Use of electron-activated dissociation (EAD) on the ZenoTOF 7600 system to elucidate PFAS structures

The Power of Precision

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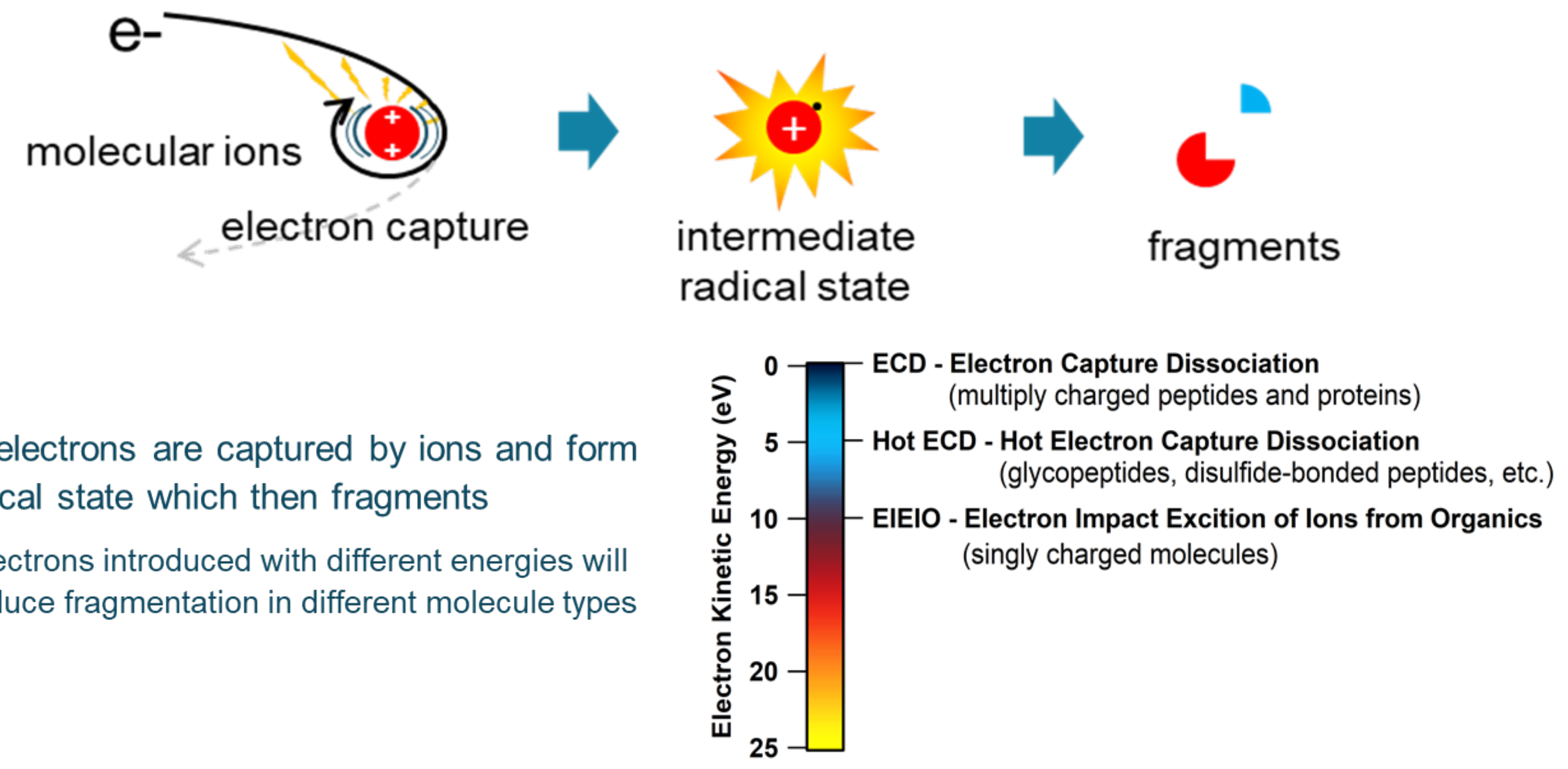
INTRODUCTION

