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Fluorotelomer alcohols, and related volatile and semivolatile PFAS compounds – occurrence, and pending regulations

Liquid chromatography, coupled with tandem mass spectrometry, in a technique commonly abbreviated to LCMSMS is typically the go to choice for analytical chemists when it comes to PFAS.

LCMSMS is an ideal way to measure PFOA, PFOS and many of the other per- and polyfluoroalkyl acids included in routine PFAS test suites. However, there are limits to what LCMSMS can achieve, and some types of PFAS, such as the fluorotelomer alcohols (FTOHs) are better investigated by other means.

Volatile PFAS

Fluorotelomer alcohols (FTOHs), fluorotelomer acrylates (FTACs), and fluorotelomer acetates (FTOAcs) are best measured by gas chromatography (GC). As for PFAAs, detection is still by tandem mass spectrometry, and between GCMSMS and LCMSMS it is possible to measure plethora organic compounds. What sets FTOHs, FTACs, and FTOAcs apart from routine PFAS compound types (e.g., PFCAs, PFSAs, FTSAs, and FASAs) is that they don't typically contain charged functionalities – i.e., the headgroups don't possess the same acidic/anionic characteristics of the more notorious PFAS family members.

Awareness of FTOH, FTACs, and FTOAcs is not new, but it has only been in recent times that commercial laboratories have begun to offer services for them. In the diagram below, summarising the aerobic biotransformation of 8:2 FTOH, the parent compound degrades through a series of steps to terminal products including the recalcitrant perfluorocarboxylic acids (PFCAs).

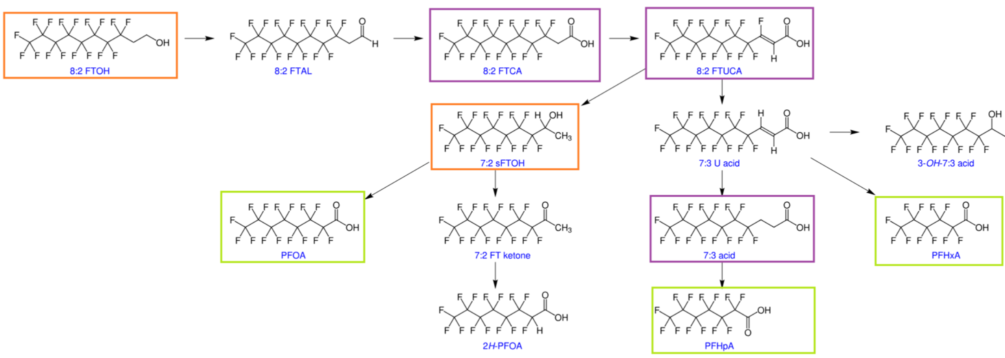

Figure 1: Aerobic biotransformation of 8:2 FTOH in soil – compounds in green boxes are included in ALS's 30 analyte PFAS suite, compounds in purple boxes are included in ALS's extended 54 analyte suites, while compounds in orange boxes are included in the new FTOH service offering. [1]

[1] https://commons.wikimedia.org/wiki/File:Aerobic_biotransformation_8-2_FTOH_soil_labeled.svg.

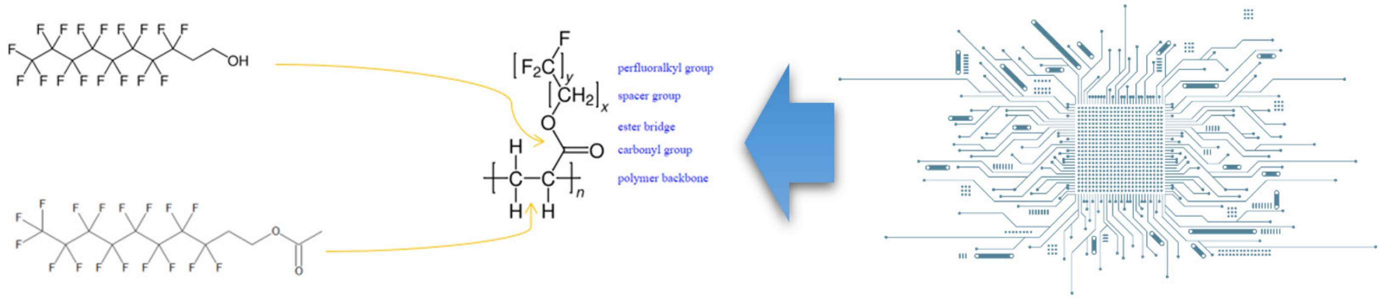

Figure 2: SCFPs have been used in resins for semiconductors. A schematic structure of an SCFP and two potential pathways that may liberate 8:2 FTOH and 8:2 FTOAc are displayed here.

Uses and origins

Fluorotelomer alcohols (FTOHs) are polyfluoroalkyl substances and were used heavily in syntheses of surfactants, and as intermediates in the manufacture of diverse products including textiles, polymers, paints, adhesives, waxes, and cleaning agents. They act as surfactants, lubricants and intermediates in manufacturing processes and can be emitted into the atmosphere during production of fluoropolymers.

FTOHs are also a constituent in aqueous film-forming foams (AFFF) and byproducts in fluorotelomer-based AFFFs – 8:2 FTOH concentrations in AFFF were found to range from 8 to 26.5 mg/L (Favreau, 2017). Detection of FTOHs at AFFF-impacted sites is thus likely to increase as analytical methods improve and become more widely available and utilised.

