

# ENVIRONMENTAL SCREENING OF WATER SAMPLES UTILIZING ION MOBILITY ENABLED HRMS

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## INTRODUCTION

Companies and environmental regulatory authorities are under pressure to monitor a wide array of contaminants varying in chemical property and thus analytical requirements. Many are turning to high resolution mass spectrometry (HRMS) as part of the solution. Modern-non-targeted, HRMS screening methods are capable of collecting accurate mass spectra, with isotopic fidelity, for both precursor and product ions in a single injection. In combination with ion mobility separations, an additional property of collisional cross section (CCS) is obtained for the ion, increasing confidence of identification in matrix. Here, we demonstrate how the use of several chromatographic and ionization techniques in combination with ion mobility and informatics can comprehensively screen environmental water samples for a range of legacy and emerging perfluorinated contaminants.

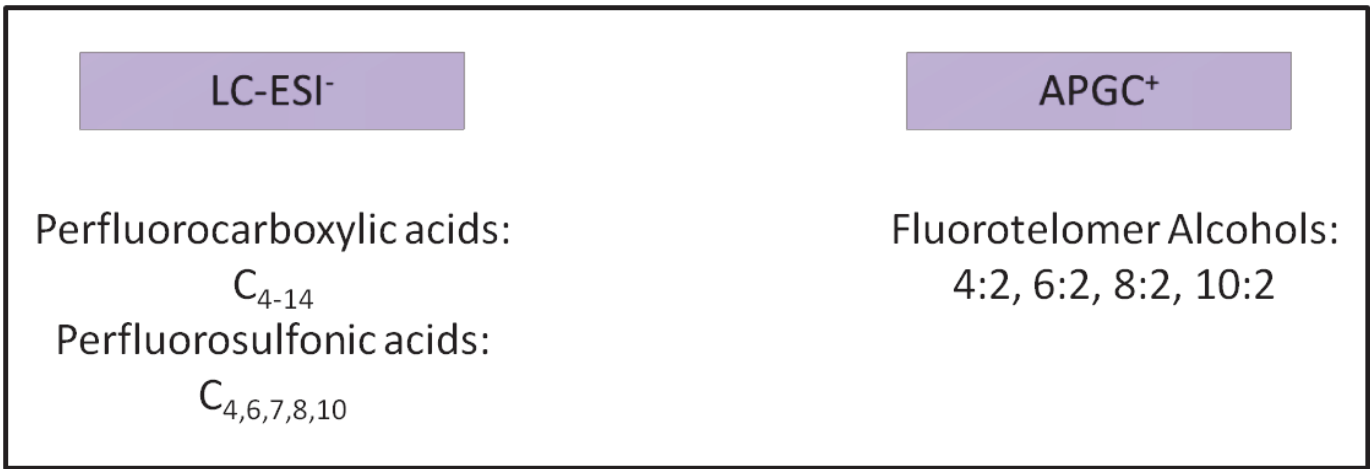


Figure 1: Perfluorinated compounds analyzed as standards in this study.



Figure 2: ESI and APGC MS sources enable easy exchange between LC and GC interfacing for atmospheric ionization used in this work.

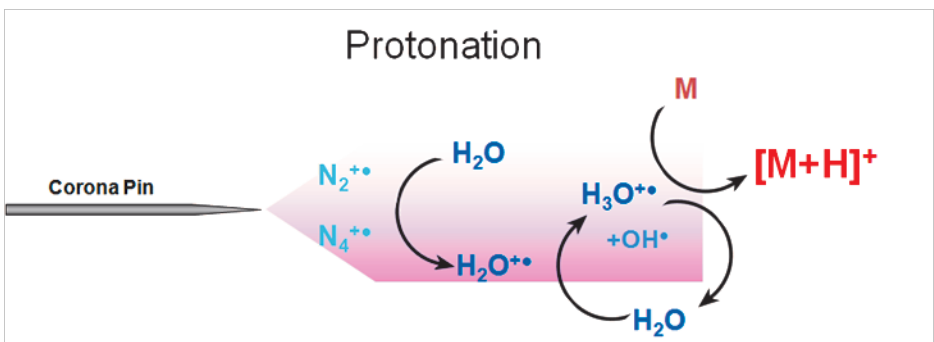


Figure 3: Protonation ionization mechanism used for APGC analysis.

