



Comparison of Three Different Mass Spectrometers in LC-MS Analysis of Perfluoroalkylated Surfactants



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Introduction

Perfluoroalkylated surfactants (PFAS) are employed in the large-volume production of fire-fighting foams, herbicides and insecticides, paints, lubricants and adhesives. Perfluorooctane sulfonate (PFOS), a representative of this group, has recently gained considerable attention because of its wide distribution in the environment. Fluorotelomer alcohols (FTOHs) are compounds with long polyfluorinated chains. They are employed for comparable applications.

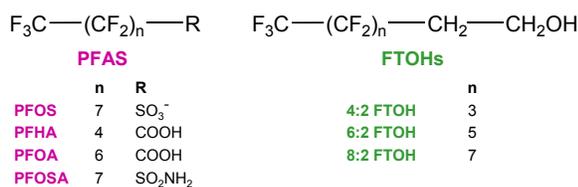


Figure 1. Structures of target analytes PFAS and FTOHs.

Experimental

- Column: C_{18} phase, 3 μm particles, 100 Å pore size, 150 mm length, 2.1 mm i.d. (Ace 3 C18; Advanced Chromatography Technologies)
- Gradient: Methanol-water (FTOHs) or 2 mM NH_4OAc in methanol-water (PFAS), 200 $\mu l/min$
- Ion trap (IT) MS: LCQ (Finnigan MAT) with APCI or ESI ion source, negative ion mode (-)
- Time-of-flight (TOF) MS: LCT™ (Micromass®) with ESI(-)
- Triple quadrupole (TriQ) MS: Quattro LC™ (Micromass®) with ESI(-)

Chromatograms of PFAS and FTOHs

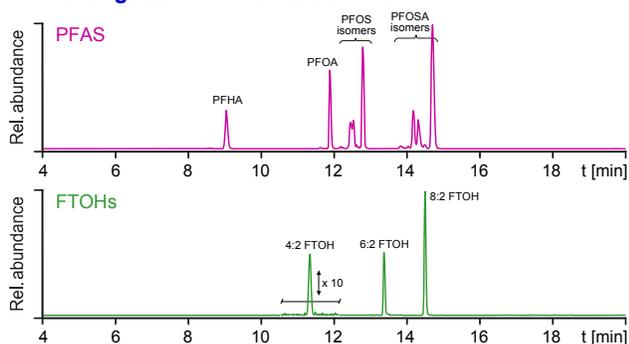


Figure 2. Chromatograms of PFAS (4 ng each) and FTOHs (5 ng each) recorded by full scan ESI(-) TOF MS.

Selectivity, detection limits and linear ranges

Table 1. Comparison of LC-MS instruments and methods concerning analysis of the target analytes in ESI(-) mode

Instrument	TOF	TriQ	TriQ	IT	IT
MS experiment	full scan	SIM	MRM	full scan	MRM
Selectivity	+	-	++	-	+++
	(high resol.)				
LOD PFAS (pg injected)	2-10	0.5-10	10-100	25-100	2500-5000
LOD FTOHs (pg injected)	5-150	2-20	0.5-20	not analysed	not analysed
Linear range PFAS (ng inj.)	0.01-1	0.01-1	0.05-5	0.05-2.5	5-100*
Linear range FTOHs (ng inj.)	0.05-1	0.02-2	0.01-5	not analysed	not analysed

Abbreviations: SIM, selected ion monitoring; MRM, multiple reaction monitoring
LOD, instrumental limit of detection (signal to noise ratio 3:1)

* Amounts above 100 ng injected were not analysed

MS and MS-MS fragmentation patterns of PFOS

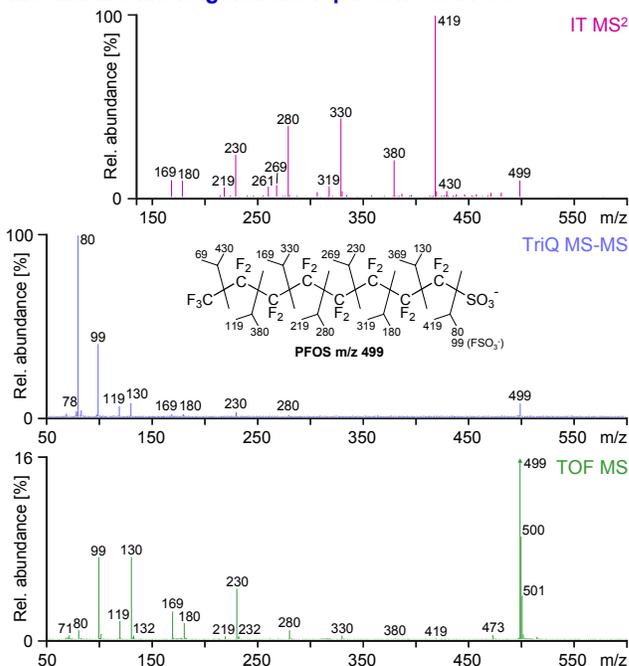


Figure 3. Helium collision induced dissociation (CID; m/z 499) by IT MS²
Argon CID (m/z 499) by TriQ MS-MS
Cone voltage induced fragmentation by TOF MS

Fragmentation pathways and efficiencies

Table 2. Comparison of MS instruments and methods concerning fragmentation efficiencies of the target analytes. Parent ion m/z → daughter ion m/z is given as well as relative daughter ion intensity (percentage of parent ion intensity).

Instrument	TriQ ESI(-)	IT ESI(-)	IT APCI(-)
PFOS	499 → 80; 1.6 %	499 → 419; 0.3 %	499 → 419; 1.9 %
PFHA	313 → 269; 12 %	313 → 269; 1.7 %	313 → 269; 1.3 %
PFOA	413 → 369; 10 %	413 → 369; 0.4 %	413 → 369; 4.2 %
PFOSA	498 → 78; 3.2 %	498 → 478; 8.0 %	498 → 478; 18 %
4:2 FTOH	263 → 155; 5.8 %	203 → 155; 50 %	Fragmentation unstable
6:2 FTOH	363 → 255; 5.6 %	303 → 283; 62 %	Fragmentation unstable
8:2 FTOH	463 → 355; 4.1 %	403 → 383; 20 %	Fragmentation unstable

Conclusions

- ❖ Concerning fragmentation efficiencies of PFAS, APCI(-) at the IT instrument gives superior results compared to ESI(-).
- ❖ Fragmentation with the IT instrument forms daughter ions with higher m/z ratios and, hence, is more selective than TriQ MS-MS. This might be due to the collision cell (ion trap vs. hexapole) or the collision gas (helium vs. argon).
- ❖ The TriQ instrument is more sensitive for PFAS than the ion trap.
- ❖ Tandem MS (MRM) gives best selectivity and leads to very low background noise. However, only compounds with good fragmentation efficiencies (e.g. FTOHs, see Table 2) can be analysed at very low concentration levels in tandem MS.