Poly- and perfluoroalkyl substances (PFAS) are well-known environmental contaminants and are widely detected in humans and wildlife, water, soil and air. PFAS are primarily used for their stain repellency properties and their surfactant characteristics, for example, in foams to combat petroleum fires. Even though there are an estimated 5,000 unique PFAS industrially manufactured, most monitoring efforts are focused on only 20-30 compounds. Non-target acquisition using high-resolution, accurate mass spectrometry is beneficial for elucidating unknown compound structures, such as PFAS. However, traditional fragmentation methods using collision-induced dissociation (CID) can be too aggressive to form diagnostic MS/MS spectra. Alternatively, electron-activated dissociation (EAD) has shown potential as a form of fragmentation.

MATERIALS AND METHODS

Standard solutions of 50 PFAS compounds including 5:3 FTB, 5:1:2 FTB, AmPr-FHxSA, TAmPR-FHxSA, and 6:2 FTSA-PrB were purchased from Wellington Laboratories (Guelph, ON). The standards were infused on the ZenoTOF 7600 system using both CID and EAD fragmentation modes in effort to compare the spectra generated by the two unique techniques. In separate EAD experiments, the kinetic energy (KE) was ramped from -10 to 25 eV and the electron beam current was ramped from 0 to 8000 V. Further, 10, 35 and 100 ms reaction times were tested. Finally, an AFFF mixture was injected on a reverse-phase LC column and subjected to gradient conditions for the purposes of comparing EAD and CID fragmentation in a real-world PFAS sample.

EAD FRAGMENTATION



- Free electrons are captured by ions and form a radical state which then fragments
  - Electrons introduced with different energies will induce fragmentation in different molecule types

Figure 1. Mechanism of EAD fragmentation.

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RESULTS

Kinetic energy (KE) ramping

Initial EAD KE ramping experiments were performed using the 5:3 FTB. Results showed that low KE values (<3 eV) were insufficient to cause precursor compound fragmentation (Figure 2). However, fragmentation was observed as the KE increased to the “hot ECD” and “EIEIO”. Specifically, fragments m/z 369, m/z 354, m/z 102 and m/z 58 were detected as the KE values increased greater to >5 eV. All fragments showed maximum intensity in the EIEIO region, except for the m/z 369 fragment.

