

Biotransformation of the ^{14}C -labeled Fluorotelomer 8-2 Telomer B Alcohol†

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8-2 Telomer B Alcohol: $\text{C}_8\text{F}_{17}\text{CH}_2\text{CH}_2\text{OH}$ (8-2 TBA; CAS# 678-39-7)

Background Information

A key raw material used in the manufacture of sales products.
May be a transformation product of fluorotelomer based sales products.

Key Questions

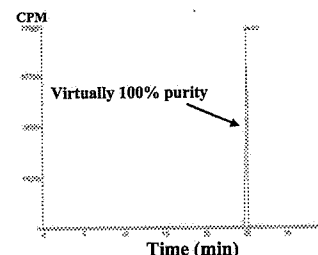
Is it biotransformable? Under what conditions?
What are the major transformation products?
What are the likely biotransformation pathways?

Physical Properties and Purity of the Test Substance

"A Difficult to Test Substance"

- Low solubility
• ~ 150 $\mu\text{g L}^{-1}$
- Vapor pressure
• 3 Pa at 21 °C
- Adsorption to surfaces

A Chromatogram of HPLC Characterization of Radiochemical Purity of the Test Substance



EXPERIMENTAL METHODS

Modified OECD 301D Closed Bottle Test.

Experimental System: Closed bottles (30 mL of test substance solution in 120-mL glass serum bottles crimp-sealed with PTFE septa).

Concentration of the test substance: 337 $\mu\text{g L}^{-1}$ dispersed in mineral medium.

Additional organic carbon source: 13 mg L^{-1} of ethanol (as co solvent).

Inoculum: Fresh sludge from Municipal POTW (Non-acclimated, 5 mL sludge L^{-1} test solution, ~ 10^4 cells).

Experimental Duration: 28 days at room temperature.

EXPERIMENTAL METHODS (Continued)

Analytical methods:

Sample extraction: Acetonitrile for ^{14}C -labeled parent and transformation products; alkaline lysis for fluoride ion.

Parent ($\text{F}(\text{CF}_2)_8\text{CH}_2\text{CH}_2\text{OH}$) was quantified by GC/MS and fluoride ion by ion selective electrode.

LC/ARC (On-line liquid chromatography/accurate radioisotope counting) was used for separation and quantification of ^{14}C -labeled parent and transformation products.

Identification of the transformation products was conducted by Q-TOF-MS method.

Spike recovery of ^{14}C -labeled parent and cold standard fluorinated acids from the sample matrices was analyzed by liquid scintillation counting and LC/MS/MS, respectively.

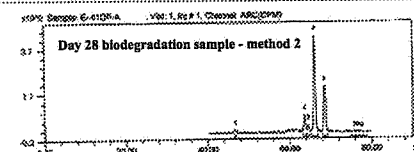
RESULTS

Spike recovery of $\text{F}(\text{CF}_2)_7^{14}\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$ and other standard fluorinated acids from the sample matrices

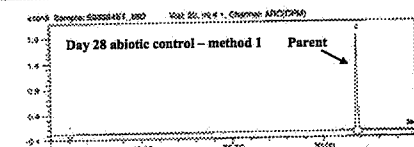
Substance spiked (dosed)	% Recovery*
$\text{F}(\text{CF}_2)_7^{14}\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$	92 ± 7
$\text{F}(\text{CF}_2)_7\text{CF}_2\text{CH}_2\text{COO}^-$	100 ± 20
$\text{F}(\text{CF}_2)_7\text{CF}=\text{CHCOO}^-$	81 ± 21
$\text{F}(\text{CF}_2)_7\text{COO}^-$	104 ± 14
$\text{F}(\text{CF}_2)_5\text{COO}^-$	120 ± 11

*: Average value for days 0, 7, 14 and 28.

LC/ARC Analysis of ^{14}C -labeled Transformation Products



Peaks 1, 2, 3, & 4 are observed transformation products and peak 5 is the parent.



(Abiotic control - 5 mL autoclaved sludge L^{-1} test solution + 0.5 mM NaCN)

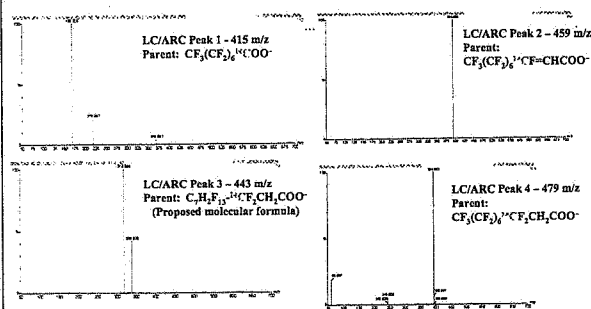
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Identification of Transformation Products



