

Discovery of Telomerized Fluorinated Sulfonates in a Groundwater System

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Overview

Purpose:

To develop a quantitative LC MS/MS method for the detection of both electrochemically fluorinated and fluorotelomerized surfactants.

Method:

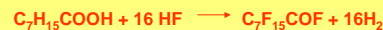
1. No sample clean-up or pre-concentration necessary.
2. Analysis by LC ESI MS/MS
3. Quantitation based on calibration curves constructed from standards.

Results:

First known detection of telomerized fluorinated sulfonates in the environment.

Fluorinated surfactants synthesized by one of two ways:

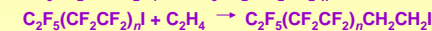
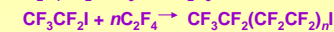
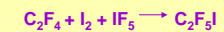
Electrochemical Fluorination (ECF)¹ (3M)



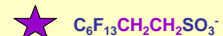
* Converted to amides or other intermediates required for the production of repellents



Fluorotelomers¹ (DuPont)



* Perfluoroalkylethyl iodides are usually derivatized to fluorotelomer alcohols or sulfonates



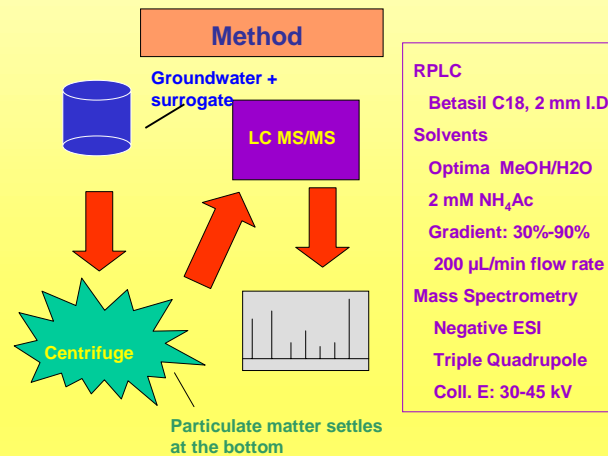
ECF:
 odd & even numbered carbons;
 branching present;
 all carbons fluorinated

Telomers:
 only even numbered carbons;
 no branching;
 C₂H₄ spacer present

AFFF should not contain telomers, 3M product

ECF sulfonates & carboxylates not found to biodegrade & are persistent in the environment²

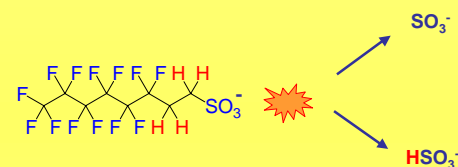
Telomers are found to biodegrade due to the H at the alpha carbon to the functional group²



Introduction

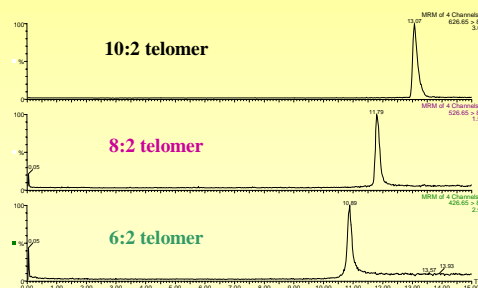
Results

Tandem Mass Spectrometry Fragmentation

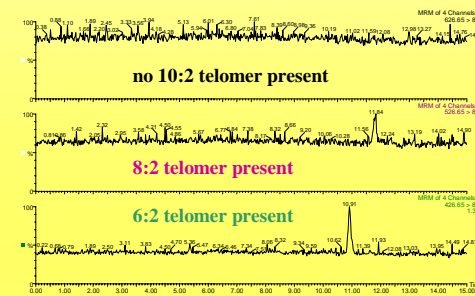


"6:2 telomeric sulfonate"
 6 fluorinated carbons
 2 non-fluorinated carbons

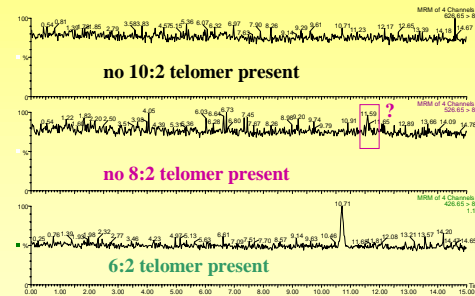
DuPont's Zonyl® TBS mixture



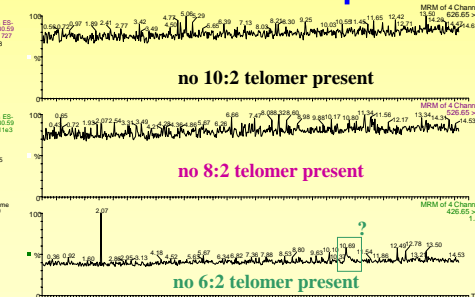
FT 1 (-46m)



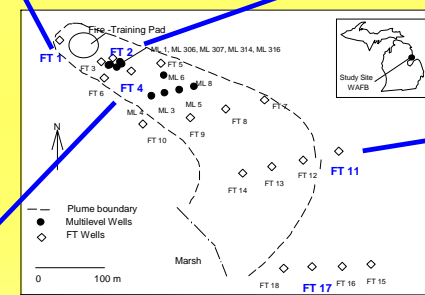
FT 4 (53m)



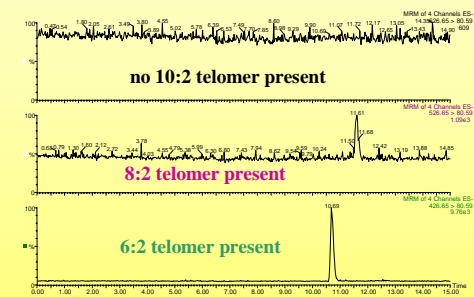
FT 17 (540m)



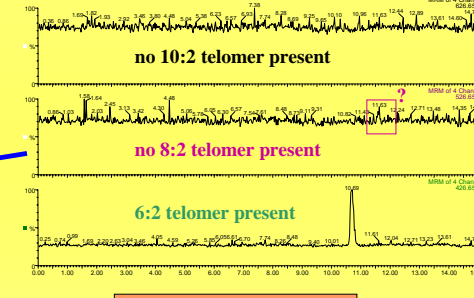
Wurtsmith Site Map



FT 2 (17m)



FT 11 (305m)



Conclusions

- Telomeric sulfonates exist in WAFB groundwater
- Telomeric sulfonates and ECF surfactants in WAFB groundwater can be quantitated
- Outside sources are a significant source of interference in quantitation
- RSD's = 3-15% (requiring no sample clean-up)
- Detection limits on order of 0.1 pg on column

References
 1. Banks, R.E.; Smart, B.E.; Tatlow, J.C. *Organofluorine Chemistry*; Plenum Press: New York, 1994.
 2. 3M Report to EPA: *Sulfonated Perfluorochemicals in the Environment: Sources, Dispersion, Fate & Effects*, March 1, 2000

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