Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

Pyrolysis-GC-HRMS with Soft Ionization

Rachel Sanig

Senior Scientist, *Waters Corporation*

Overview

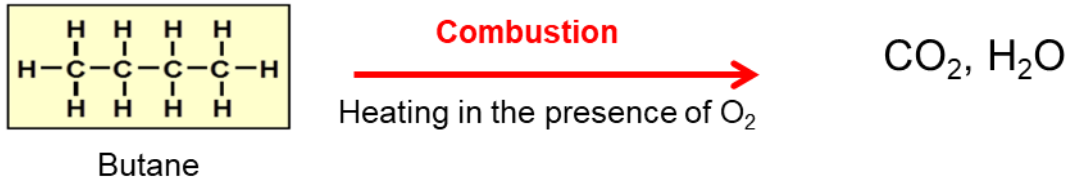
Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

- Introduction to pyrolysis
- Pyrolysis-GC/HRMS with soft ionization
- Applications
  - Comparison to Py-GC/MS with EI
  - Analysis of biobased plastics
  - Statistical analysis
  - Other applications

Pyrolysis

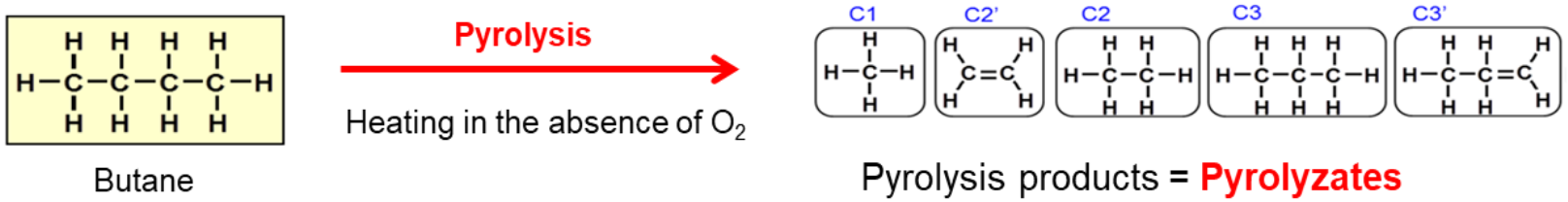
Combustion

- Hydrocarbon reacts with oxygen to produce carbon dioxide and water



Pyrolysis

- Pyrolysis process is done in the absence of oxygen.



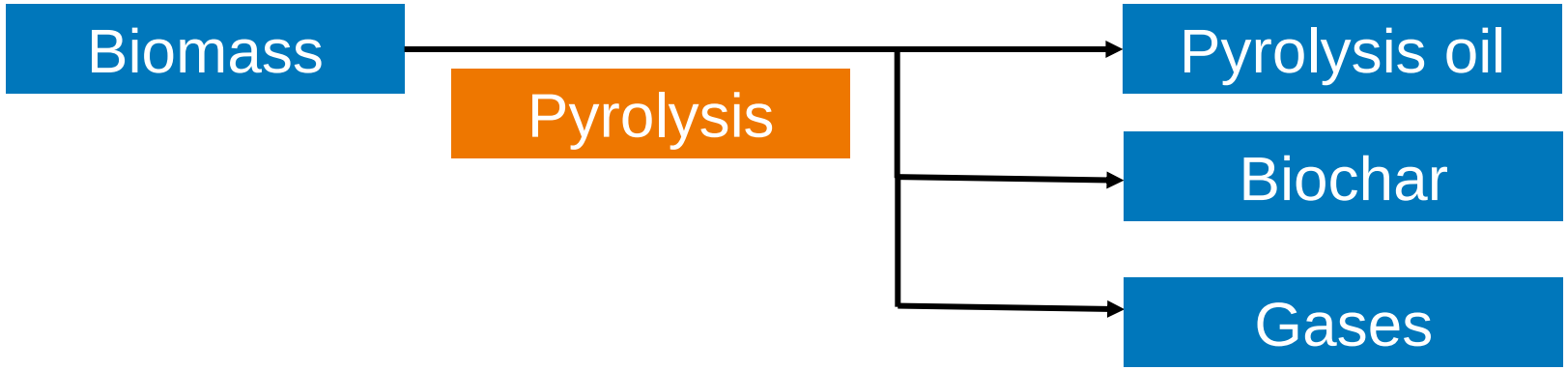
Applied vs Analytical

- There are two key applications for this technique.

