

UTILIZING ION MOBILITY TO ENHANCE TARGETED AND NON-TARGETED ANALYSIS OF PFAS FROM ENVIRONMENTAL SAMPLES COLLECTED AT A SKI RESORT

Sarah Dowd,¹ Kari Organtini,¹ Marian Twhig,¹ Frank Dorman,^{1,2} Jean Carlan²

¹Waters Corporation 34 Maple Street, Milford, MA ²Dartmouth College, Department of Chemistry, Hanover, NH

INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are a group of commonly used compounds in industrial and consumer goods, known particularly for their hydrophobic, non-stick properties. Their unique chemistry led to their use in ski waxes. While regulations are changing for the manufacture of ski wax to exclude PFAS, the persistence of PFAS means they could still be detected for years. Given the hazards and global concern about PFAS, we investigated if the contamination could be detected at a local ski area that supports a high-level race program. While previous studies of PFAS at ski areas have used targeted analysis for a set of known PFAS¹⁻³, this study used high-resolution mass spectrometry (HRMS) and ion mobility to look for new and unexpected PFAS. Data collection was done with ion mobility enabled data-independent acquisition on a SELECT SERIES™ Cyclic™ IMS QTOF.

SAMPLES AND SAMPLE PREPARATION

Water samples were collected from a variety of locations (Table 1) within a New Hampshire ski area that is known for its elite racing program. The samples were acidified and extracted using weak anion exchange (Oasis™ WAX Cartridge) solid phase extraction (Figure 1).

Table 1. Sample names and locations used in this study.

Sample ID	Location	Location Details
B11	Pool A 2	Base of ski slopes (highest in flow gradient)
B12	Running 1	Stream (runoff) flowing into retention pond
B13	Cars 2	Base of ski area – Parking lot
B14	Reservoir 1	Snowmaking retention pond
B15	Spiked Reservoir 2	Snowmaking retention pond - spike
B16	Pool B 2	Base of ski slopes (slightly lower in gradient)

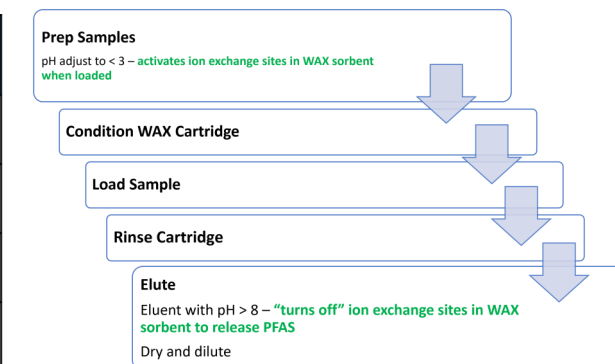


Figure 1. Solid phase extraction protocol used for isolating and concentrating PFAS from the samples.

LC-MS EXPERIMENTAL PARAMETERS

LC Parameters

Analytical Column: ACQUITY UPLC™ BEH™ C18, 1.7 μm; 2.1mm x 100 mm
Mobile phase A: Water + 2 mM Ammonium Acetate
Mobile Phase B: Methanol
Column Temperature: 35°C

LC Gradient:

TIME (min)	FLOW (ml/min)	%A	%B
Initial	0.30	95	5
1.0	0.30	75	25
6.0	0.30	50	50
13.0	0.30	15	85
14.0	0.30	5	95
17.0	0.30	5	95
18.0	0.30	95	5
22.0	0.30	95	5

MS Parameters

Instrument: SELECT SERIES Cyclic IMS
Ionization: ESI⁺
Capillary Voltage: 0.5 kV
Cone Voltage: 10 V
Desolvation Gas Flow: 800 L/hr (N₂)
Desolvation Temperature: 350°C
MS Analyzer Mode: V Mode (Resolution ~50,000 FWHM)
Mass Range: m/z 50-2000
Acquisition: DIA HDMS^E
Ion Mobility Resolution: ~ 65 Ω/ΔD (FWHM)

