Use of Electron Activated Dissociation (EAD) on the SCIEX ZenoTOF 7600 system to elucidate PFAS structures

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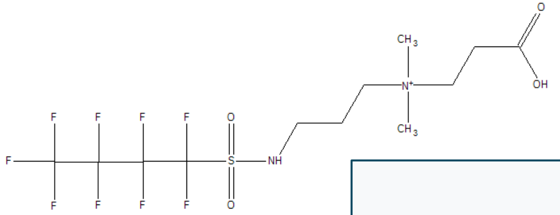
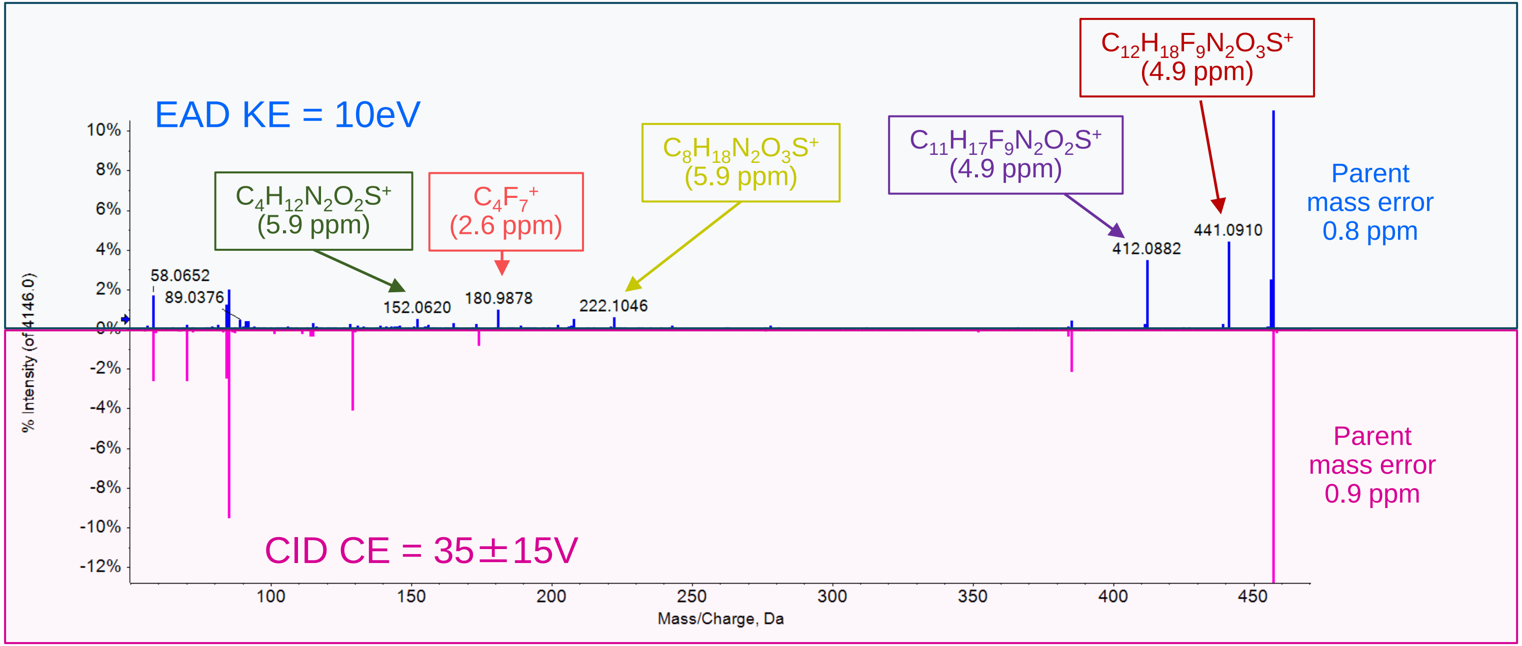
The Power of Precision

EAD provides more structural information than CID

PERFLUOROBUTANE SULFONAMIDO PROPYL DIMETHYL QUATERNARY AMINE PROPANOATE





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Outline

- Aqueous film forming foam (AFFF) is complex mixture of PFAS compounds, poorly understood
- SCIEX 7600 ZenoTOF system has alternative fragmentation mechanism, electron activated disassociation (EAD)
- EAD fragmentation is “softer” than traditional CID, provides additional structural information
- Application of EAD fragmentation to AFFF sample

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Early awareness of PFAS in AFFF

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Novel 2001 paper from Analytical Chemistry

- PFAS in Etobicoke Creek near Pearson Airport (Toronto, ON)
- 22,000 L spill of AFFF
- Total PFAS measured using 19F NMR
- PFOS, PFHxS, PFOA by LC-MS/MS

Anal. Chem. **2001,** *73,* 2200−2206

Determination of Perfluorinated Surfactants in Surface Water Samples by Two Independent Analytical Techniques: Liquid Chromatography/Tandem Mass Spectrometry and ^{19}F NMR

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Department of Chemistry, 80 St. George Street, University of Toronto, Toronto, Ontario, Canada M5S 3H6, Department of Environmental Biology, University of Guelph, Guelph, Ontario, Canada N1G 2W1, National Water Research Institute, Environment Canada, 867 Lakeshore Road, Burlington, Ontario, Canada L7R 4A6

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Introduction: characterizing PFAS in AFFF

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Environmental Science & Technology
Article
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Discovery of 40 Classes of Per- and Polyfluoroalkyl Substances in Historical Aqueous Film-Forming Foams (AFFFs) and AFFF-Impacted Groundwater

Krista A. Barzen-Hanson,[†] Simon C. Roberts,[∇,‡] Sarah Choyke,[§] Karl Oetjen,[‡] Alan McAlees,[∥] Nicole Riddell,[∥] Robert McCrindle,[⊥] P. Lee Ferguson,[§] Christopher P. Higgins,[*,‡] and Jennifer A. Field[*,#]

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[#]Department of Environmental and Molecular Toxico
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Supporting Information

ABSTRACT: Aqueous film-forming foams (AFFFs
(PFASs), are released into the environment durin
historical applications of AFFF at military sites w
equipment testing. Recent data on AFFF-impacted
remain unidentified. In an attempt to close the n
fluorotelomer-based AFFFs, commercial products,
military bases was conducted to identify the remai
time-of-flight mass spectrometry was used for c
Kendrick mass defect plots and a "nontarget" R scrip
of previously reported PFASs. Forty classes of nov
discovered, and an additional 17 previously reporte
and/or AFFF-impacted groundwater. All 57 classes r
from collective author knowledge. Thirty-four of t
electrochemical fluorination (ECF) processes, mos
newly discovered PFASs found only in AFFF-impac
two classes are fluorotelomer-derived, which sugge
environment.

