Application Note

Application Snap-Shot: Focus on PFAS

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Expand Your PFAS Analysis. Screen for Targets and Identify Unknowns Simultaneously

Key Words: PFAS, GC-MS, HR-MS, TOFMS, Environmental Analysis, Pollutants, Emerging Substances, Non-target, NTS, Screening

Background and Description

Research into the prevalence of Per- and polyfluoroalkyl substances (PFAS) chemicals—also known as "forever chemicals" due to their high stability in our environment and food chain—continues to grow. At the same time, regulatory control of these species in our water and food supplies continues to gain momentum. However, analysis of PFAS in complex environmental samples can be challenging due to the enormous number and variety of PFAS chemicals. New analytical methods must be developed to monitor PFAS in the environment.

This application snapshot focuses on the rapidly expanding area of PFAS analysis and highlights how screening for known PFAS targets, as well as discovering and identifying unknown PFAS chemicals, can be performed using high-performance GC-TOFMS. New libraries are being developed to facilitate the screening of these pollutants in samples.

Sources and Types of PFAS

A huge array of products, that we use and are exposed to daily, contain PFAS (Figure. 1). There are thousands of different PFAS molecules used in the industries producing these materials. PFAS have been categorized into different groups depending on their functionality. For example, PFAS that are currently screened by LC-MS and GC-MS methods include perfluoroalkylcarboxylic acids (PFCA), perfluoroalkanesulfonates (PFSA), perfluoroalkanesulfonamides (FASA), and fluorotelomer alcohols (X:2FTOH). The perfluorinated sections (alkyl backbone), vary in length and may be branched. Several representative, commercially available PFAS are provided (Figure 2). 1) Perfluorooctanoic acid (PFOA), 2) Perfluorooctanesulfonic acid (PFOS), 3) Perfluorooctanesulfonamide (PFOSA), and 4) 2-perfluorooctyl ethanol (8:2FTOH).

Figure 1. PFAS Sources.

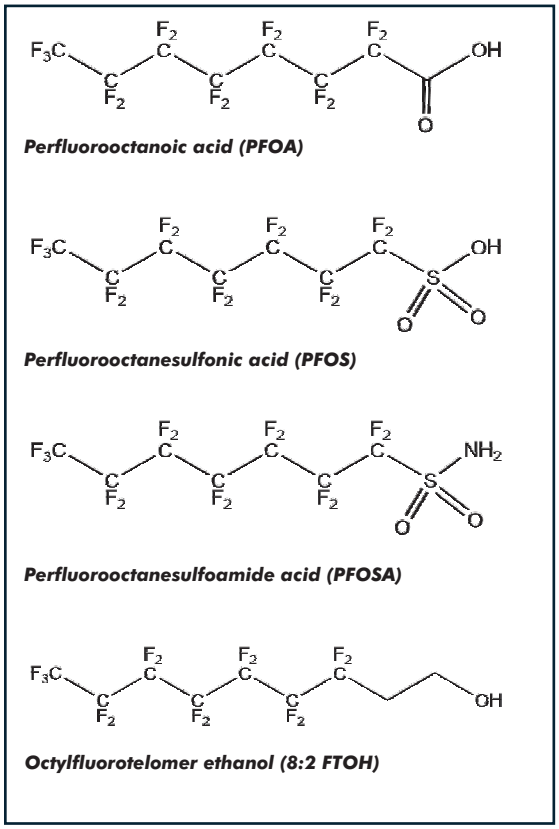


Figure 2: Examples of some common PFAS types (some available as analytical standards).

PFAS Screening Using GC-TOFMS

With huge numbers of PFAS varieties in existence, the use of powerful screening technologies is vital. For volatile and semi-volatile PFAS analysis, Gas Chromatography (GC) with Time-of-Flight Mass Spectrometry (TOFMS) is ideal, due to the ability to collect sensitive, full mass range data, at high acquisition rates. This allows a variety of real-world sample matrices to be analyzed, such as a set of commercially available "Anti-Fog and Demisting," products. These products contain a variety of PFAS as indicated by Stapleton and coworkers.[1] Simultaneous target and non-target screening (NTS) of these products was performed using a **LECO Pegasus® BT GC-TOFMS** system. For example, analysis of an anti-fog spray product (Figure. 3), revealed some known target PFAS compounds, but also an array of unknowns as well, where EI-MS spectral fragmentation indicated that they could be assigned as PFAS candidates.

