) showing homologue series peaks in the FTOH derived fluoroacrylate Zonyl TM.

In this way 'unknown' FTOH-derived substances can be detected in samples by making EICs of FTOH product ions, adducts by accurate MS, or by search for neutral HF losses in QqQ instruments.