Environmental Science & Technology
Article
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Identification of Novel Fluorinated Surfactants in Aqueous Film Forming Foams and Commercial Surfactant Concentrates

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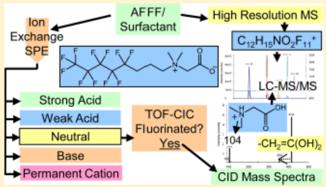
Department of Chemistry, University of Toronto, 80 St George Street, Toronto, M5S 3H6 Ontario, Canada

Supporting Information

ABSTRACT: Recent studies comparing the results of total organofluorine-combustion ion chromatography (TOF-CIC) to targeted analysis of perfluoroalkyl and polyfluoroalkyl substances (PFASs) by liquid chromatography tandem mass spectrometry (LC-MS/MS) have shown that a significant yet variable portion of the total organofluorine in environmental and biological samples is in the form of unknown PFASs. A portion of this unknown organofluorine likely originates in proprietary fluorinated surfactants not included in LC-MS/MS analyses and not fully characterized by the environmental science community, which may enter the environment through use in aqueous film forming foams (AFFFs) for firefighting. Contamination of water, biota, and soils with various PFASs due to AFFF deployment has been documented. Ten fluorinated AFFF concentrates, 9 of which were obtained from fire sites in Ontario, Canada, and two commercial fluorinated surfactant concentrates were characterized in order to identify novel fluorinated surfactants. Mixed-mode ion exchange solid phase extraction (SPE) fractionated fluorinated surfactants based on ionic character. High resolution mass spectrometry assigned molecular formulas to fluorinated surfactant ions, while collision induced dissociation (CID) spectra assisted structural elucidation. LC-MS/MS detected isomers and low abundance fluorinated chain lengths. In total, 12 novel and 10 infrequently reported PFAS classes were identified in fluorinated chain lengths from C3 to C15 for a total of 103 compounds. Further research should examine the environmental fate and toxicology of these PFASs, especially their potential as perfluoroalkyl acid (PFAA) precursors.



AFFF is more complex than only PFOS & PFOA!

Contains >40 classes of PFAS; some classes can degrade to perfluorinated carboxylates & sulfonates

High-resolution mass spectrometry used to identify novel PFAS classes

Mass spectral libraries are built to aid compound identification

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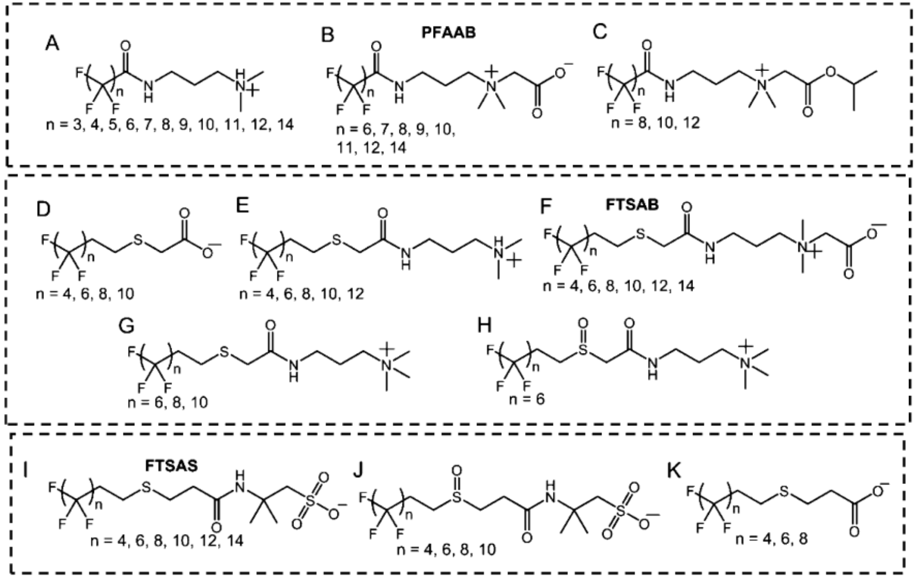
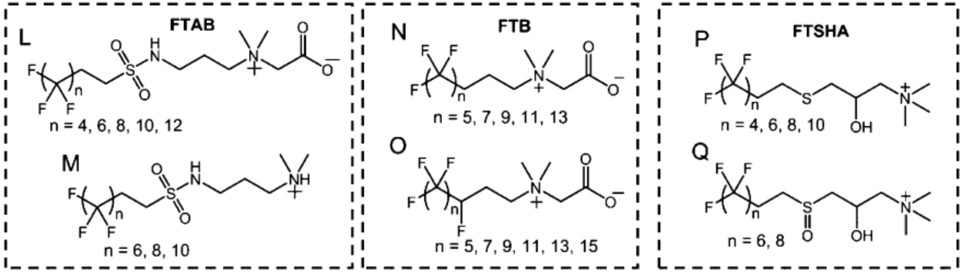
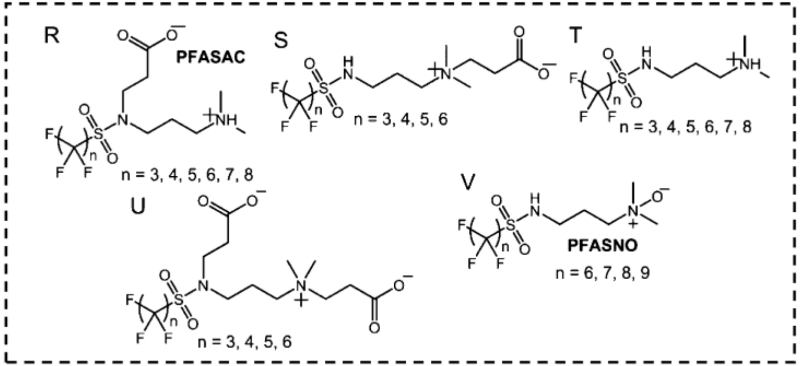
Introduction: characterizing PFAS in AFFF



Unique AFFF-derived PFAS contain perfluorinated tail and complex alkyl headgroups





Source: D’Agostino & Mabury. *Environ. Sci. Technol.* **2014**, 48(10): 121-129

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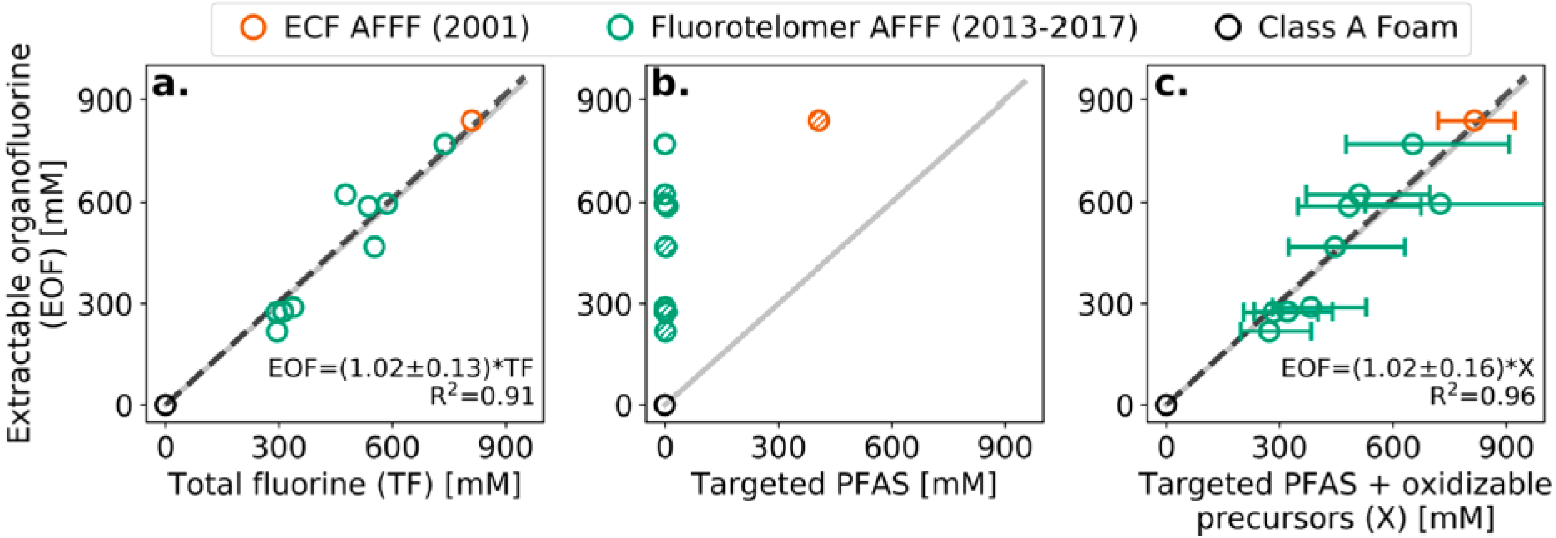
Introduction: characterizing PFAS in AFFF