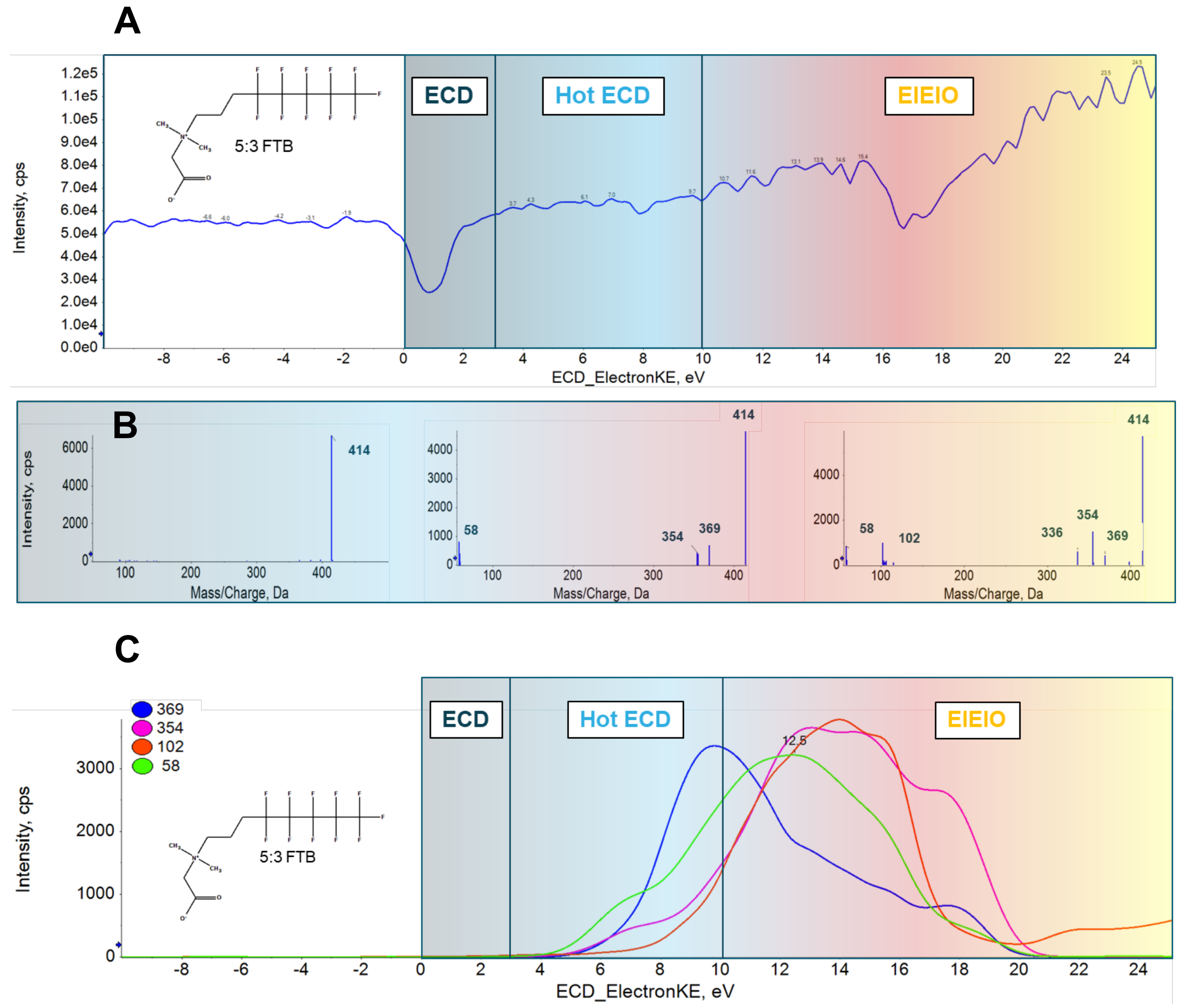
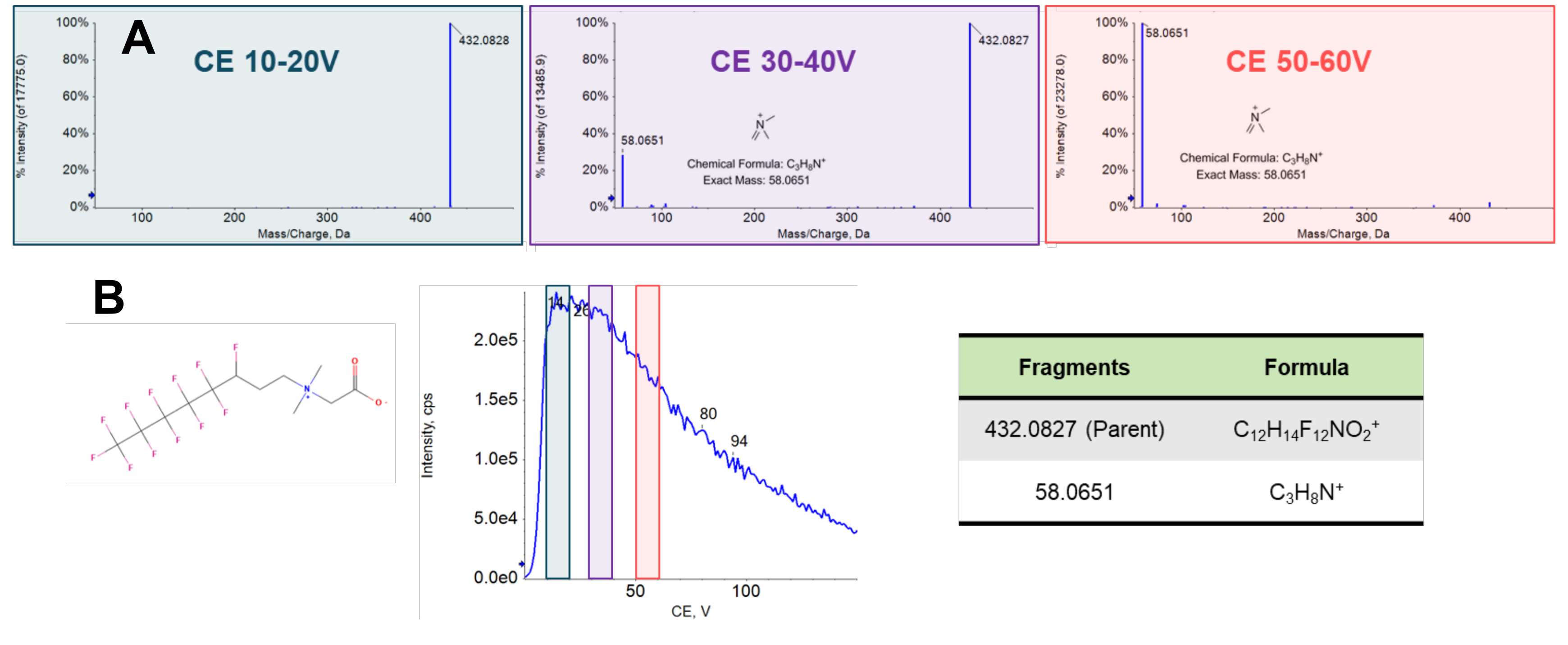