## ANALYSIS APPROACH

A subset of perfluoroalkyl standards were injected under either LC or GC conditions based on previously established methods<sup>1,2</sup>, with minor modifications. A summary of the standards analyzed in these respective conditions are shown in Figure 1. The LC analysis utilized electrospray ionization operated in the negative polarity (ESI<sup>-</sup>), and for GC atmospheric pressure chemical ionization (APGC) in the positive polarity (Figure 2). The ionization mechanism for APGC was protonation (Figure 3), which was achieved by placing water in the source. The HRMS system acquired spectra in both low and elevated collision energies, referred to as MS<sup>E</sup>, and fragmentation patterns were established and collated. Example spectrum are shown for both analysis conditions in Figures 4A and B. Following standards analysis, local lake and tap water samples were collected and extracted<sup>3</sup> for PFASs. In addition to using fragment ions, RT and isotope scoring, an ion mobility experiment was performed to establish CCS values for the compounds of interest prior to sample analysis. Figure 5A and B shows the results of screening using this information, and conservation of CCS despite variations in response between the samples.

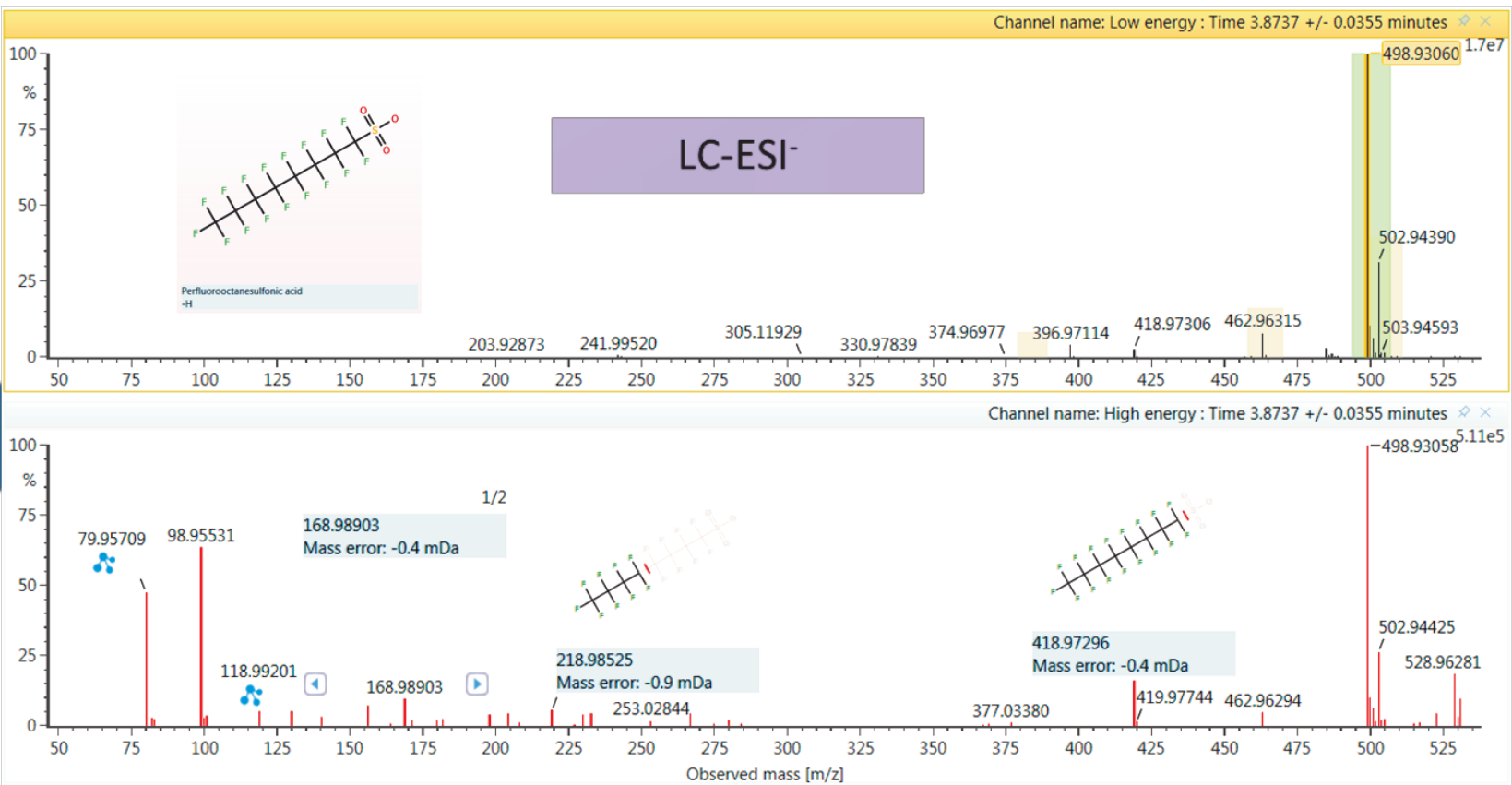


Figure 4A: PFOS low (top) and elevated (bottom) collision energy spectra.