- Targeted LC-MS/MS methods **poorly quantify** PFAS in AFFF
- Majority of “unknown” PFAS are precursors to perfluorinated acids

Source: Ruyle et al. *Environ. Sci. Technol. Lett.* **2021**, 8: 59-65

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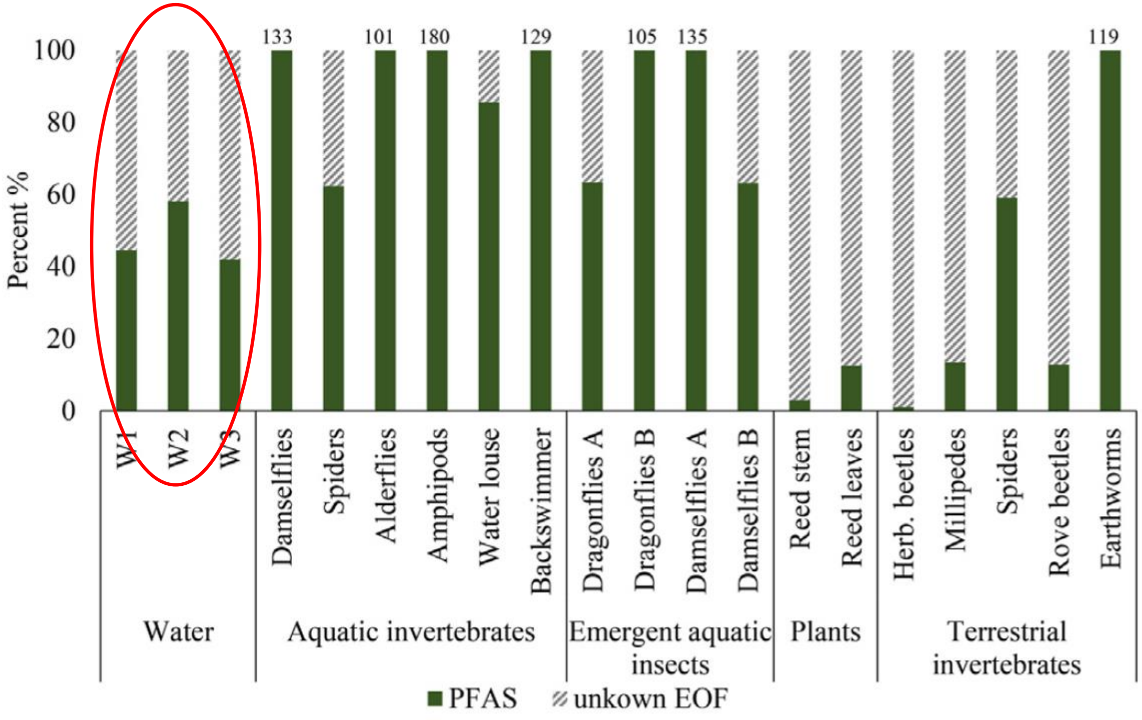
Unknown PFAS in an AFFF-impacted environment



- AFFF-contaminated pond
- Total fluorine (TF), extractable organic fluorine (EOF), targeted analysis, suspect screening
- 42-58% of EOF in pond water not explained by targeted analysis
- **Non-target analysis needed to understand PFAS environmental burden**

Source: Koch et al. *Chemosphere* **2021**, 276: 130179

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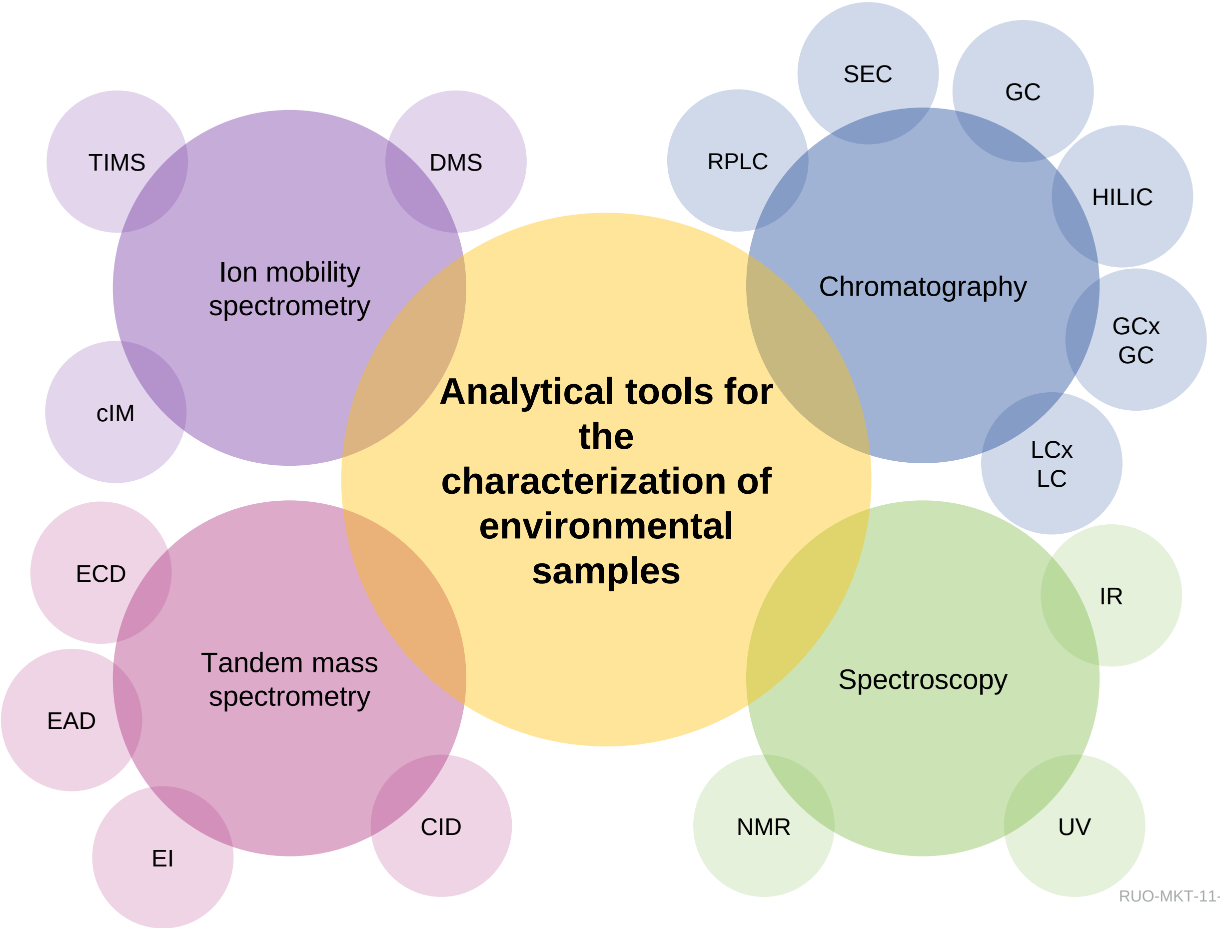
Characterization of environmental samples