Figure 2. Kinetic energy ramping from -10 to 25 eV using EAD fragmentation mode for 5:3 FTB. More fragments were generated at KE values associated with “hot ECD” (3-10 eV) and “EIEIO” (10-25 eV).
A) Spectra intensity versus KE. B) MS/MS spectra generated during ECD, hot ECD and EIEIO. C) Fragment intensity versus KE.

Comparing CID and EAD fragmentation

To further explore the potential benefits of EAD fragmentation, the 5:1:2 FTB solution was infused using both CID and EAD fragmentation modes. The MS/MS spectra generated from CID fragmentation showed only formation of the m/z 58.0651 Da fragment ($C_3H_8N^+$) during the 3 ranges of collision energy (CE) tested: 10-20 eV, 30-40 eV and 50-60 eV (Figure 3A). In contrast, the MS/MS spectra generated from EAD fragmentation showed many more fragments, particularly at KE=16 eV (Figure 4).



Fragments	Formula
432.0827 (Parent)	$C_{12}H_{14}F_{12}NO_2^+$
58.0651	$C_3H_8N^+$

Figure 3. A) Fragmentation spectra generated using CID fragmentation of the 5:1:2 FTB at CE ramps from 10-20 eV (far left), 30-40 eV (center) and 50-60 eV (far right). The only fragment observed during CID was the $C_3H_8N^+$ fragment at m/z 58.0651. B) 5:1:2 FTB structure, and intensity vs. CE profile showing highlighted CE regions