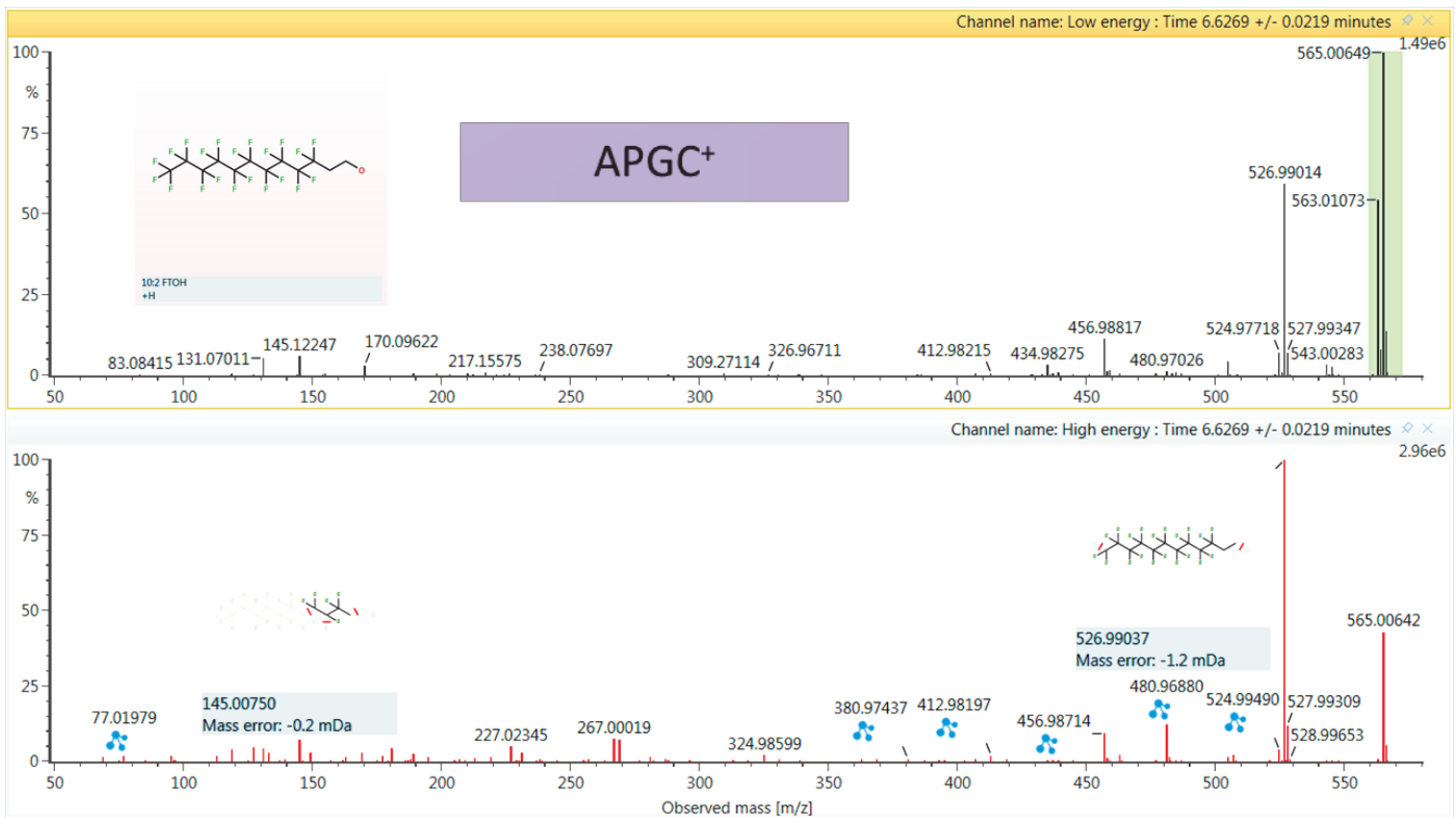


Figure 4B: 10:2 FTOH low (top) and elevated (bottom) collision energy spectra.

