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Publication date:
2013

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

Link back to DTU Orbit

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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+CO2]− were observed in MS spectra (Fig. 2) and MMS spectra (Fig. 3) of 4, 2, 1, 13C-6-2 and 13C-8-2 FTOHs. FTOHs were separated on a C18 UHPLC column with methanol /water as eluent and NH3 as additive (Fig. 3A). Elemental compositions of product ions and neutral losses were assigned considering their accurate mass, DBE and loss of 13C isotopes, with a mass accuracy of 1-10 ppm. The proposed fragmentation paths (Fig. 1) show neutral losses of HF, CO2, CH2O and F2. Base peak ions were typically
- [M-H][13C-8]- e.g. m/z 403 product ion
- [M-H][13C-8]- e.g. m/z 355 product ion
- [M-H][13C-8]- e.g. m/z 333 product ion
- [M-H][13C-8]- e.g. m/z 507 adduct ion
- [M-H][13C-8]- depending on the instrument and the fluorocarbon chain length (Fig. 2). Other minor series were observed including the [M+H][13C-8]-, typical for perfluorinated ion series x03 and x55 from an industrial blend of fluoroacrylates (Zonyl TM) showed homologues series of fluoroacrylates also forming FTOH ions (Fig. 3B)

Instruments and methods

Results
Two major ionisation series from [M-H]− and [M+H+CO2]− were observed in MS spectra (Fig. 2) and MMS spectra (Fig. 3) of 4, 2, 1, 13C-6-2 and 13C-8-2 FTOHs. FTOHs were separated on a C18 UHPLC column with methanol /water as eluent and NH3 as additive (Fig. 3A). Elemental compositions of product ions and neutral losses were assigned considering their accurate mass, DBE and loss of 13C isotopes, with a mass accuracy of 1-10 ppm. The proposed fragmentation paths (Fig. 1) show neutral losses of HF, CO2, CH2O and F2. Base peak ions were typically
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Discussion
The Micromass QTOF MS produced a major ion series of [M-H]− (m/z 463) and a minor series of [M+H+CO2]−(m/z 507), while the Bruker Maxis QTOF MS only produced the [M+H+CO2]−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+CO2]−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 CO2 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.

Conclusions
FTOHs were shown to fragment by two pathways in ESI− MS, from [M-H]− and [M+H+CO2]−. 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.