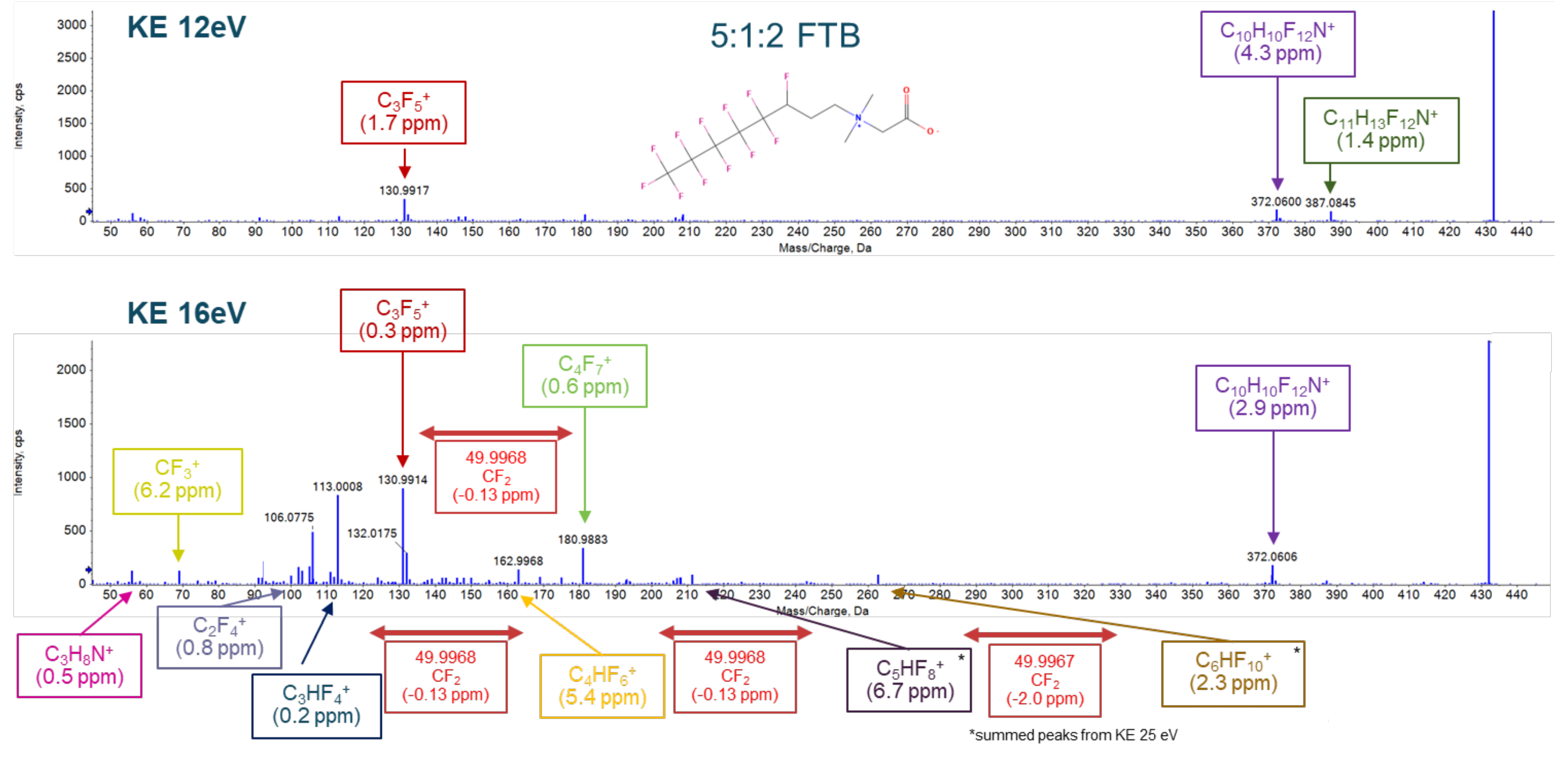


Figure 4. Fragmentation spectra generated using EAD fragmentation of the 5:1:2 FTB at KE values of 12 eV (top) and 16 eV (bottom). The KE=12 eV spectrum showed the formation of 3 fragments, while the KE=16 eV spectrum showed the formation of 16 unique fragments.

Using EAD fragmentation to identify PFAS in an AFFF mixture

The AFFF mixture that was separated using the LC column and gradient conditions showed the presence of the perfluorobutane sulfonamido propyl dimethyl quaternary amine propanoate using both EAD and CID fragmentation (molecular structure shown in Figure 5). However, the EAD fragmentation spectrum showed additional, unique fragments that were not observed during CID fragmentation (Figure 5). Therefore, EAD fragmentation might act as an additional, orthogonal source of confirmation for the identification of unknown PFAS compounds.

