Analyzing Compounds of Environmental Interest Using an LC/Q-TOF Part 2: Fluorotelomer Unsaturated Acids

Application

Environmental

Authors

Jim Lau, Chin-Kai Meng, and Jennifer Gushue
Agilent Technologies, Inc.
2850 Centerville Road
Wilmington, DE 19808
USA

Robert J. Letcher and Shaogang Chu
Wildlife and Landscape Science Directorate
Science and Technology Branch
Environment Canada
National Wildlife Research Centre
Carleton University
Ottawa, Ontario, K1A 0H3
Canada

Abstract

Perfluoroalkyl substances (PFASs) have been widely used in a variety of products due to their chemical inertness, resistance to heat, and ability to repel water and oils. PFASs exhibit a high propensity for persistence and bioaccumulation in wildlife, which is causing concern. Due to different manufacturing and degradation processes, different chain lengths and functional groups of PFAS exist in the environment. An LC/Q-TOF is best suited to screen, identify, and quantify many perfluoroalkyl compounds in different matrices.

This LC/Q-TOF application shows good mass accuracy (well below 3 ppm) and good resolution (> 13,500). Excellent quantification results for selected PFASs were obtained from extracts derived from blind liver samples.

Introduction

Environment Canada is tasked with risk assessment and the evaluation of impact of a variety of compounds in environmental matrices, including wildlife tissues, water, sediment, and air [1, 2]. A number of compounds classified as perfluoroalkyl substances (PFASs) have been widely used in a variety of products due to their chemical inertness, resistance to heat, and ability to repel water and oils. Some of the commercial PFAS products include lubricants, adhesives, stain and soil repellents, paper coatings, and fire-fighting foams. Due to their unique chemical and biological stability, some PFASs exhibit a high propensity for persistence and bioaccumulation in wildlife. In recent years, particular environmental concern has arisen as a number of PFASs have been reported in tissues of marine mammal, seabird, and fish species inhabiting various regions of the Arctic. More specifically, some PFASs, such as perfluorooctane sulfonate (PFOS) [$CF_3(CF_2)_7SO_3H$] and C8 to C15 chain length perfluorinated carboxylates (PFCAs), have been reported present at similar or higher concentrations than persistent organochlorines (OCs) in polar bears [3–5].

Many of the PFASs originate from the two manufacturing processes of electrochemical fluorination (perfluoroalkyl sulfonamido alcohols degrade to PFOS) and telomerization (fluorotelomer alcohols [FTOHs] are transformed to PFOA). The degradation pathway for telomers is:

From 8:2 fluorotelomer alcohol (8:2 FTOH) to:

- Major products: 8:2 fluorotelomer aldehyde (8:2 FTAL), 8:2 fluorotelomer carboxylate (8:2 FTCA), and perfluorooctanoic acid (PFOA) [$CF_3(CF_2)_6CO_2H$]
- Minor products: 8:2 fluorotelomer unsaturated carboxylate (8:2 FTUCA, $CF_3(CF_2)_6CF{=}COOH$) and perfluorononanoic acid (PFNA)

Then from 8:2 FTCA and 8:2 FTUCA (degradation products from above) to:

- Major product: PFOA
- Minor product: PFNA

This application uses fluorotelomer unsaturated carboxylates (FTUCAs – metabolites of telomer alcohols) to demonstrate the mass accuracy, resolution, and the quantification capability of the LC/Q-TOF.

Experimental

Samples

This study analyzed three standard solutions of the following three target compounds at 1, 100, and 250 ppb. Three internal standards (ISTDs) at 50 ppb each were also added to each of the three solutions. A fourth sample was a blind liver extract with an undisclosed concentration of the three target compounds.

Target Compounds:

F**H**UEA (C8, **6**:2 FTUCA)	2H-Perfluoro-2-octenoic acid $CF_3(CF_2)_4CF{=}CH{-}COOH$
F**O**UEA (C10, **8**:2 FTUCA)	2H-Perfluoro-2-decenoic acid $CF_3(CF_2)_6CF{=}CH{-}COOH$
F**D**UEA (C12, **10**:2 FTUCA)	2H-Perfluoro-2-dodecenoic acid $CF_3(CF_2)_8CF{=}CH{-}COOH$

ISTDs:

MFHUEA	2H-Perfluoro-[1,2-$^{13}C_2$]-2-octenoic acid $CF_3(CF_2)_4CF{=}C^{13}H{-}C^{13}OOH$
MFOUEA	2H-Perfluoro-[1,2-$^{13}C_2$]-2-decenoic acid $CF_3(CF_2)_6CF{=}C^{13}H{-}C^{13}OOH$
MFDUEA	2H-Perfluoro-[1,2-$^{13}C_2$]-2-dodecenoic acid $CF_3(CF_2)_8CF{=}C^{13}H{-}C^{13}OOH$

Instrument Parameters

All sample analyses were performed on an Agilent 1200 SL Rapid Resolution LC coupled to an Agilent 6520 Q-TOF.

All sample analyses were performed under LC/Q-TOF autotune conditions. Mass accuracy, sensitivity, and resolution for all samples were measured without any changes to 6520 Q-TOF instrument parameters, except ion source conditions appropriate for the spray chamber type, LC flow, and sample thermal stability.