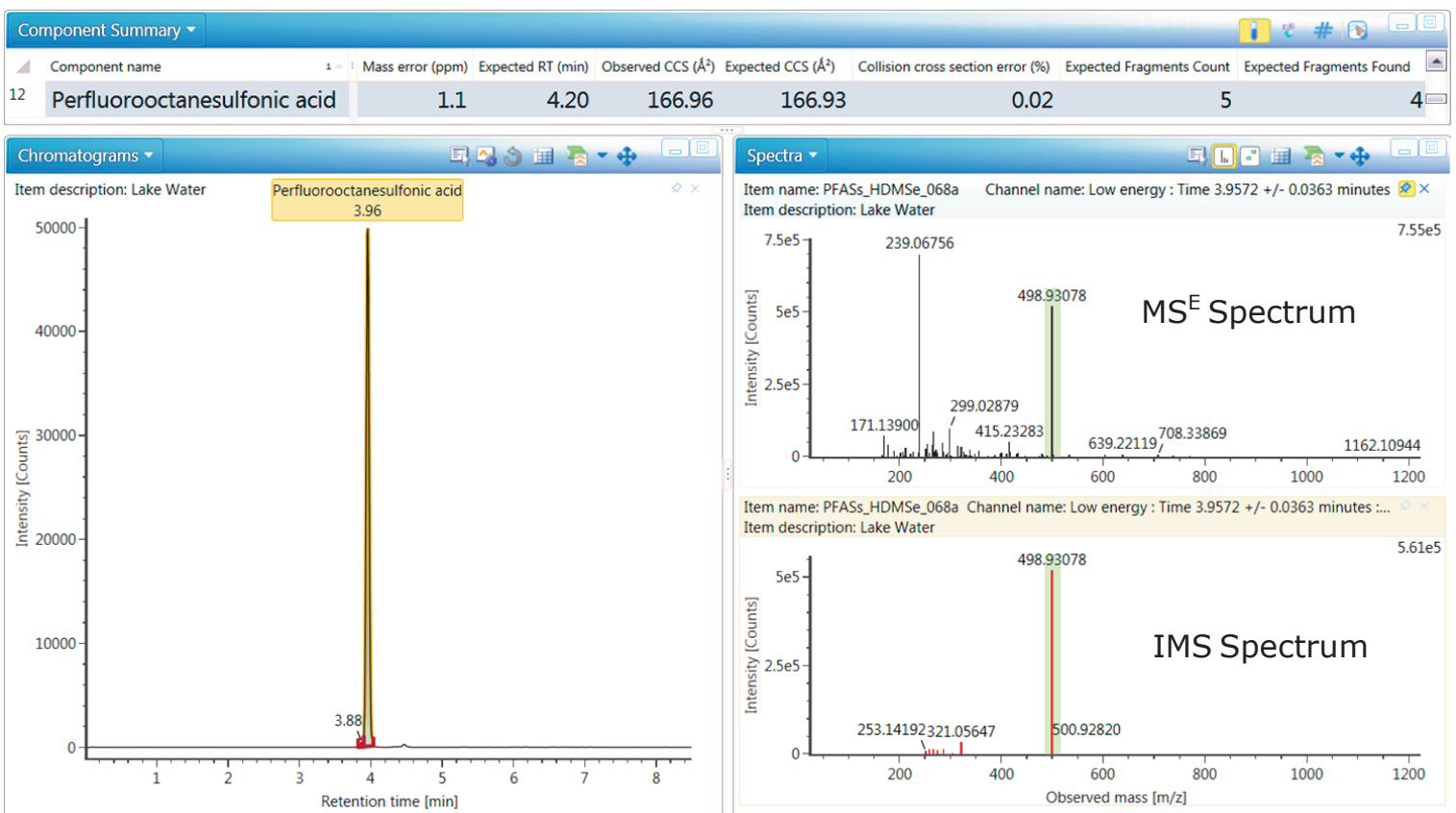


Figure 5A: PFOS spiked into lake water with identification results including CCS. Ion mobility removes additional