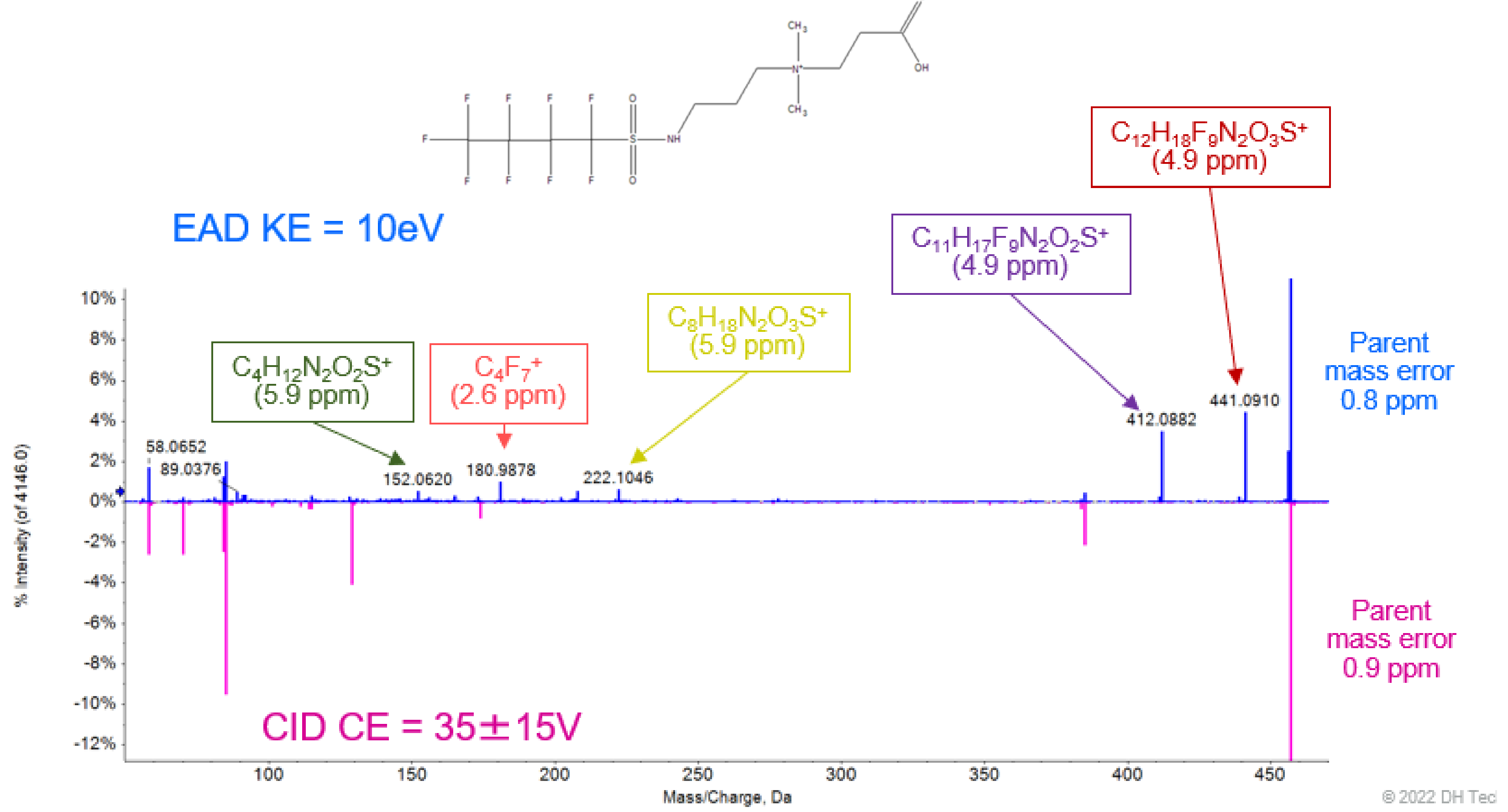


Figure 5. Fragmentation spectra generated using EAD fragmentation in an AFFF mixture. EAD showed the generation of several unique fragments as compared to CID fragmentation.

CONCLUSIONS

In conclusion, EAD fragmentation of PFAS compounds using the ZenoTOF 7600 system showed the formation of unique fragments, as compared to traditional CID fragmentation. In general, the MS/MS spectra generated by EAD showed more fragments which could be beneficial for confirming compound identity during non-target analysis.

TRADEMARKS/LICENSING