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ZenoTOF 7600 system

ZenoTOF 7600 System

QUALITATIVE FLEXIBILITY COMBINED WITH QUANTITATIVE POWER

- ZenoTOF 7600 system combines the flexibility of multiple fragmentation options
- High sensitivity MS/MS with the ZenoTOF 7600 system
- SCIEX OS software provides an intuitive workflow interface for easy acquisition and data processing

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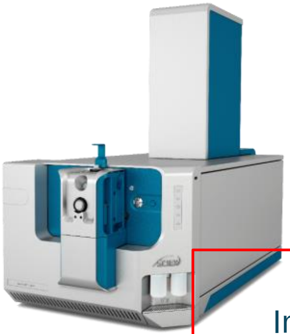
ZenoTOF 7600 system

ZenoTOF 7600 System

HARDWARE ADVANCEMENTS

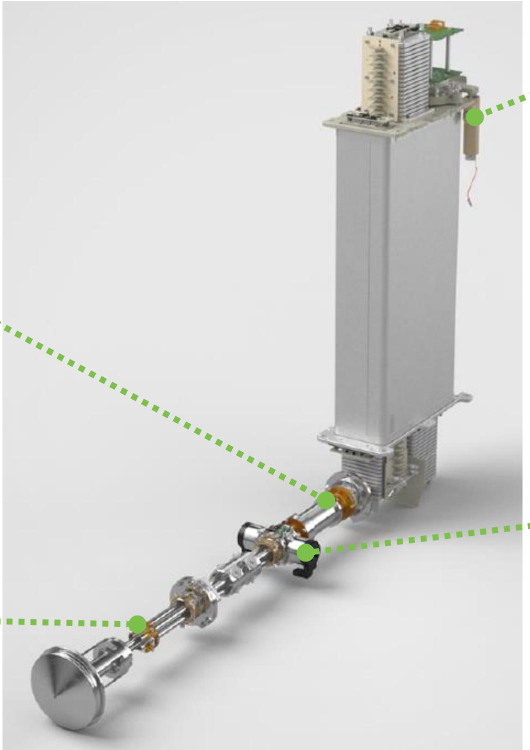


New

Zeno trap
Improved MS/MS
duty cycle gain ≥90%

New

New Q0 design for
improved ion transmission
and maintenance



New

Wide dynamic range

- 5GHz, 10bit ADC with 40GHz TDC timing with 25 psec detection rate. High speed pulse counting to maintain resolution and mass accuracy >130Hz and over 5 orders LDR

New

Complementary fragmentation with increased sensitivity using the EAD cell

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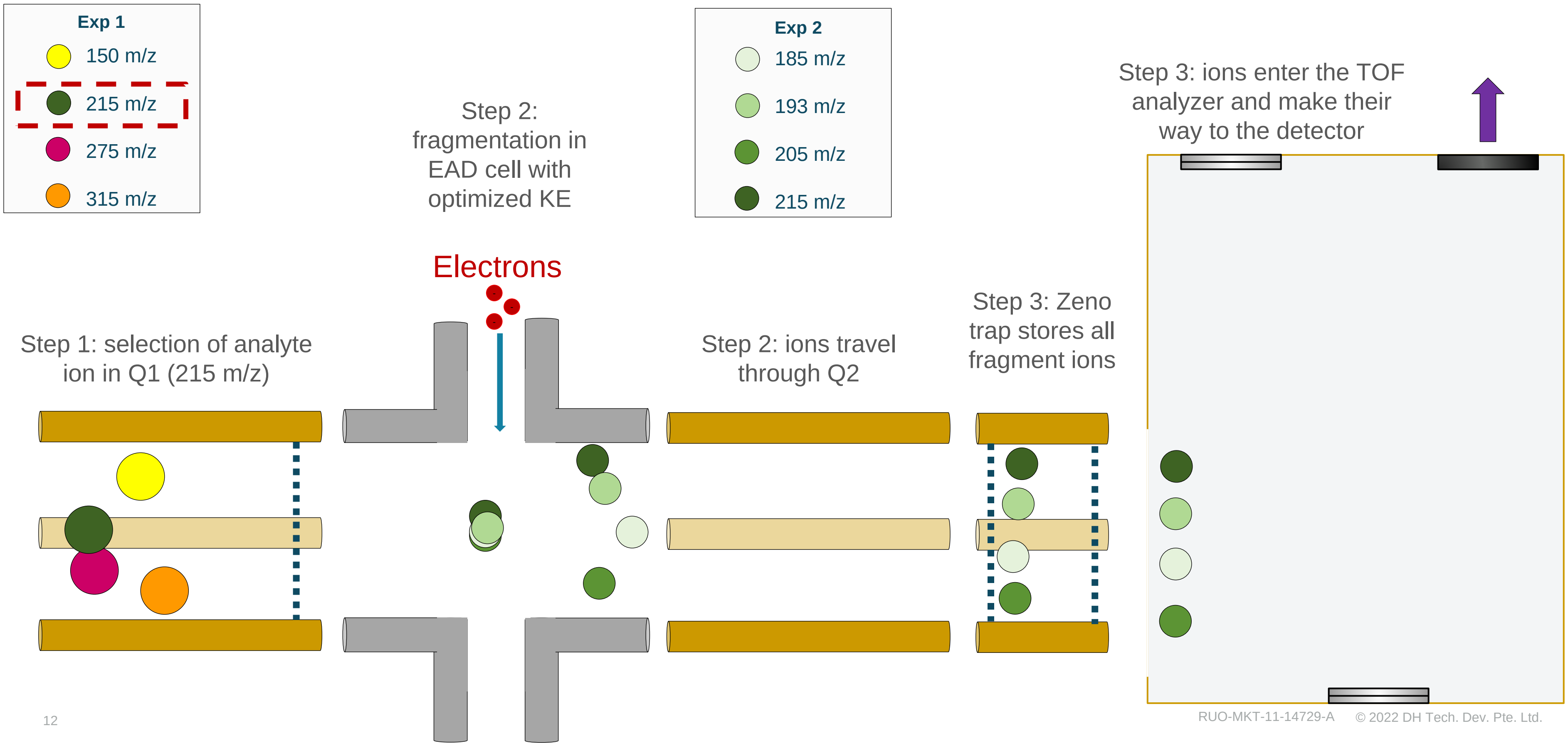
Electron activated dissociation (EAD)