spectral peaks from the selected component, resulting in a cleaner spectrum.

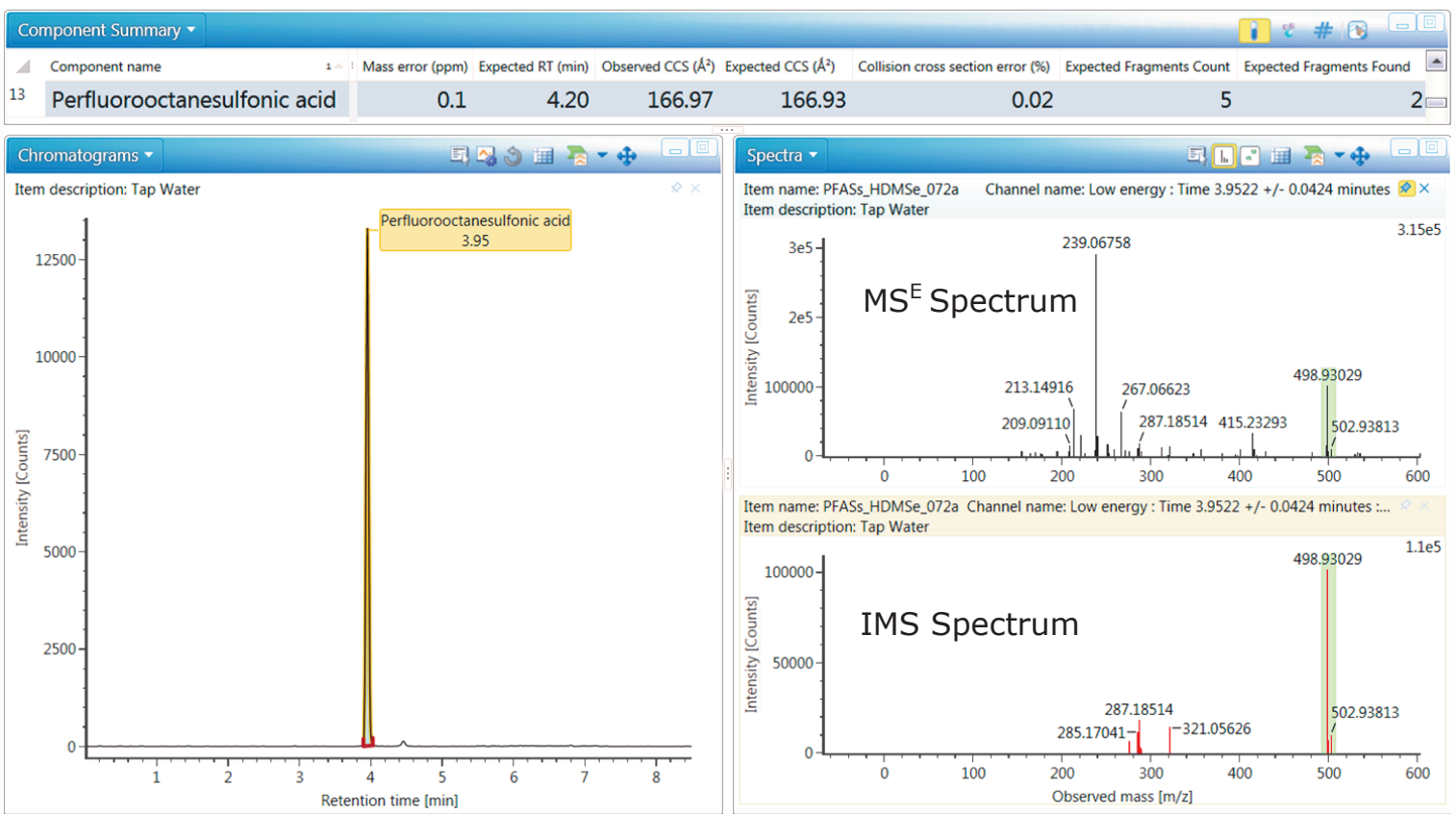
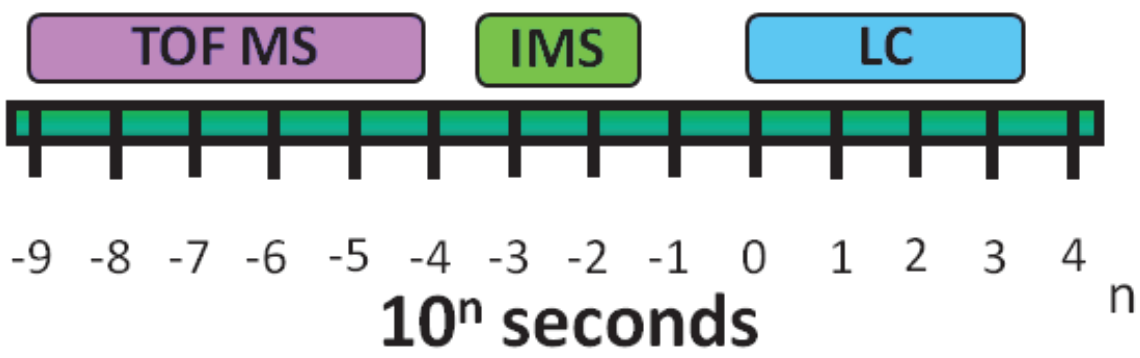


