A Highly Sensitive and Specific GC-PCI-MS/MS Method for the Analysis of Fluorinated Alkyl Compounds

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Introduction

Increasing numbers of researchers have shown that fluorotelomer alcohols can degrade to fluorinated carboxylic acids under certain environmental conditions. Fluorotelomer alcohols are manufactured and used as building blocks for fluorinated polymers and may potentially be intermediate degradation products from those polymers. Robust analytical methodology is required to study the fate and transport of fluorotelomers in the environment, investigate degradability of fluoropolymers, and gain understanding of human exposure and toxicity. Herein, we present a GC-PCI-MS/MS method for trace level analysis of fluorinated alkyl compounds in complex matrices such as biosolids. The method employs cold, splitless injection and capillary flow technology to enable backflush of matrix and unwanted interferences and maintain retention time precision.

Background

Fluorinated alkyl compounds (PFCs) studied for fate, transport, potential human exposure and toxicities

Fluorotelomer alcohols (FTOHs) degrade to PFCs both atmospherically and biologically

Some of the PFCs have been found to be toxic and widespread throughout the world

The source of the PFCs remains yet unknown
- Speculated
  - Wastewater treatment plants
  - Direct emission from manufacturers
  - Degradation of precursor materials

Purpose of Study

Develop robust, sensitive and selective GC-MS/MS method in bio-solid matrix from waste water treatment plants

Study the fate and transport of fluorotelomers in the environment

Investigate degradation pathways of fluoropolymers

Gain understanding of human exposure and toxicity

Evaluate gas chromatography-quadrupole time of flight mass spectrometry (GC Q-TOF MS)

Experimental

GC-PCI-MS/MS Conditions

GC Run Conditions	
Column 1	HP-INNOWax (Agilent Santa Clara, CA)
Column 2	0.7 m x 0.15 mm fused silica
Injection mode	pulsed, cold splitless
Inlet temperature program	65 °C (0.01 min), 300 °C/min to 250 °C
Cryo	Compressed air
Injection volume	2 microliters
Carrier gas	Helium, constant flow mode, 1.0 ml/min
Oven program	45 °C (0 min hold), 60 °C/min to 60 °C (1 min), 3 °C/min to 75 °C (0 min), 20 °C/min to 210 °C (0 min)
Transfer line temperature	210 °C
GC Post-Run Conditions	
Backflush device	Purged Ultimate Union (Agilent Santa Clara, CA) controlled by electronic pressure control module at 1 psi, constant presssure
Backflush conditions	Column 1: -10.866 ml/min; Column 2: 60 psi, 4 minutes
MS conditions	
Tune	Autotune
Gain factor	100
Acquisition parameters	Positive Chemical Ionization, multiple reaction monitoring
Collision gas	Nitrogen, 1.5 ml/min; Helium quench gas 2.25 ml/min
Solvent delay	3.2 minutes
MS temperatures	Source 250 °C, Quadrupoles 150 °C

MRM Table

Compounds	Quantifying MRM	CE (V)	Qualifying MRM	CE (V)
10:1 FTOH	551 -> 49	40	527 -> 481	27
10:2 FTOH	565 -> 527	10	551 -> 531	3
11:1 FTOH	601 -> 581	3	601 -> 49	40
4:2 FTOH	265 -> 227	5	227 -> 181	15
5:1 FTOH	301 -> 281	3	301 -> 49	40
6:1 FTOH	351 -> 331	3	351 -> 49	40
6:2 FTOH	365 -> 327	5	327 -> 281	17
7:1 FTOH	401 -> 381	3	401 -> 49	40
7:2 FTOH	377 -> 77	10	377 -> 69	25
8:1 FTOH	451 -> 49	40	427 -> 381	23
8:2 FTOH	465 -> 427	5	451 -> 431	3
9:1 FTOH	501 -> 481	3	501 -> 49	40
EtFOSE	572 -> 554	5	554 -> 71	20
MeFOSE	540 -> 57	20	558 -> 540	5

Experimental

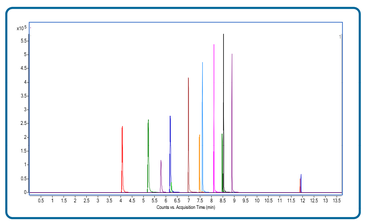
Standards and Samples

- Solvent standards, 100 ng/µl in MTBE
- Two bio-solid extracts prepared in EtOAc
- One 1% and the other 5% lime treated
- Each extract split 50/50
- One spiked with analytes and IS @ 50 ng/ml, the other not spiked