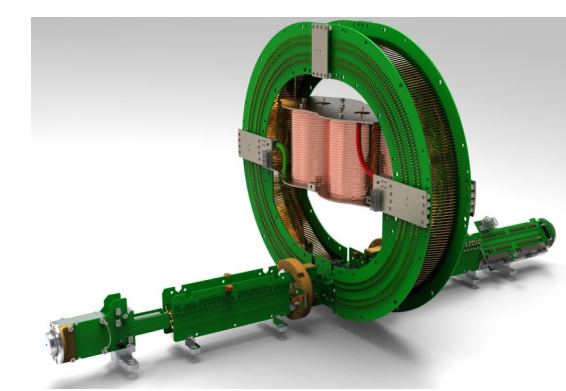


Figure 2. The cyclic ion mobility ion optics in the SELECT SERIES Cyclic IMS.

RESULTS: TARGETED SCREENING OF PFAS

After data acquisition, detected peaks were first compared to an internal HRMS PFAS library.⁴ Identification criteria included accurate mass (5ppm), detected fragments, and RT error. The added dimension of IMS can be used for spectral clean-up (Figure 3) that can be helpful for confirmation of target ions and elucidation of unknowns. A standard of 30 PFAS (Wellington Labs PFAC30PAR) was analyzed to confirm observed CCS values. Results are presented in Table 2.

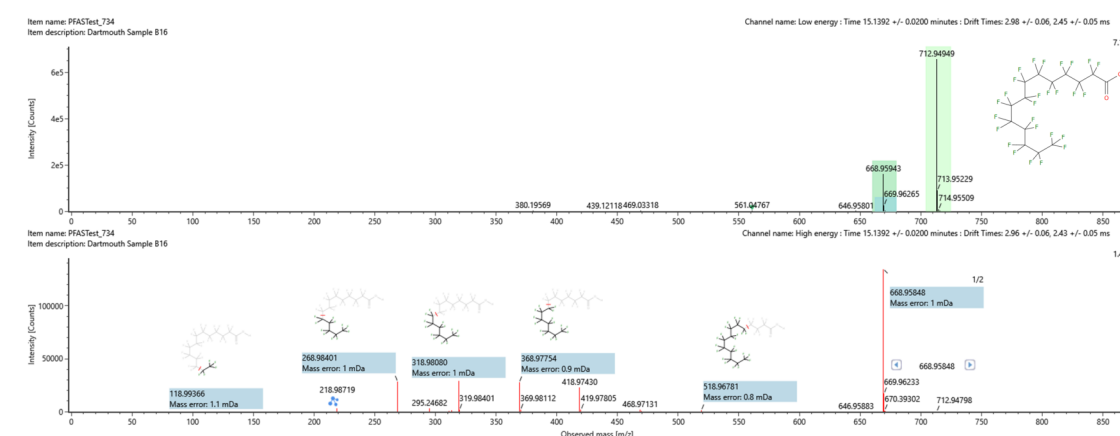


Figure 3. Time and drift-aligned low collision energy (top) and high collision energy (bottom) spectra for PFTrDA from sample B16. The high collision energy spectrum is annotated with theoretical fragments for PFTrDA.

Table 2. Identified PFAS compounds from Targeted Screening Analysis. Observed CCS is an average of the calculated CCS in the environmental samples and PFAS standards.