Daughter ion spectra of ions obtained for a day-28 sample by Q-TOF-MS

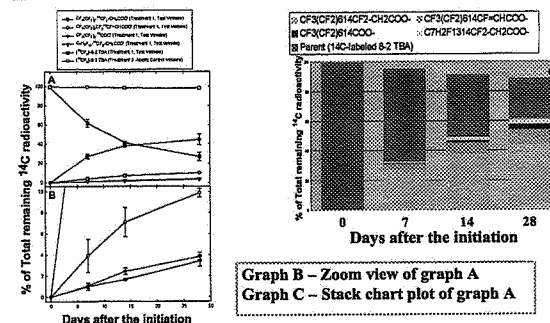
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Accurate Mass Measurement for Observed Transformation Products

Determined mass	^{14}C -labeled transformation products	Elemental composition	Calculated mass	Error in ppm
478.9803	$\text{CF}_3(\text{CF}_2)_6^{14}\text{CF}_2\text{CH}_2\text{COO}^-$	$12\text{C } 9 \ 14\text{C } \text{H}_2 \ \text{O}_2 \ \text{F}_{17}$	478.9816	-2.6
458.9764	$\text{CF}_3(\text{CF}_2)_6^{14}\text{CF}=\text{CHCOO}^-$	$12\text{C } 9 \ 14\text{C } \text{H} \ \text{O}_2 \ \text{F}_{16}$	458.9753	+2.3
414.9771	$\text{CF}_3(\text{CF}_2)_6^{14}\text{COO}^-$	$12\text{C } 7 \ 14\text{C } \text{O}_2 \ \text{F}_{15}$	414.9691	+19.3
443.0037	$\text{C}_7\text{H}_2\text{F}_{13}^{14}\text{CF}_2\text{CH}_2\text{COO}^-$	$12\text{C } 9 \ 14\text{C } \text{H}_4 \ \text{O}_2 \ \text{F}_{15}$	443.0004	-7.4

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Time Course of ^{14}C -labeled Transformation Product Formation



Graph B - Zoom view of graph A
Graph C - Stack chart plot of graph A

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Mass Balance of Transformation Products at Day 28

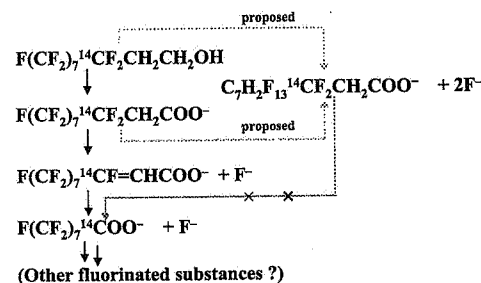
Transformation Products	% Total
Peak 1 - $\text{F}(\text{CF}_2)_7^{14}\text{COO}^-$	2.0
2 - $\text{F}(\text{CF}_2)_7^{14}\text{CF}=\text{CHCOO}^-$	5.9
3 - $\text{C}_7\text{H}_2\text{F}_{13}^{14}\text{CF}_2\text{CH}_2\text{COO}^-$	2.3
4 - $\text{F}(\text{CF}_2)_7^{14}\text{CF}_2\text{CH}_2\text{COO}^-$	26.6
5 - $\text{F}(\text{CF}_2)_7^{14}\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$ (parent)	16.1
$\text{F}(\text{CF}_2)_7^{14}\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$ (parent) adsorbed by the test vessel surface§	~ 40
Sum	93*

§: Estimated.

*: Other unidentified minor transformation products together accounted for < 10% of mass balance, with each of them accounted for < 1% of mass balance.

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Potential Biotransformation Routes (Not include the unidentified minor transformation products)



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CONCLUSIONS

- Four biotransformation products ($\text{F}(\text{CF}_2)_7^{14}\text{CF}_2\text{CH}_2\text{COO}^-$, $\text{F}(\text{CF}_2)_7^{14}\text{CF}=\text{CHCOO}^-$, $\text{C}_7\text{H}_2\text{F}_{13}^{14}\text{CF}_2\text{CH}_2\text{COO}^-$, and $\text{F}(\text{CF}_2)_7^{14}\text{COO}^-$) were formed over the 28 days; the concentration of the transformation products did not reach steady-state. It cannot be concluded from this study whether these are the ultimate products of biotransformation.
- The observed transformation product $\text{C}_7\text{H}_2\text{F}_{13}^{14}\text{CF}_2\text{CH}_2\text{COO}^-$ accounted for 3.8% of remaining ^{14}C radioactivity in the test solution at day 28. The formation and increase of this product over 28 days indicated that biotransformation pathways for $\text{F}(\text{CF}_2)_7^{14}\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$ most likely diverged at the point of the parent (itself) or $\text{F}(\text{CF}_2)_7^{14}\text{CF}_2\text{CH}_2\text{COO}^-$, with one transformation path proceeding through $\text{F}(\text{CF}_2)_7^{14}\text{COO}^-$ (PFOA) and an alternative path proceeding through $\text{C}_7\text{H}_2\text{F}_{13}^{14}\text{CF}_2\text{CH}_2\text{COO}^-$. PFOA formation will not occur through the alternative path.
- Although PFOA is one of the identifiable metabolites, it accounted for approx. 2% of mass balance at day 28.
- Biotransformation of $\text{F}(\text{CF}_2)_7^{14}\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$ may be facilitated by the presence of ethanol (13 mg L^{-1}) as a co-solvent.

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