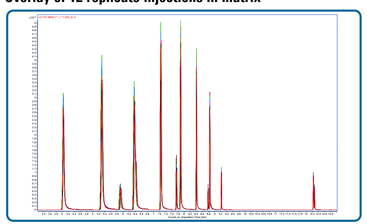
ID	Solvent	Vol (mL)	Description
1	Ethyl acetate	1	Extracted solvent, 1% lime treated biosolid
2	Ethyl acetate	1	Standards in extracted solvent
3	Ethyl acetate	1	Extracted solvent, 5% lime treated biosolid
4	Ethyl acetate	1	Standards in extracted solvent

Biosolid samples were extracted 3 times with methyl tert-butyl ether via 30-min sonication followed by 30-min shaking. All extracts were centrifuged for 10 min at 3000 rpm then combined. The extracts were then treated by solid phase extraction for further clean up. Prior to analysis, sample extracts were frozen at –80°C for 30 min to remove water.

MRMs



Overlay of 12 replicate injections in matrix



Results & Discussion

Area Precision at 50 pg on column

Sample	Injection	4:2 FTOH	5:1 FTOH	6:2 FTOH	6:1 FTOH	7:2 FTOH	7:1 FTOH
Data File	Number	Area	Area	Area	Area	Area	Area
1% lime treated - vial 1	1	770372	780203	191544	484227	202027	462117
1% lime treated - vial 1	2	791988	794505	196308	494719	201631	474574
1% lime treated - vial 1	3	797961	807048	195345	485956	201126	472518
1% lime treated - vial 2	1	815268	823303	203368	511424	214294	510761
1% lime treated - vial 2	2	819729	832375	206549	468437	212621	502528
1% lime treated - vial 2	3	838986	843641	208300	519692	214490	503993
		% RSD	2.99	2.95	3.38	3.82	3.24	4.18

Sample	8:2 FTOH	8:1 FTOH	9:1 FTOH	10:2 FTOH	10:1 FTOH	11:1 FTOH	MeFOSE	EtFOSE
Data File	Area	Area	Area	Area	Area	Area	Area	Area
1% lime treated - vial 1	194986	360154	233693	66002	172257	72622	52349	37306
1% lime treated - vial 1	198713	365775	240025	66967	176801	74053	51874	36519
1% lime treated - vial 1	201814	370929	245253	67636	178756	75262	52659	37042
1% lime treated - vial 2	208950	388089	263460	69781	188766	80666	55799	38753
1% lime treated - vial 2	206685	397540	263452	68031	189377	80261	55807	38946
1% lime treated - vial 2	208881	387945	264234	70021	189277	80669	55718	38665
	2.84	3.92	5.44	2.32	4.13	4.77	3.56	2.74

Sample	Injection	4:2 FTOH	5:1 FTOH	6:2 FTOH	6:1 FTOH	7:2 FTOH	7:1 FTOH
	Number	Area	Area	Area	Area	Area	Area
5% lime treated - vial 1	1	822104	835995	201828	521148	215060	515108
5% lime treated - vial 1	2	808261	822110	192428	502187	206797	495274
5% lime treated - vial 1	3	779078	781190	184528	477415	197952	480935
5% lime treated - vial 2	1	747749	767019	182643	474199	190738	465050
5% lime treated - vial 2	2	747430	725434	179494	463952	188150	455082
5% lime treated - vial 2	3	725129	712423	171405	427678	179695	430268
		% RSD	4.94	6.44	5.70	6.74	6.59	6.36

Sample	8:2 FTOH	8:1 FTOH	9:1 FTOH	10:2 FTOH	10:1 FTOH	11:1 FTOH	MeFOSE	EtFOSE
	Area	Area	Area	Area	Area	Area	Area	Area
5% lime treated - vial 1	181813	399943	263344	68021	193088	80541	54726	38407
5% lime treated - vial 1	176363	382338	253529	65531	186323	79300	52196	36218
5% lime treated - vial 1	174462	381721	244776	63520	180684	75925	50769	36051
5% lime treated - vial 2	171177	366063	236982	62233	171562	72234	51615	36603
5% lime treated - vial 2	166233	357142	231167	61478	169218	71473	50869	36111
5% lime treated - vial 2	159522	339585	216155	58584	160184	67267	48787	33616
		4.59	5.76	6.94	5.20	6.84	6.80	3.81	4.24