Name	Formula	Observed Ion	Observed CCS (Å²)	B11	B12	B13	B14	B15	B16
PFBS	C4HF9O3S	[M-H] ⁻	132.6 ± 0.5	✓	✓	✓	✓	✓	✓
4:2 FTS	C6H5F9O3S	[M-H] ⁻	149.5 ± 0.1				✓	✓	✓
PFHxA	C6HF11O2	[M-HCO2] ⁻	124.7 ± 0.3		✓	✓	✓	✓	✓
FBSA	C4H2F9NO2S	[M-H] ⁻	134.0 ± 0.1	✓				✓	✓
PFPeS	C5HF11O3S	[M-H] ⁻	141.2 ± 0.4			✓	✓	✓	✓
GenX	C6HF11O3	[M-HCO2] ⁻	127.1 ± 0.1					✓	✓
PFHpA	C7HF13O2	[M-HCO2] ⁻	133.4 ± 0.2	✓	✓	✓	✓	✓	✓
L-PFHxS	C6HF13O3S	[M-H] ⁻	149.4 ± 0.2	✓	✓	✓	✓	✓	✓
6:2 FTS	C8H5F13O3S	[M-H] ⁻	165.2 ± 0.2	✓	✓	✓	✓	✓	✓
PFOA	C8HF15O2	[M-HCO2] ⁻	141.0 ± 0.2	✓	✓	✓	✓	✓	✓
PFHpS	C7HF15O3S	[M-H] ⁻	157.3 ± 0.7			✓	✓	✓	✓
FHxSA	C6H2F13NO2S	[M-H] ⁻	150.7 ± 0.4	✓	✓	✓	✓	✓	✓
PFNA	C9HF17O2	[M-HCO2] ⁻	149.0 ± 0.2	✓	✓	✓	✓	✓	✓
L-PFOS	C8HF17O3S	[M-H] ⁻	165.6 ± 0.1	✓			✓	✓	✓
9Cl-PF3ONS	C8HClF16O4S	[M-H] ⁻	170.2 ± 0.1			✓	✓	✓	✓
PFDA	C10HF19O2	[M-HCO2] ⁻	156.5 ± 0.4	✓	✓	✓	✓	✓	✓
8:2 FTS	C10H5F17O3S	[M-H] ⁻	182.4 ± 0.1				✓	✓	✓
N-MeFOSAA	C11H6F17NO4S	[M-H] ⁻	189.2 ± 0.6				✓	✓	✓
FOSA	C8H2F17NO2S	[M-H] ⁻	166.5 ± 0.3			✓	✓	✓	✓
N-EiFOSAA	C12H8F17NO4S	[M-H] ⁻	193.6 ± 0.3		✓	✓	✓	✓	✓
PFUnDA	C11HF21O2	[M-HCO2] ⁻	164.6 ± 1.1				✓	✓	✓
11Cl-PF3OUdS	C10HClF20O4S	[M-H] ⁻	186.6 ± 0.1				✓	✓	✓
PFDoDA	C12HF23O2	[M-HCO2] ⁻	171.6 ± 0.2				✓	✓	✓
N-MeFOSA	C9H4F17NO2S	[M-H] ⁻	170.4 ± 0.2	✓	✓	✓	✓	✓	✓
PFTrDA	C13HF25O2	[M-HCO2] ⁻	179.7 ± 0.5	✓	✓	✓	✓	✓	✓
N-EiFOSA	C10H6F17NO2S	[M-H] ⁻	175.6 ± 0.3	✓	✓	✓	✓	✓	✓
PFTrEDA	C14HF27O2	[M-H] ⁻	206.6 ± 0.2	✓	✓	✓	✓	✓	✓
PFHxDA	C16HF31O2	[M-H] ⁻	224.7 ± 0.1	✓	✓	✓	✓	✓	✓
PFODA	C18HF35O2	[M-H] ⁻	242.7	✓	✓	✓	✓	✓	✓

RESULTS: NON-TARGETED SCREENING OF PFAS

A challenge with non-targeted screening is being able to find PFAS among thousands of detected peaks. For this study, we used IMS to select for potentially fluorinated or halogenated compounds. Previous studies^{5,7} have shown that the CCS values of per- and poly-fluorinated compounds are lower than the CCS of un-halogenated compounds of similar m/z .