Figure 5B: PFOS spiked into tap water at a 10x lower concentration than lake water. CCS values are conserved despite this difference in concentration, whereas low abundance fragment identifications are missing.

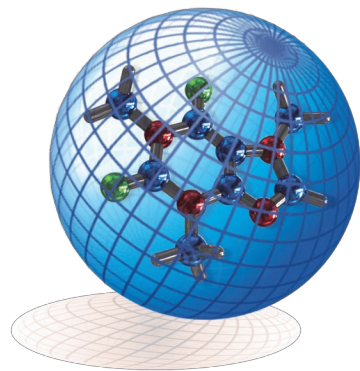
## CONCLUSIONS

- **Universal ionization coverage affords comprehensive coverage of analyte classes which vary in physical and chemical properties and require GC and LC analyses**
- **Accurate mass low and elevated collision energy spectrum provides fragmentation pathway information which can be used for further screening analyses and isotope fidelity for both low and high energy**
- **Including ion mobility separation experiments in the screening workflow add an additional identification parameter, CCS, which is conserved despite variations in concentration and retention time**

## Ion Mobility Separation



CCS values are calculated for every molecular ion. CCS is a robust and precise physico-chemical property of an ion.



## REFERENCES

1. Mullin et al. Screening for Perfluoroalkyl Substances in Wildlife Samples Using a Highly Selective LC-QToF MS. Waters Poster PSTR134854034
2. Portoles et al. Gas chromatography-tandem mass spectrometry with atmospheric pressure chemical ionization for fluorotelomer alcohols and perfluorinated sulfonamides determination. J. of Chrom. A 1413 (2015) 107-116
3. Lee et al. ACQUITY UPLC system solution for quantifying trace levels of perfluorinated compounds with an ACQUITY PFC analysis kit. Waters Application Note APNT10090111