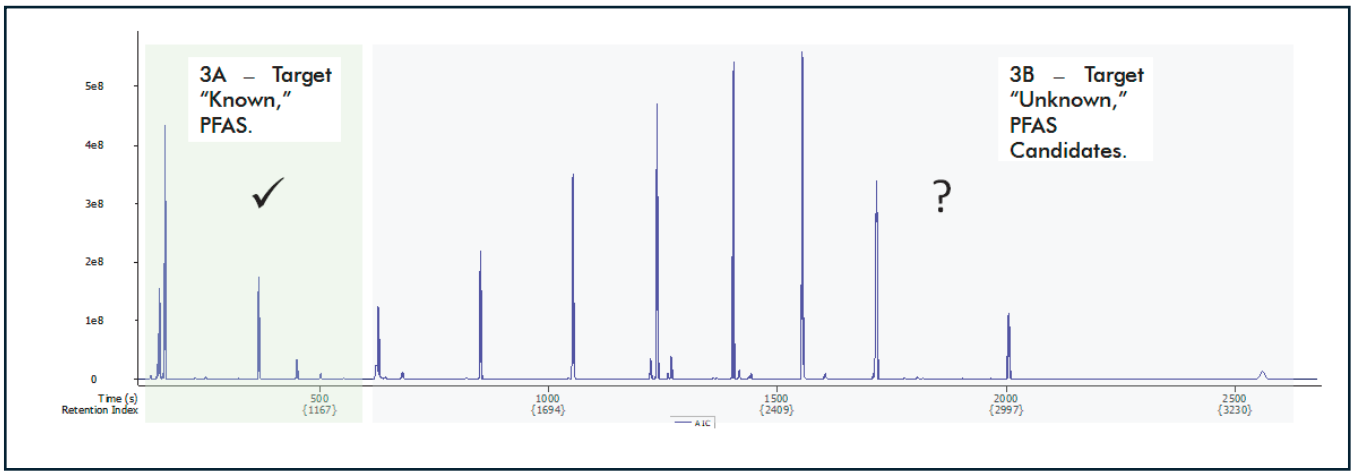
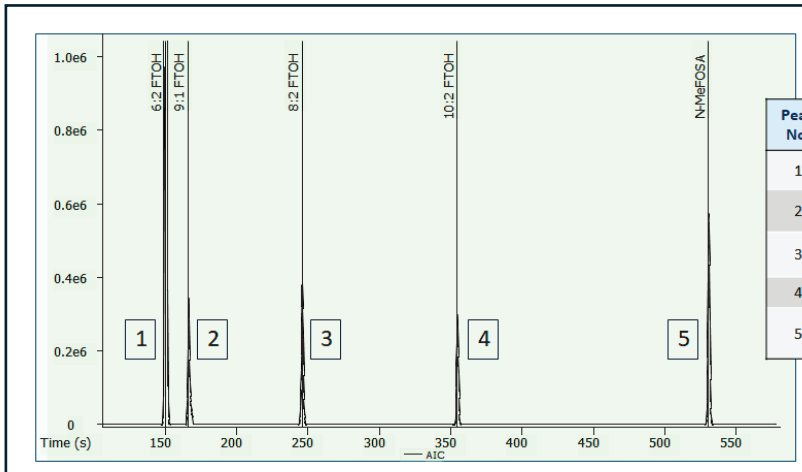


Figure. 3. Simultaneous target and non-target screening of a commercially available "anti-fog," spray. Sections of "known," PFAS targets (3A. highlighted in green) and "unknown," PFAS candidates (3B. highlighted in grey) are displayed.

The presence of five PFAS target compounds (Figure 3A) was confirmed using analytical standards and similarity matching to NIST 2023 mass spectral and retention index (RI) library entries. These five species are highlighted in the zoomed-in section of the chromatogram and table below (Figure 4).