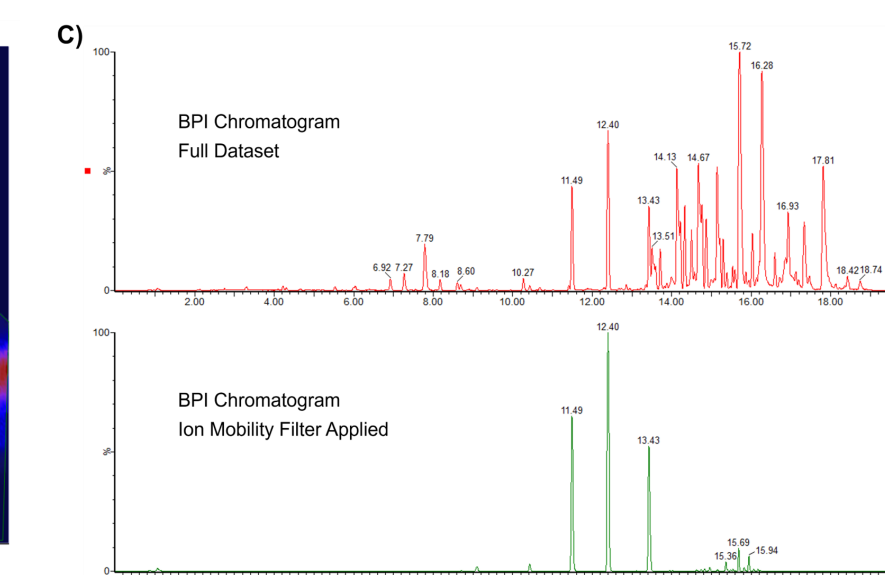
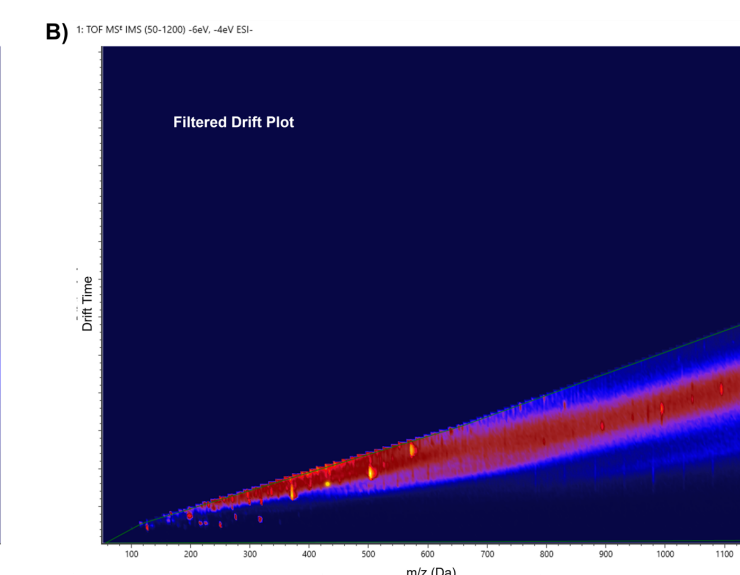
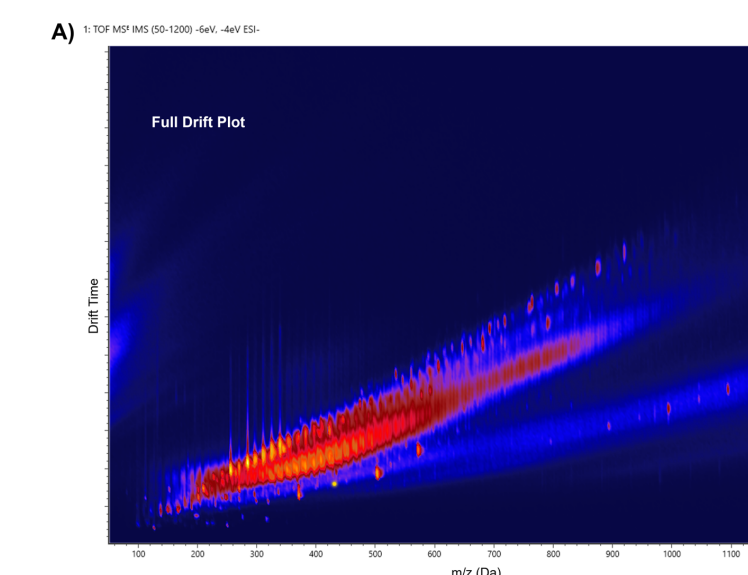