Sidechain fluorinated polymers (SCFPs) comprise another, lesser-known group of PFAS and are characterised by inclusion of fluorinated side chains on larger polymer backbones. The presence of fluorinated side chains helps instil the types of properties to materials for which PFAS have been highly effective, for instance in high temperature resistant, waterproofing and surface coatings formulations.

Fate and transport

Due to the volatility of FTOHs, they can undergo long-range environmental transport. Landfill leachate (Titaley et al., 2023) and wastewater treatment works are potential sources of FTOHs (Wang et al., 2020). FTOHs have been found ubiquitous in water (Ayala-Cabrera et al., 2020; Dimzon et al., 2017), while other studies have shown that FTOHs can breakdown into persistent, bioaccumulative PFCAs by various biotransformation mechanisms (Dinglasan et al., 2004; Ellis et al., 2004; Wang et al., 2009; Yu et al., 2018; Zhao et al., 2013). As such, FTOHs are an indirect source of PFCAs in the environment. In soils, FTOHs have been found to persist for long periods under reducing (redox) conditions. In reducing environments, they may persist for many years (Henderson et al., 2024).

Regulatory interest

European regulations are currently pending for 6:2 and 8:2 FTOH which propose their inclusion within a regulated sum of twenty-four per- and polyfluorinated alkyl substances (PFAS) of primary concern.[2] Additionally, the US EPA recently issued a test order for 6:2 fluorotelomer acrylate noting that "even small amounts can significantly contribute to people's long-term exposure and health risk for cancers, impacts to the liver and heart, and immune and developmental damage to infants and children."[3] Understanding FTOH, FTAC, and FTOAc contamination levels is also important because their degradation products – such as those included in the Stockholm Convention's list of Persistent Organic Pollutants (POPs) – are regulated widely.

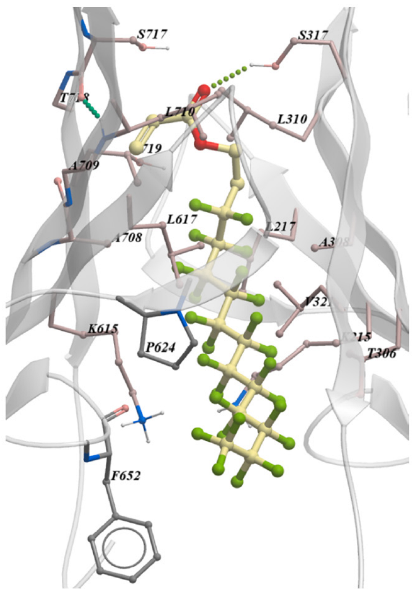

Figure 3: A gull docking model of 8:2 Fluorotelomer acrylate in the binding pocket of transthyretin (a transport protein that transports thyroid hormone and retinol in biochemical processes)[4]

[2] Proposal for a DIRECTIVE OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL amending Directive 2000/60/EC establishing a framework for Community action in the field of water policy, Directive 2006/118/EC on the protection of groundwater against pollution and deterioration and Directive 2008/105/EC on environmental quality standards in the field of water policy, European Commission, Brussels, Oct 2022.

[3] EPA Issues Test Order for PFAS Used in Manufacturing Under National Testing Strategy | US EPA

[4] Homology modeling to screen for potential binding of contaminants to thyroid hormone receptor and transthyretin in glaucous gull (Larus hyperboreus) and herring gull (Larus argentatus), (Mortensen et al.).

Testing options for FTOHs, FTACs and FTOAcs

The new service offering includes the ten compounds listed below, and consequentially, combinations of test suites can enable efficient accounting of many of the precursors, intermediates and terminal products that might be involved in PFAS degradation pathways (refer to figure 1).

Table 1: ALS Australia now offers the below analyte suite in water and soil samples to the listed LORs.

VOLATILE PFAS IN WATER AND SOIL			
Analyte	**water LOR (µg/L)**	**soil LOR (µg/kg)**	**CAS#**
FBET (4:2 FTOH)	1	20	2043-47-2
FHET (6:2 FTOH)	1	20	647-42-7
FOET (8:2 FTOH)	1	20	678-39-7
FDET (10:2 FTOH)	1	20	865-86-1
5:2 sFTOH (5:2 secondary fluorotelomer alcohol)	1	20	914637-05-1
7:2 sFTOH (7:2 secondary fluorotelomer alcohol)	1	20	24015-83-6
8:2 FTAC	1	20*	27905-45-9
10:2 FTAC	1	20*	17741-60-5
8:2 FTOAc	1	20*	37858-04-1
10:2 FTOAc	1	20*	37858-05-2

*Short holding times apply for these analytes in soil matrices

Sampling and analysis requirements

The lists of compounds above have holding times of 14 days from collection, except for soil testing of FTACs and FTOAcs which have been observed to degrade rapidly (24-48 hours) under certain conditions. Water samples are collected in pink/grey labelled polypropylene test tubes, pre-charged with 2 mL of a preservative solution containing methanol and sodium thiosulfate, while soil samples are collected in standard Teflon free, HDPE sampling containers used for routine PFAS sampling. To request analysis for these compounds, ALS method code EP133 should be included on analysis requisition documentation.

Get in touch with us

We would love to hear about how our services for this emerging class of PFAS might assist with your project needs, and we welcome feedback on how we might improve or expand our services to meet your needs. Don't hesitate to get in contact with your nearest ALS laboratory to discuss your PFAS testing requirements.

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