Peak No.	Name	Formula	RT (s)	MS Similarity	RI
1	6:2 FTOH	$C_8H_5F_{13}O$	150	955	823
2	9:1 FTOH	$C_{10}H_3F_{19}O$	166	745	842
3	8:2 FTOH	$C_{10}H_5F_{17}O$	246	706	931
4	10:2 FTOH	$C_{12}H_5F_{21}O$	355	768	1034
5	N-MeFOSA	$C_9H_4F_{17}NO_2S$	531	850	1195

Figure 4. A zoomed-in section of the chromatogram section is highlighted in Figure 3A, and a table, showing 5 target PFAS species that were identified using standards and library data. Nomenclature used corresponds to the alkyl chain of the perfluorinated, and functional group sections of the compounds. For example, 6:2 FTOH represents a perfluorinated 6-carbon backbone tail, with an ethanol head.

In addition to the target PFAS molecules found, the non-target data collected also revealed several other components (Figure 3B), which were judged to be possible PFAS candidates. The nine most prominent peaks showed similar mass spectral fragmentation, indicating the presence of fluoroalkyl and ethoxy groups, but elution times were spread out rather evenly as the GC temperature gradient increased, suggesting a homologous series of PFAS. To investigate the identification of these species, further analysis was performed using a **LECO *Pegasus* HRT+**, high resolution, accurate mass GC-TOFMS system, equipped with a **Multi-Mode Ion Source® (MMS®)**, allowing electron ionization (EI), as well as positive and negative chemical ionization (PCI and NCI), to be performed.