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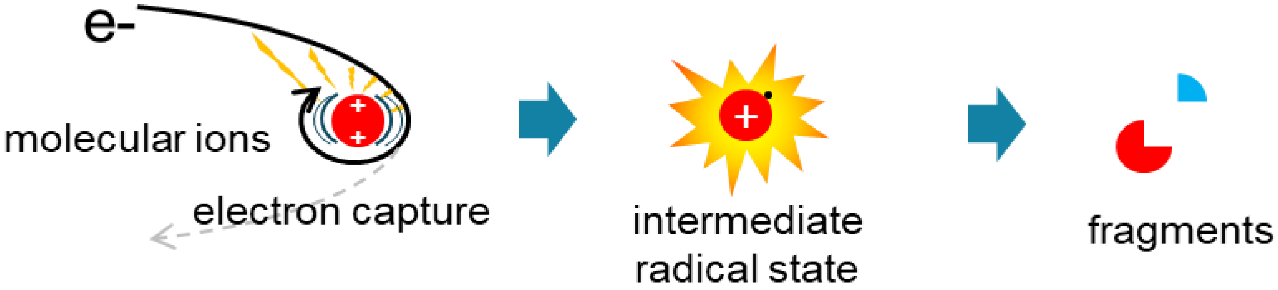
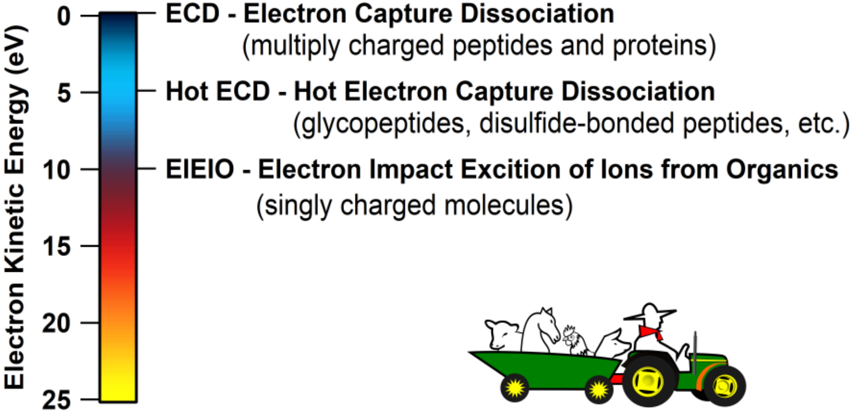
Electron activated dissociation (EAD)



- 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



T. Baba *et al. Anal.Chem*. 2014

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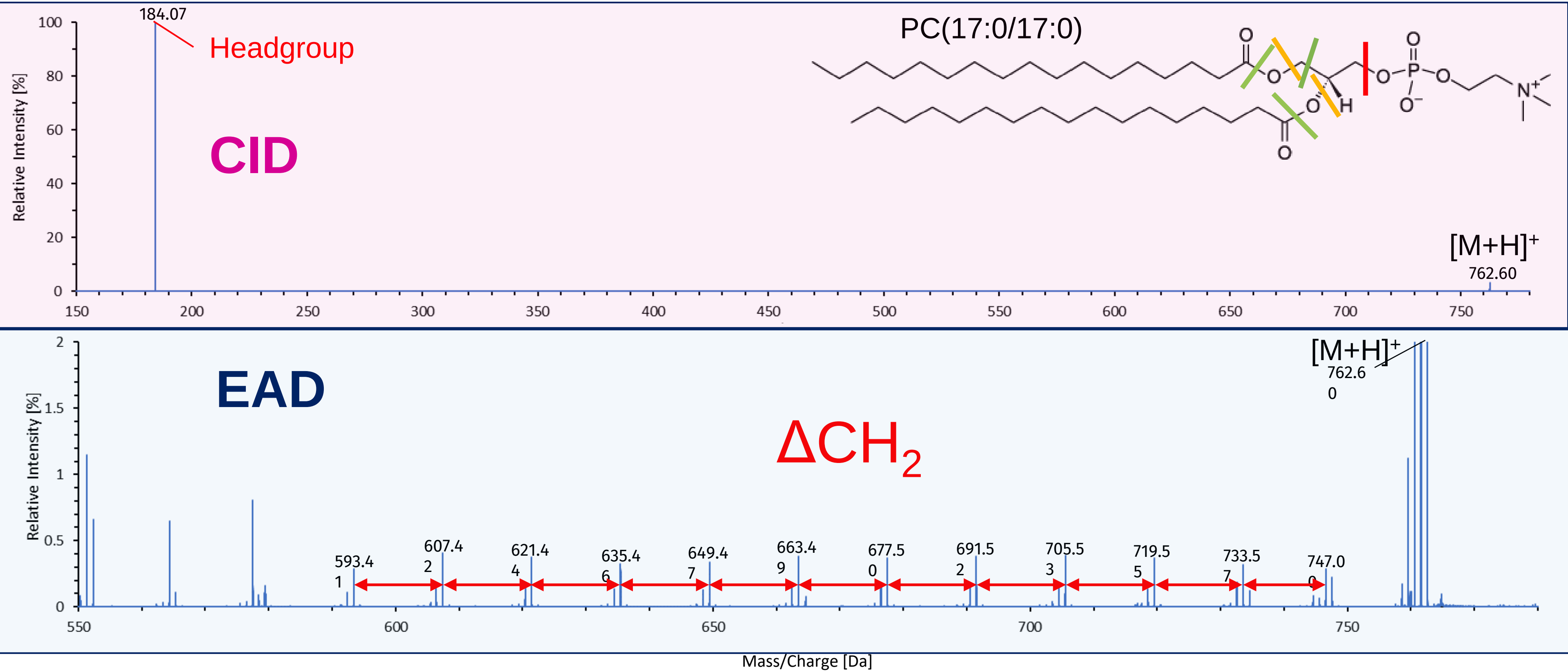
CID vs EAD



Courtesy of DSM

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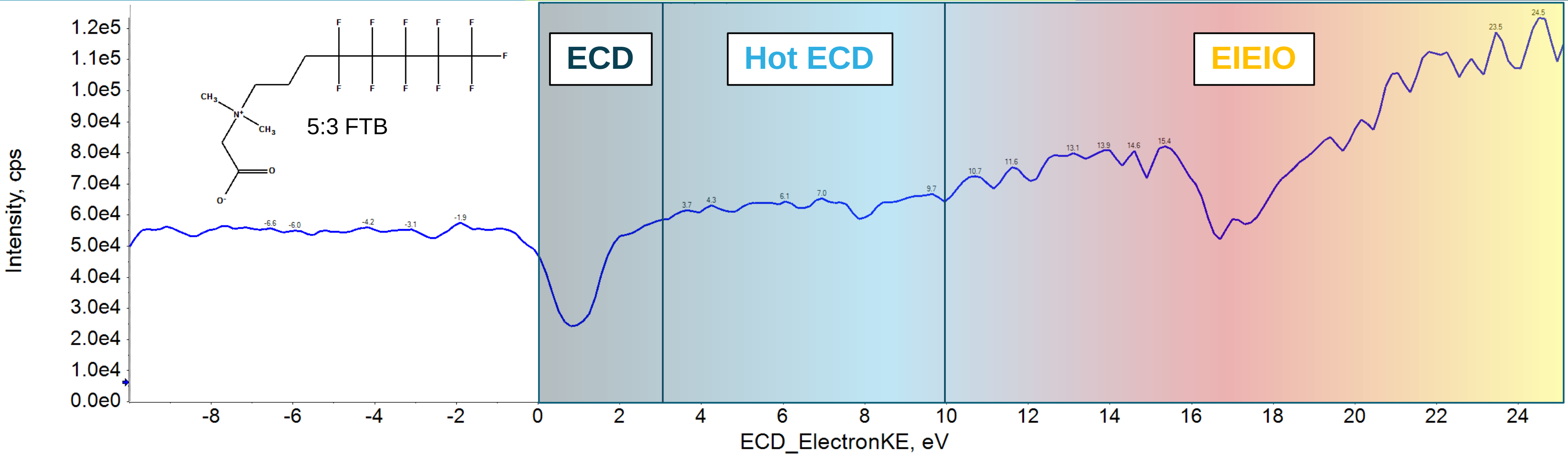
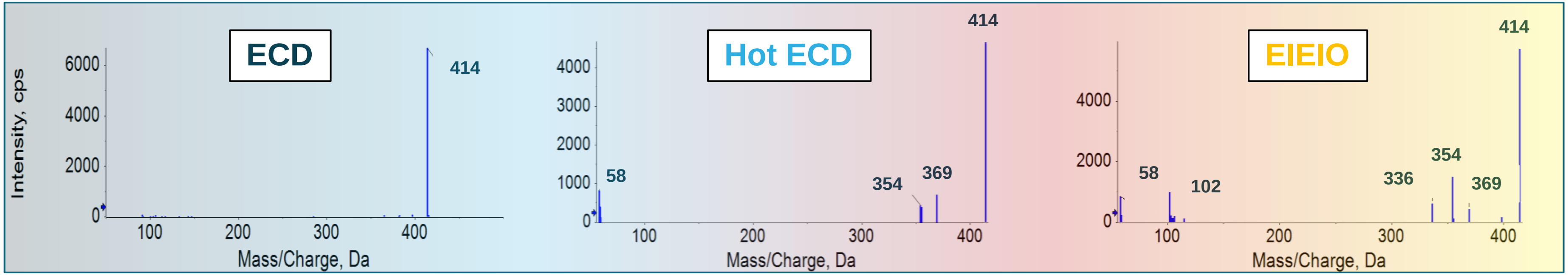
Ramping the kinetic energy