Figure 4. A) Plot of drift time versus mass to charge (m/z) for the full data set for sample B11. B) Plot of drift time vs m/z filtered for potential PFAS compounds. Tools within the ion mobility data viewer were used to select for this drift region. Due to the density of fluorine, the drift time for PFAS compounds is shorter than compounds of similar m/z that do not contain halogens. C) Comparison of the base peak intensity chromatogram before (top) and after (bottom) drift time filter was applied.

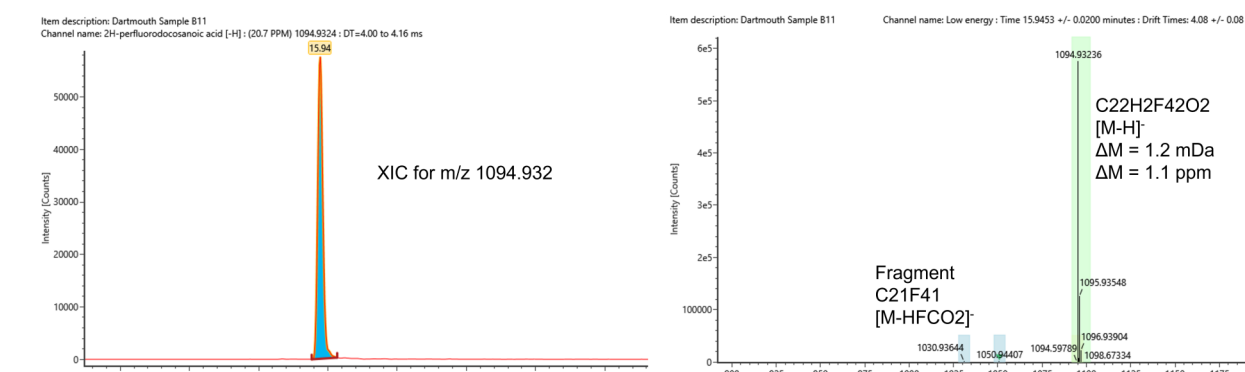


Figure 5. Left: Extracted ion chromatogram for m/z 1094.932, which was an ion that passed the drift filter applied to find unknown PFAS in Sample B11. Right: Time and drift-aligned low collision energy spectrum for the selected peak. The best match by elemental composition was C22H2F24O2, an H-substituted perfluorocarboxylic acid (PFCA) was the proposed structure.