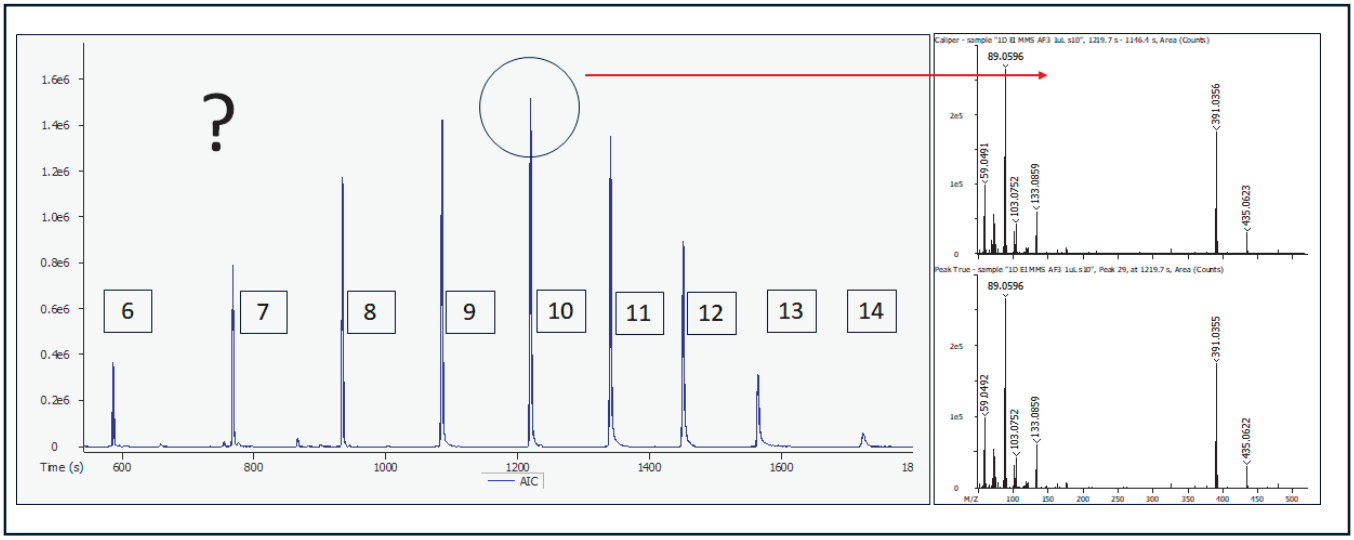
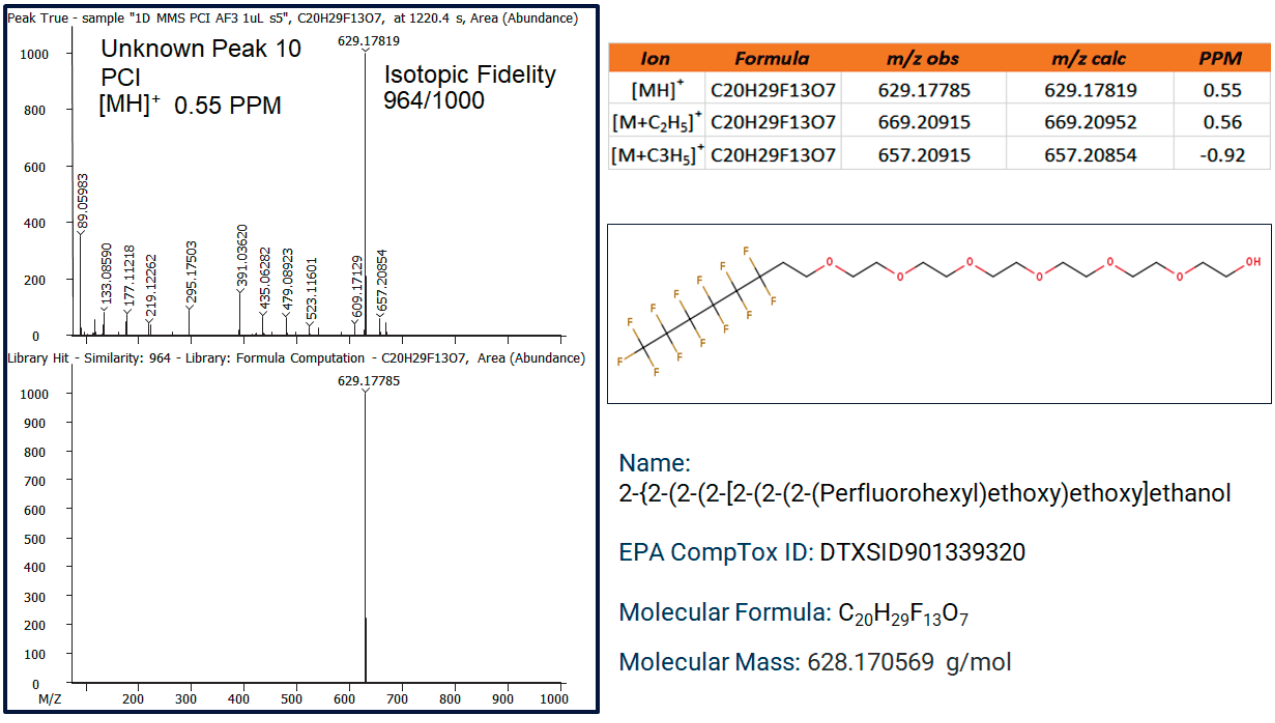


Figure 5. 5A) The chromatogram section featuring unknown PFAS candidates, peaks 6-14. ***5B) The EI mass spectra for peak 10.***

The most prominent unknown peaks (6-14, Figure 5A) all showed very similar EI mass spectral accurate mass fragments (Figure 5B, representative MS spectrum for unknown 10), which was useful in confirming the possibility that they were PFAS candidates. To obtain further structural information and identify the species, with higher confidence, positive chemical ionization data was collected, facilitating the generation of intense protonated molecular adducts.



Ion	Formula	m/z obs	m/z calc	PPM
$[MH]^+$	C20H29F13O7	629.17785	629.17819	0.55
$[M+C_2H_5]^+$	C20H29F13O7	669.20915	669.20952	0.56
$[M+C3H_5]^+$	C20H29F13O7	657.20915	657.20854	-0.92

Name:
2-{2-(2-(2-[2-(2-(2-(Perfluorohexyl)ethoxy)ethoxy]ethanol

EPA CompTox ID: DTXSID901339320

Molecular Formula: $C_{20}H_{29}F_{13}O_7$

Molecular Mass: 628.170569 g/mol

Figure 6. PCI Data and structural determination of unknown peak 10, using ChromaTOF® software with high-resolution accurate mass data for molecular adducts and subsequent search of the molecular formula with the EPA CompTox Chemicals Database.