To assure sample integrity and mitigate potential thermal degradation, a pulsed, cold splitless injection was used. This allowed increasing the injection volume from one to two microliters and nearly doubling signal intensity with a minimal increase in baseline noise. MRM transitions were determined for the compounds through a series of full scan and product ion scan experiments. Collision energies were optimized to facilitate the maximum response for each transition. Significant peak shifting was observed in matrix spikes on the wax column during method development. To address this issue, post-column backflush was configured using a purged union at the outlet of the analytical column and a 0.7 m restrictor into the mass spectrometer. Without backflush, retention times wandered as much as 0.2 minutes from injection to injection. After installing the backflush components, retention time reproducibility ranged from 2.3% - 6.9% RSD in the matrix spikes. Detection limits, as determined by a S/N ratio of ≥ 10:1, ranged from 2 fg – 100 fg on column.

GC Q-TOF

GC Quadrupole Time of Flight MS (GC Q-TOF)

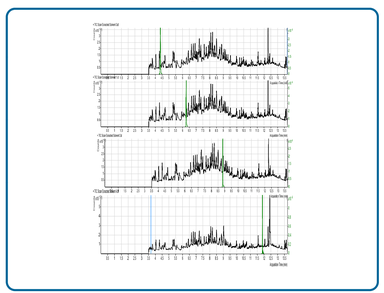
As a follow up study that presented herein, the authors investigated GC Q-TOF as an alternative analytical approach with the same samples. The following represents preliminary data from the GC-PCI Q-TOF methodology.

Uncorrected Mass Accuracy at 50 pg on column

Acronym	Formula	Exact Mass + H	Observed Mass	Δppm
4:2 FTOH	$C_6H_5F_9O$	265.0269	265.0270	-0.3773
6:2 FTOH	$C_8H_5F_{13}O$	365.0206	365.0206	0.0000
8:2 FTOH	$C_{10}H_5F_{17}O$	465.0142	465.0140	0.4301
10:2 FTOH	$C_{12}H_5F_{21}O$	565.0078	565.0078	0.0000
7:2 sFTOH	$C_9H_5F_{15}O$	415.0174	415.0190	-3.8553
5:1 FTOH	$C_6H_5F_{11}O$	301.0081	301.0079	0.6644
6:1 FTOH	C7 H3 F13 O	351.0049	351.0050	-0.2849
7:1 FTOH	C8 H3 F15 O	401.0017	401.0016	0.2494
8:1 FTOH	C9 H3 F17 O	450.9985	450.9985	0.0000
9:1 FTOH	C10 H3 F19 O	500.9953	500.9956	-0.5988
10:1 FTOH	C11 H3 F21 O	550.9921	550.9922	-0.1815
11:1 FTOH	C12 H3 F23 O	600.9889	600.9896	-1.1647
MeFOSE	C11 H8 F17 N O3 S	558.0026	558.0042	-2.8674
EtFOSE	$C_{12}H_{10}F_{17}NO_3S$	572.0183	572.0167	2.7971

Resolution (50 pg on column)

Extracted Ions vs. Matrix (50 pg on column)



Conclusions

There are few references in the literature pertaining to the analysis of fluorotelomer alcohols. One reference posits complications for GC-MS due to thermal degradation of analytes in the traditionally hot inlet. Herein is presented a sensitive and selective method for the analysis of 12 fluorotelomer alcohols and 2 perfluorinated sulfonamidoethanols using GC-PCI-MS/MS equipped with cold, splitless injection and column backflushing. This method is suitable for trace level analysis of volatile fluorochemicals in complex bio-solid matrices.

Follow up studies Illustrate GC Q-TOF MS as viable for the analysis of PFCs in bio-solid matrix with excellent uncorrected mass accuracy: typically < 2 ppm. Resolving power easily extracted all analytes and labeled IS from heavy bio-solid matrix at the 50 ng/ml calibrator level and below. Comparison to MRM data suggests high fg on column detection limits. Further studies are to be undertaken to determine and validate MDLs via GC Q-TOF.

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Mention of trade names or commercial products does not constitute endorsement or recommendation for use by USEPA.

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