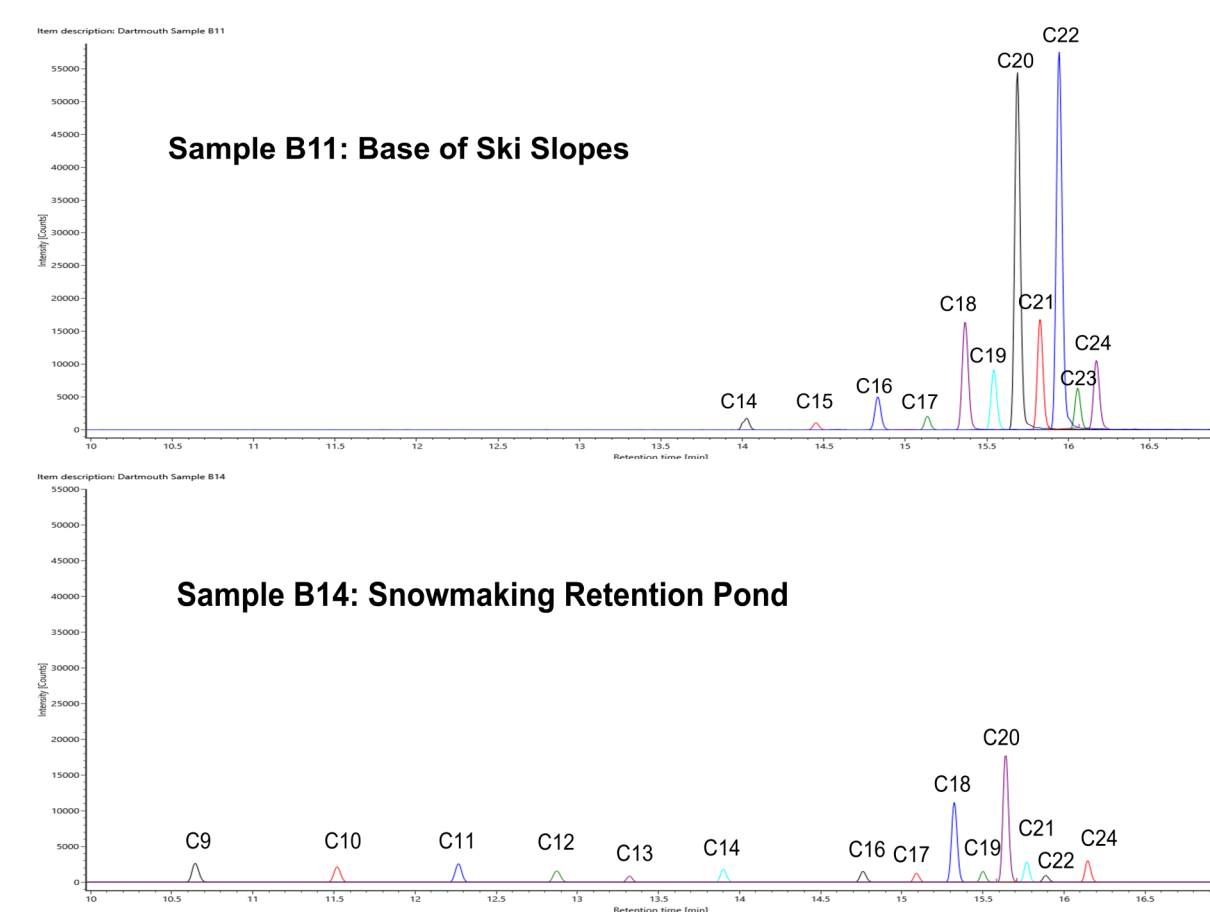


Figure 6. Extracted ion chromatograms for the series of H-substituted PFCAs (C9-C24) detected in Sample B11 (top) and B14 (bottom).

An ion mobility filter (Figure 4) was created and applied to find possible PFAS in a list of unknowns. Using this filter, a series (C9-C24) of polyfluorinated carboxylic acid compounds with one hydrogen substitution in the carbon chain were found (Figures 5 and 6). A second series (C10-C17) of dioic perfluorinated acids were tentatively identified in Sample B14 from the snowmaking retention pond (Figure 7).

RESULTS: CONFIRMATION OF PROPOSED STRUCTURES

While authentic standards were not available for many of the tentative identifications from the non-targeted screening, standards of 9H-perfluorononanoic acid and perfluorodecanedioic acid were purchased from Oakwood Chemical (SC, USA).

9H-Perfluorononanoic Acid:

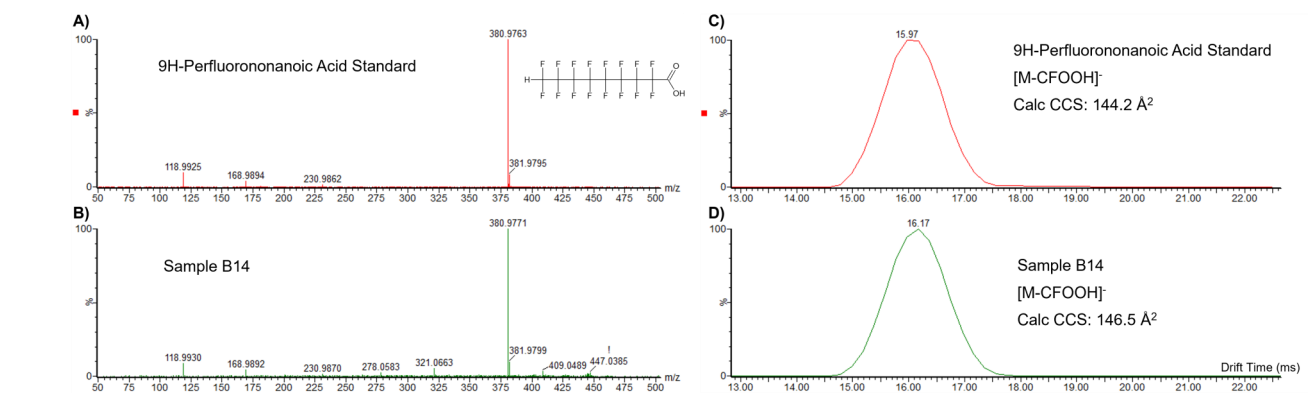


Figure 8. Left: MSMS fragmentation spectrum of m/z 448.9 at CE 30V for the standard of 9H-perfluorononanoic acid (A) and in sample B14 (B). The observed RT was the same in both injections. Right: Extracted drift traces for the m/z 380.93 [M-CFOOH]⁻ ion for the standard of 9H-perfluorononanoic acid (C) and in sample B14 (D).

Perfluorodecanedioic Acid:

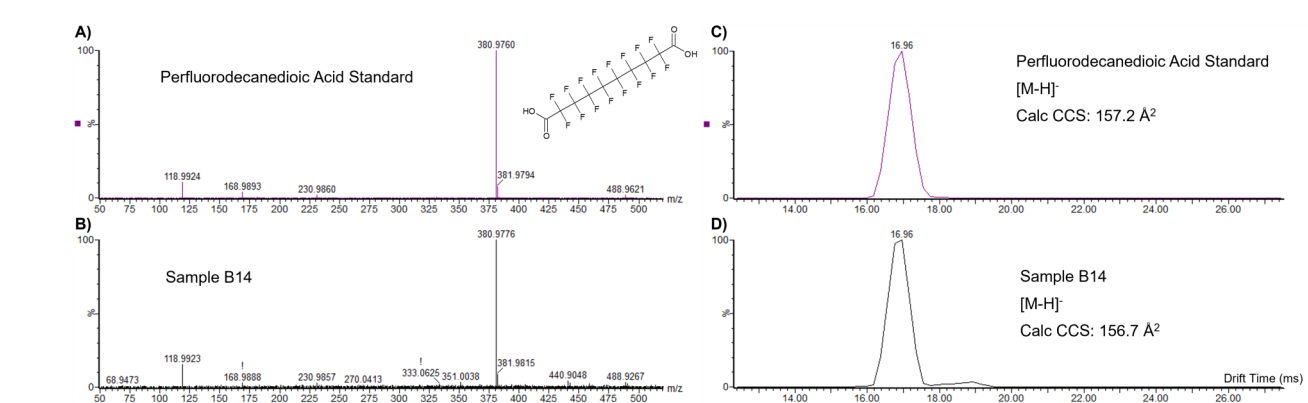


Figure 9. Left: MSMS fragmentation spectrum of m/z 488.9 at CE 30V for the standard of perfluorodecanedioic acid (A) and in sample B14 (B). The observed RT was the same in both injections. Right: Extracted drift traces for the m/z 488.93 [M-H]⁻ ion for the standard of perfluorodecanedioic acid (C) and in sample B14 (D).

CONCLUSIONS

- Targeted screening utilized the extra dimension of IMS for spectral clean up that aided in the identification of legacy and emerging PFAS.
- Ion mobility can be used to filter for possible PFAS compounds among detected peaks.
- The ion mobility filter led to the tentative identification of a series of polyfluorinated carboxylic acids and perfluorinated dioic acids in the samples collected at the ski resort.
- While authentic standards for the 'unknown' compounds are difficult to find, two standards were compared to experimental data to confirm identifications based on RT, fragment ions, and CCS.

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