Mobile A	3 mM NH_4OAc
Mobile B	MeOH
LC column	ZORBAX XDB 2.1 mm × 50 mm, C-18, 3.5-µm particle size
Flow rate	0.5 mL/min
Injection volume	10 µL
MS	Scanned at 2.5 scans/sec, 50 to 1,100 *m/z*
Negative ref. ions	*m/z* 113, 1034
Q-TOF parameters	Set by autotune
Drying gas	12 L/min N_2 at 300 °C
Nebulizer pressure	50 psi
ESI (–)	3 KV
Fragmentor	275 V

Results and Discussion

Table 1 shows the mass accuracy and resolution of the six compounds analyzed in this study. The accuracy for each compound was under 3 ppm and the resolution was > 13,500. Table 2 shows the quantitation ions and results. The quantitation ion was not the molecular ion but a fragment ion from the collision-induced dissociation (CID). The fragment ion is a lost fragment of "FCOOH" ($[M–H]^-$ – 64) from the deprotonated molecular ion. The calibration range was 1 to 250 ppb (that is, 10 pg to 2.5 ng on column). Good signal-to-noise ratios (un-smoothed signal) were observed for the three FTUCA standards at 1 ppb (see Figure 1).

A blind mixture of the three standards in liver extract was quantified by Q-TOF. Excellent quantification results were obtained for all three targets:

Compound	Measured	Actual
FOUEA	4.0 ppb	5 ppb
FHUEA	2.7 ppb	5 ppb
FDUEA	6.7 ppb	5 ppb

By comparing the ISTD responses, ion suppression (matrix effect) was observed in analyzing the liver extract. It has been shown using an LC/QQQ system with atmospheric pressure photoionization (APPI) is a more effective technique than electrospray ionization (ESI) to analyze FTOHs and perfluorinated sulfonamides [6].

Table 1. Mass Accuracy and Resolution of the Six FTUCA Analyzed in This Study

	Formula	Mass accuracy (ppm)	Resolution
FHUEA	$C_8H_2F_{12}O_2$	– 0.98	13692
MFHUEA	$[^{13}C]_2C_6H_2F_{12}O_2$	– 0.39	13789
FOUEA	$C_{10}H_2F_{16}O_2$	– 0.19	14018
MFOUEA	$[^{13}C]_2C_8H_2F_{16}O_2$	– 2.08	13564
FDUEA	$C_{12}H_2F_{20}O_2$	– 0.62	15399
MFDUEA	$[^{13}C]_2C_{10}H_2F_{20}O_2$	– 1.33	14322

Table 2. Quantification Ions and Linearity of the FTUCA (The quantitation ion is a lost fragment of "FCOOH" from the molecular ion.)

	Formula	$[M–H]^-$	Quant Ion ($[M–H]^- – 64$)	R^2 (1–250 ppb)
FHUEA	$C_8H_2F_{12}O_2$	357	293	0.9992
MFHUEA	$[^{13}C]_2C_6H_2F_{12}O_2$	359	294	–
FOUEA	$C_{10}H_2F_{16}O_2$	457	393	0.9998
MFOUEA	$[^{13}C]_2C_8H_2F_{16}O_2$	459	394	–
FDUEA	$C_{12}H_2F_{20}O_2$	557	493	0.9972
MFDUEA	$[^{13}C]_2C_{10}H_2F_{20}O_2$	559	494	–

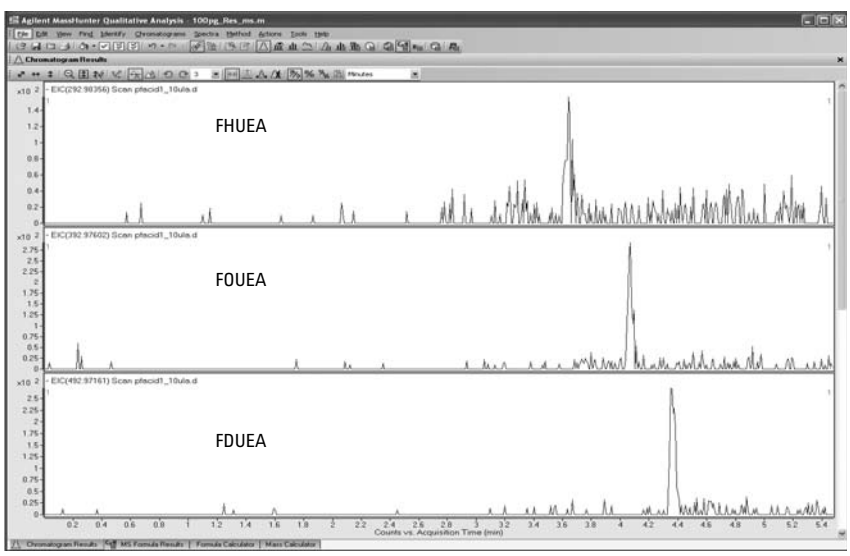

Figure 1. Expansion of EICs for quant ions of 1 ppb FTUCA standards (S/N > 5, unsmoothed signal).

Conclusions

Some of the most impressive aspects about the LC/Q-TOF were the mass accuracy, the linear dynamic range, and the signal-to-noise ratios. For environmental applications, using Q-TOF can greatly reduce interference from complex matrices and improve the accuracy of the results. This application of Q-TOF shows good mass accuracy (well below 3 ppm) and good resolution (> 13,500). Excellent quantification results were obtained from a blind liver extract.

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