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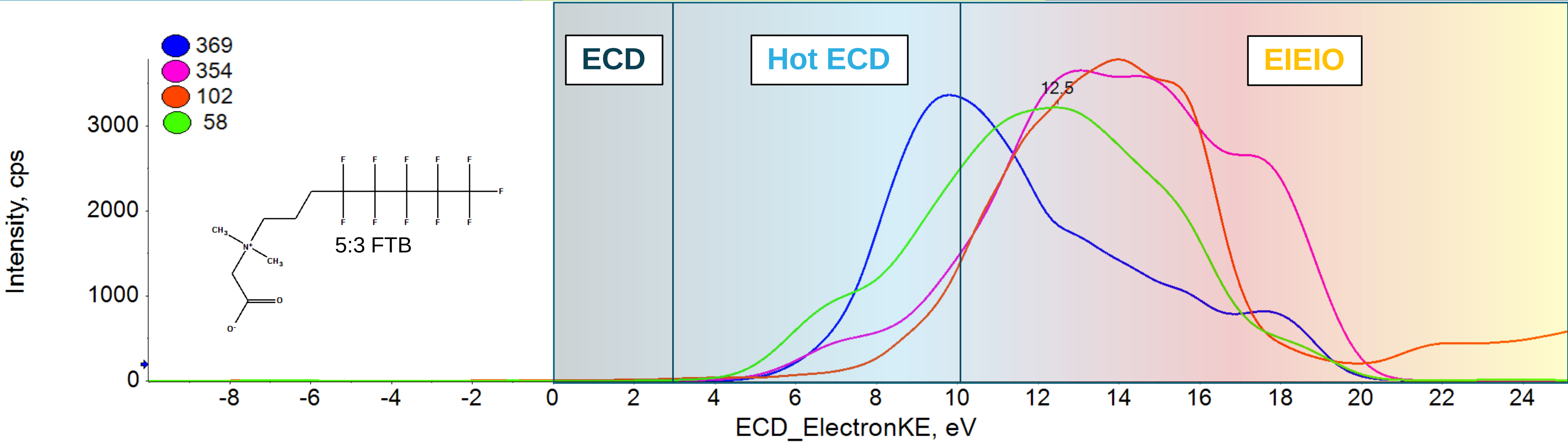
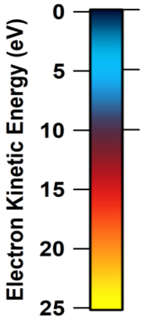
Ramping the kinetic energy





ECD - Electron Capture Dissociation
(multiply charged peptides and proteins)

Hot ECD - Hot Electron Capture Dissociation
(glycopeptides, disulfide-bonded peptides, etc.)

EIEIO - Electron Impact Excition of Ions from Organics
(singly charged molecules)

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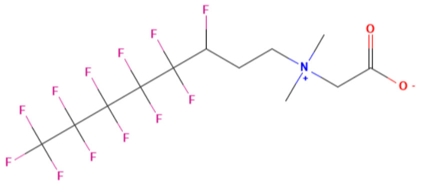
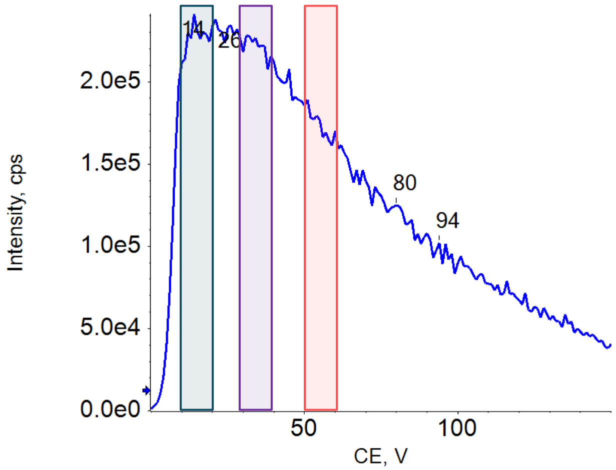
Where does EAD become useful?