The generation of accurate mass molecular ion data provided formulas for $[MH]^+$, $[M+C_2H_5]^+$ and $[M+C_3H_5]^+$ adducts with mass accuracies of <+/- 1ppm, and allowed strong tentative identification of the unknown compounds to be a group of fluorotelomer ethoxylates (FTEOs), for example as shown for peak 10 (Figure 6), via a search of the EPA CompTox Chemicals Database.[2] The list of similarly strong tentative identification formulas, for this PFAS class, reached using the same process for peaks 6-14, is provided below (Table 1).

Table 1. Unknown peaks 6-14, tentatively identified as a class of fluorotelomer ethoxylates (FTEOs), PFAS compounds

Peak	*Name*	*Formula*	*Molecular Mass*
6	2-(2-(2-(Perfluorohexyl)ethoxy)ethoxy)ethanol	$C_{12}H_{13}F_{13}O_3$	452.0657104
7	2-{2-[2-(2-(Perfluorohexyl)ethoxy)ethoxy]ethoxy}ethanol	$C_{14}H_{17}F_{13}O_4$	496.0919251
8	2-{2-(2-[2-(2-(Perfluorohexyl)ethoxy)ethoxy]ethoxy)ethoxy}ethanol	$C_{16}H_{21}F_{13}O_5$	540.1181399
9	2-{2-(2-(2-[2-(2-(Perfluorohexyl)ethoxy)ethoxy]ethoxy)ethoxy)ethoxy}ethanol	$C_{18}H_{25}F_{13}O_6$	584.1443546
10	2-{2-(2-(2-[2-(2-(2-(Perfluorohexyl)ethoxy)ethoxy]ethoxy)ethoxy)ethoxy)ethoxy}ethanol	$C_{20}H_{29}F_{13}O_7$	628.1705694
11	23-(Perfluorohexyl)-3,6,9,12,15,18,21-heptaoxatricosan-1-ol	$C_{22}H_{33}F_{13}O_8$	672.1967841
12	26-(Perfluorohexyl)-3,6,9,12,15,18,21,24-octaoxahexacosan-1-ol	$C_{24}H_{37}F_{13}O_9$	716.2229989
13	29-(Perfluorohexyl)-3,6,9,12,15,18,21,24,27-nonaoxanonacosan-1-ol	$C_{26}H_{41}F_{13}O_{10}$	760.2492136
14	32-(Perfluorohexyl)-3,6,9,12,15,18,21,24,27,30-decaoxadotriacontan-1-ol	$C_{28}H_{45}F_{13}O_{11}$	804.2754284

Conclusion

Meeting the growing environmental research and regulatory needs for PFAS analysis requires the use of powerful technologies to screen for known targets and to detect and identify unknown PFAS candidates. Here, sub-nominal mass GC-TOFMS, allowed simultaneous, full mass range, highly sensitive target, and NTS screening for PFAS in Anti-Fog/Demisting products, detecting a variety of both known PFAS and unknown PFAS candidates. The use of accurate mass GC-HR-TOFMS technology with EI and CI capabilities facilitated strong tentative identifications of the unknowns to be a class of fluorotelomer ethoxylates (FTEOs). This approach, together with the results obtained, suggests these technologies are an ideal choice for screening and identification of volatile and semi-volatile PFAS, in an array of sample types in complex matrices.

References

[1]Herkert N.J., Kassotis C.D., Zhang S., Han Y., Pulikkal V.F, Sun M., Ferguson P.L., and Stapleton H.M, Environmental Science and Technology 2022, 56(2), 1162-1173.

[2]United States Environmental Protection Agency, Computational Toxicology Chemicals Dashboard: https://comptox.epa.gov/

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Form No. 203-821-678 9/23—REV0