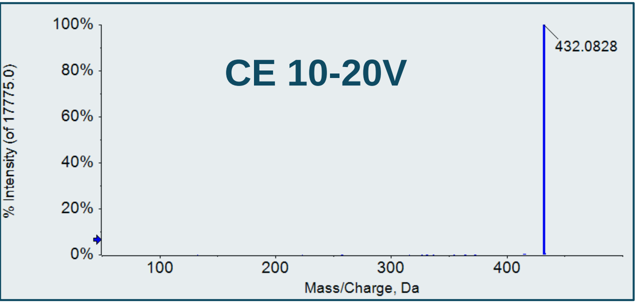
Using CID

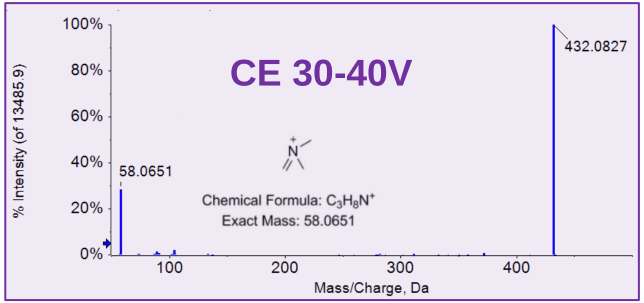


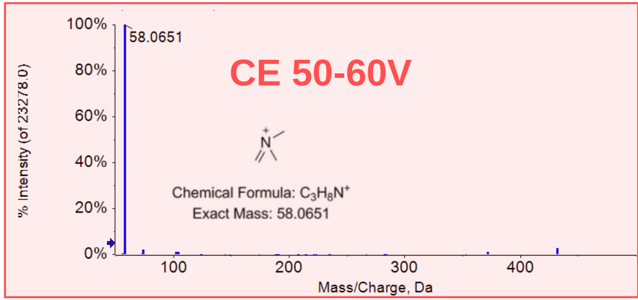
5:1:2 FTB



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







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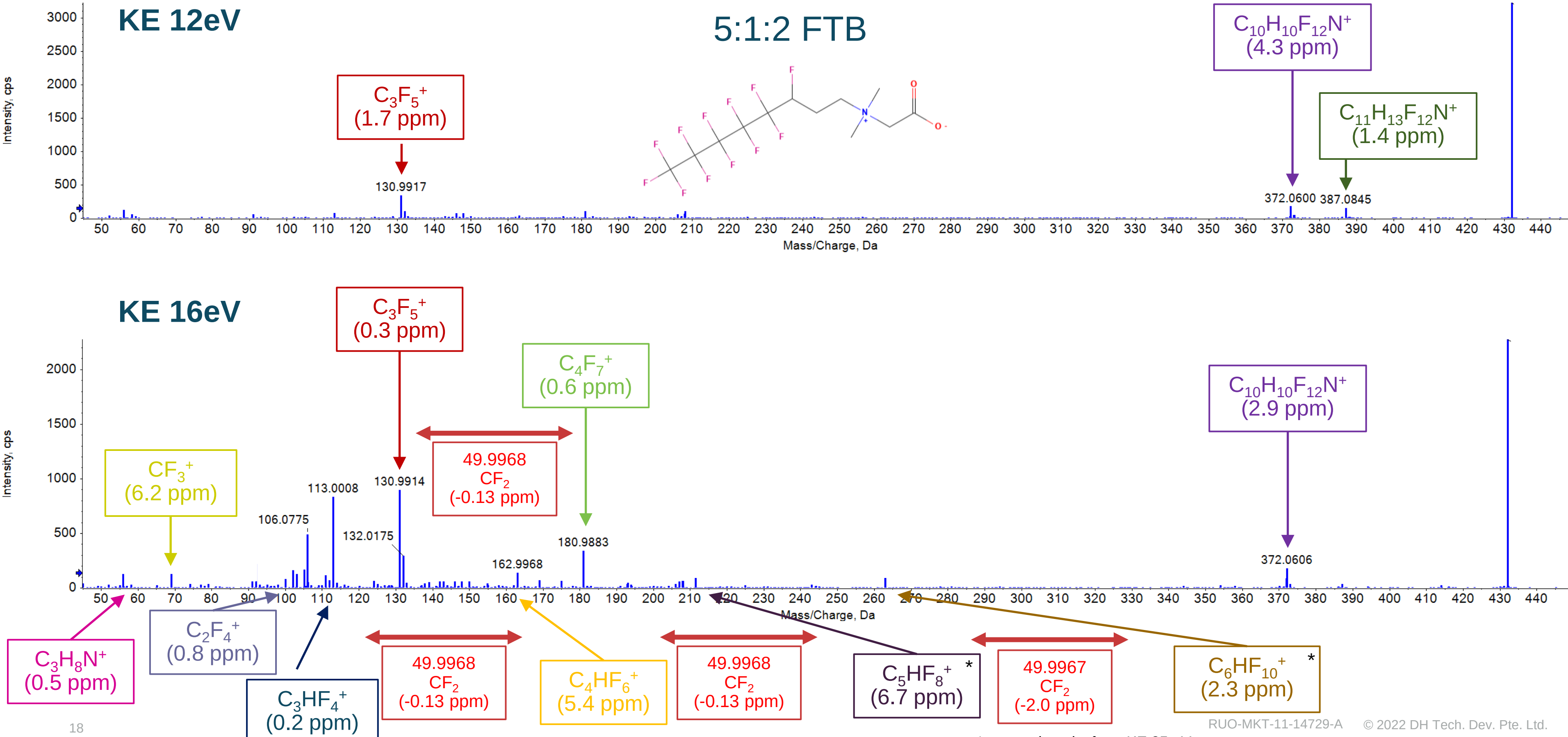
Where does EAD become useful?



*summed peaks from KE 25 eV

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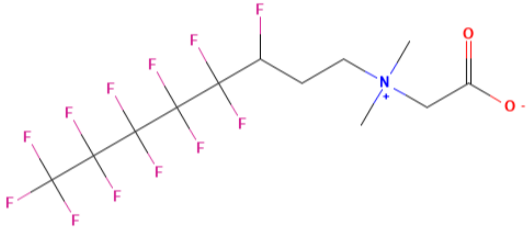
Where does EAD become useful?

5:1:2 FTB



Calculated fragments formulas	CID	EAD
$C_{12}H_{14}F_{12}NO_2^+$ (Parent)	✓	✓
$C_{11}H_{13}F_{12}N^+$		✓
$C_{10}H_{10}F_{12}N^+$		✓
$C_6HF_{10}^+$		✓
$C_5HF_8^+$		✓
$C_4F_7^+$		✓
$C_4HF_6^+$		✓
$C_3F_5^+$		✓
$C_3HF_4^+$		✓
$C_3H_8F_{12}NO^+$		✓
$C_2F_4^+$		✓
CF_3^+		✓
$C_3H_8N^+$		✓
$C_3H_8N^+$	✓	✓

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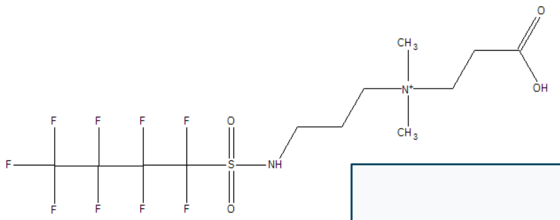
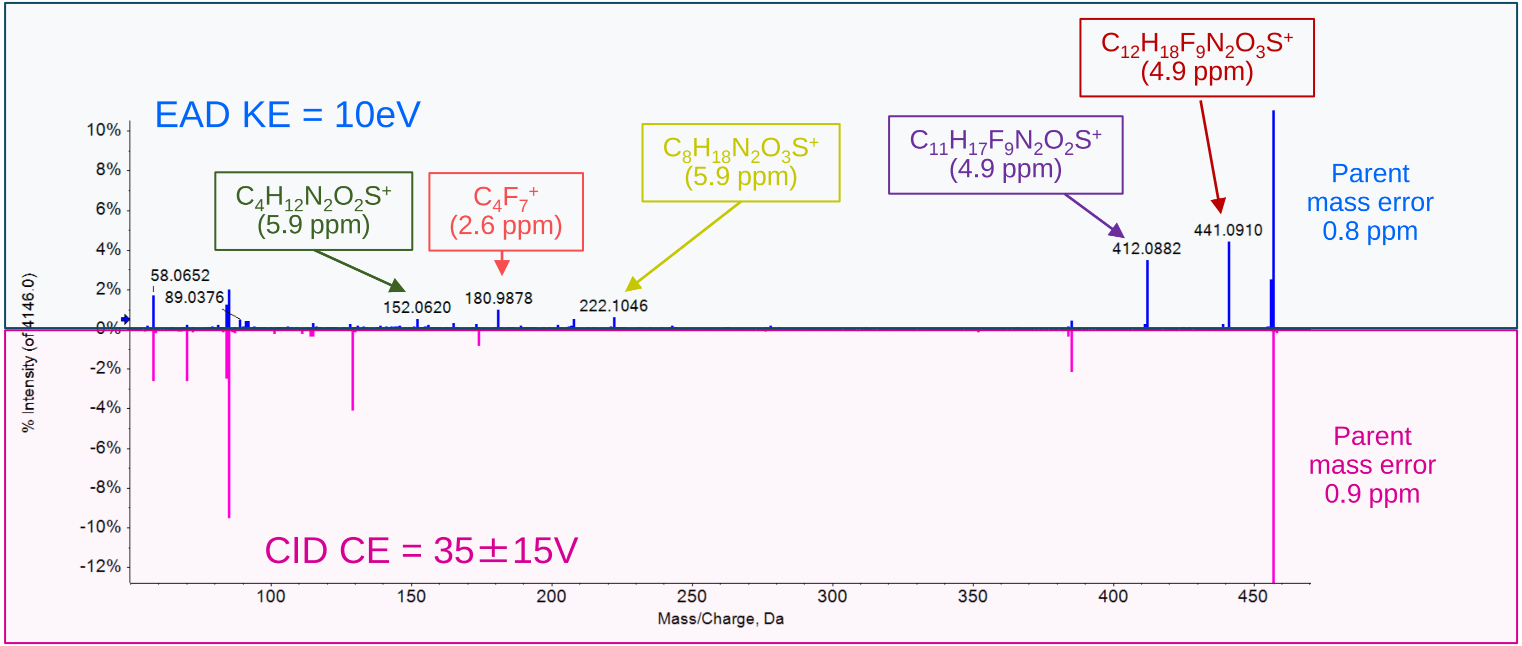
Analyzing AFFF with EAD

PERFLUOROBUTANE SULFONAMIDO PROPYL DIMETHYL QUATERNARY AMINE PROPANOATE





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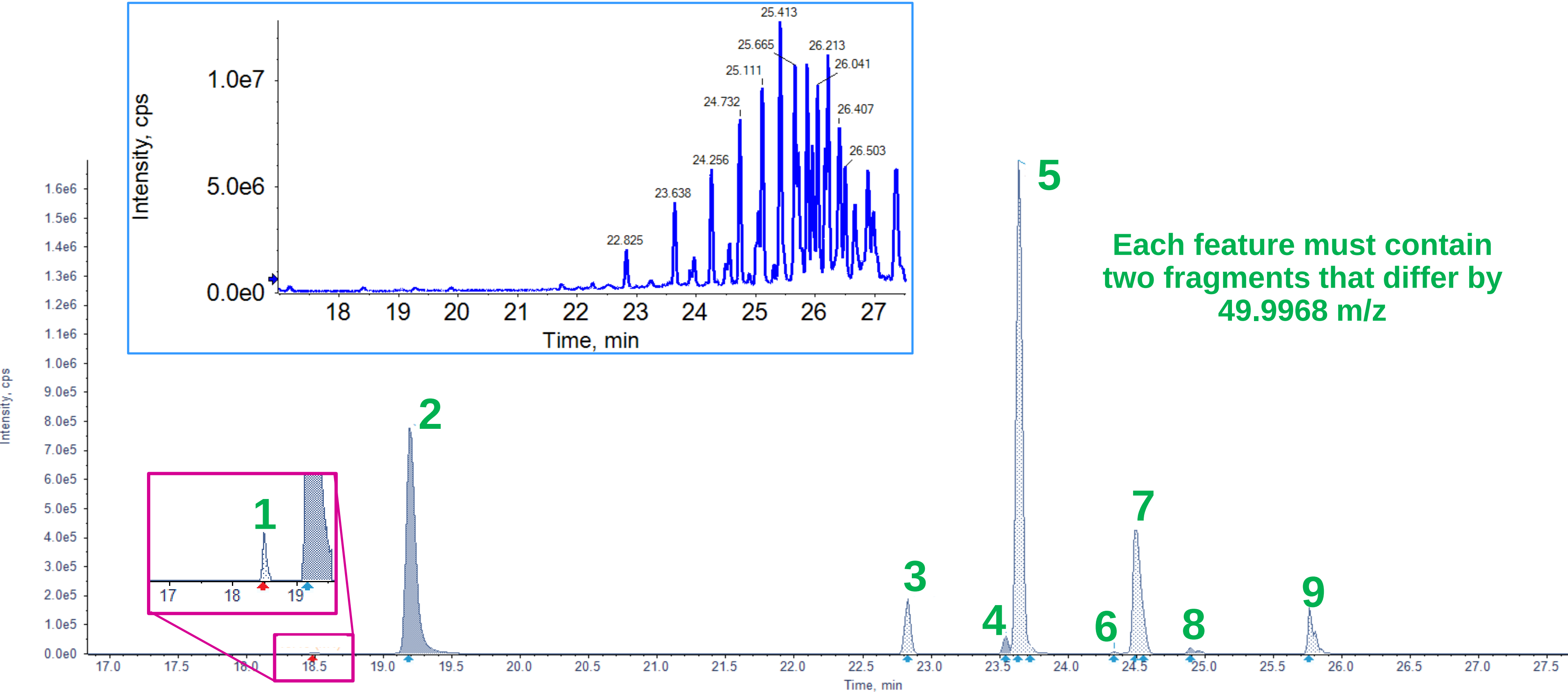
Querying EAD MS/MS spectra



Each feature must contain two fragments that differ by 49.9968 m/z

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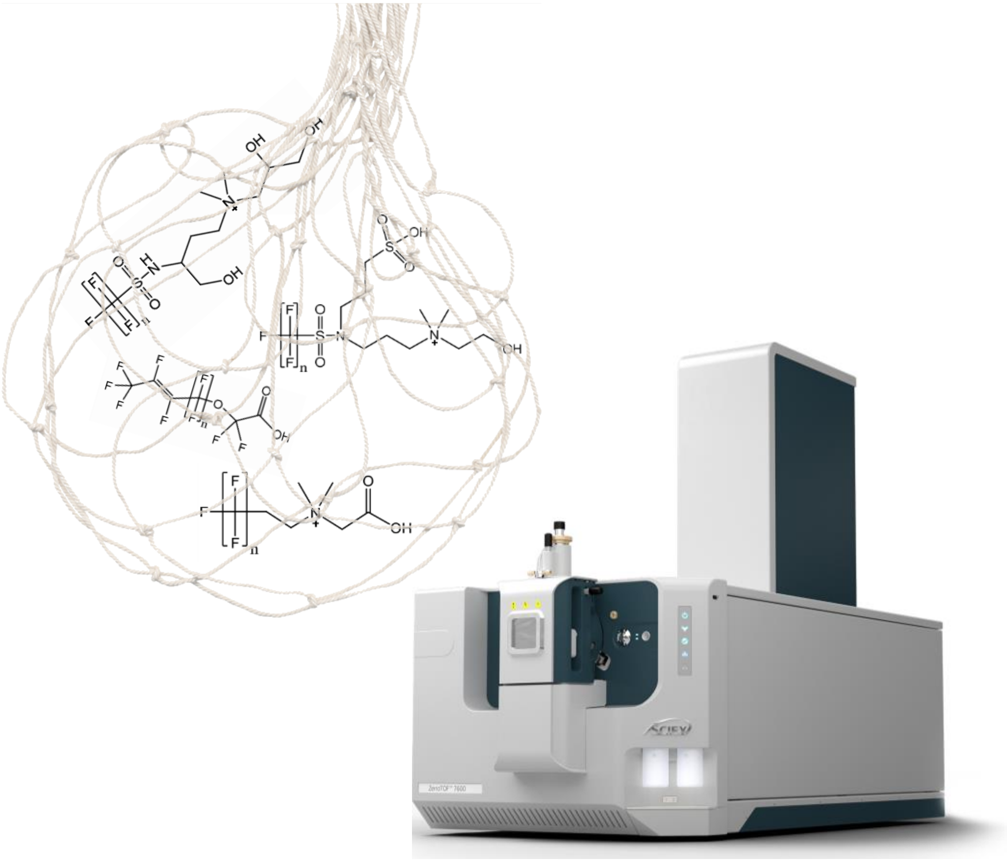
Future work

Next steps:

- Negative mode
- Structural elucidation workflows
- Identify fragments unique to PFAS compounds/classes



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Conclusions

- EAD fragmentation is an alternative to traditional CID
- EAD forms additional, diagnostic fragments that can be useful for structural elucidation of AFFF-derived PFAS
- Emerging technology with significant application in unknown screening of many environmental contaminants

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