Applied Pyrolysis

Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

Biomass decomposition



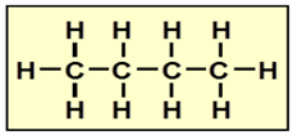
Chemical recycling

- Pyrolysis is **one of the main methods for chemical recycling of plastics**.
  - Breaks downs polymers to monomers with quality recovery of the recycled material
  - Suitable for challenging feedstocks containing mixture of several plastics and impurities

Analytical Pyrolysis

Pyrolysis

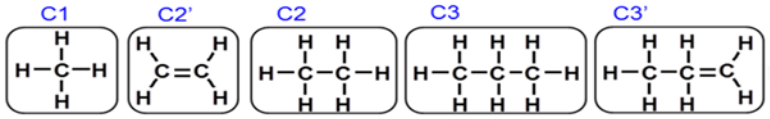
- Pyrolysis process is done in the absence of oxygen.



Butane

Pyrolysis

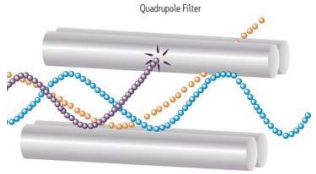
Heating in the absence of O_2



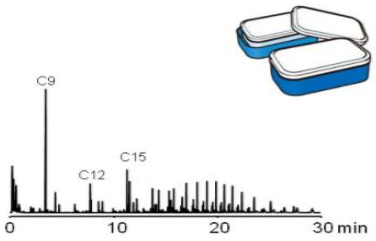
Pyrolysis products = **Pyrolyzates**

GC Separation

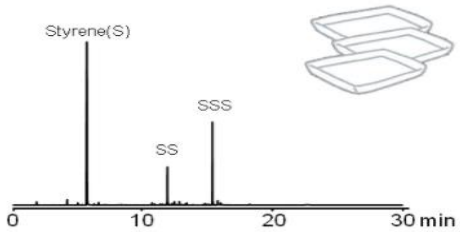
Mass Detection



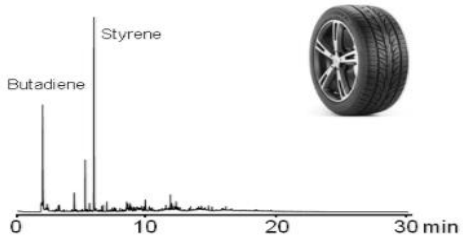
Pyrogram



Polypropylene (PP)



Polystyrene (PS)



Styrene-butadiene rubber (SBR)

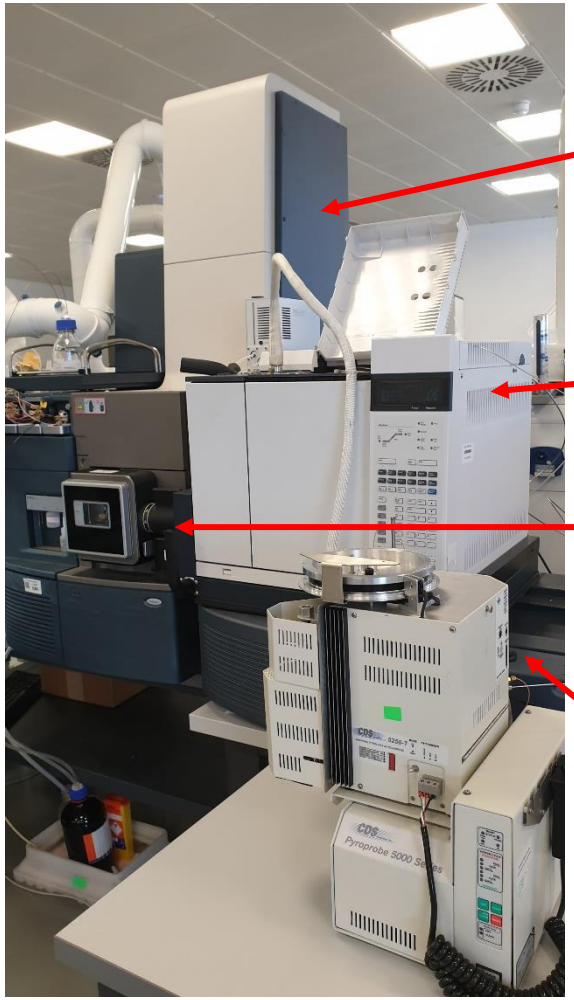
Pyrolysis-GCMS - Challenges and Limitations

Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

- Database search
  - While some monomers are listed in the database, not all pyrolyzates spectrum are registered.
- Analyzing unknowns
  - The pyrolysis process and electron ionization, or electron impact, (EI) do not generate intact molecular ions of pyrolyzates
  - Quad mass resolution is also too low to do elucidation and identify true unknowns
- Sensitivity of high mass range
  - High mass pyrolyzates, trimers and higher, are often sensitivity challenged
  - EI can make it difficult to confirm the molecular ion of high molecular weight polymers as these often are fragmented in the ionization process

Py-APGC HRMS can help with these analytical challenges

Connecting up the instruments



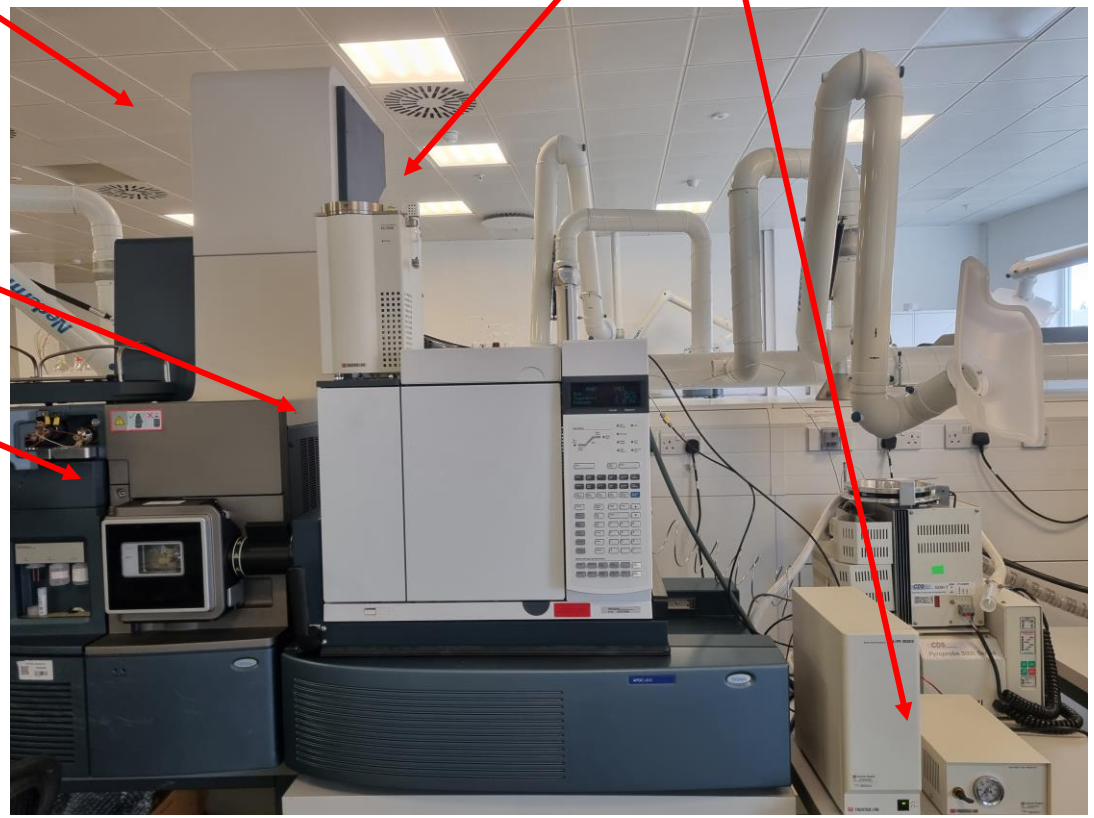
Xevo G2-XS QTof

GC

APGC Source

CDS Pyroprobe 5000 Series with autosampler

Frontier Auto-Shot Sampler (AS-1020E)

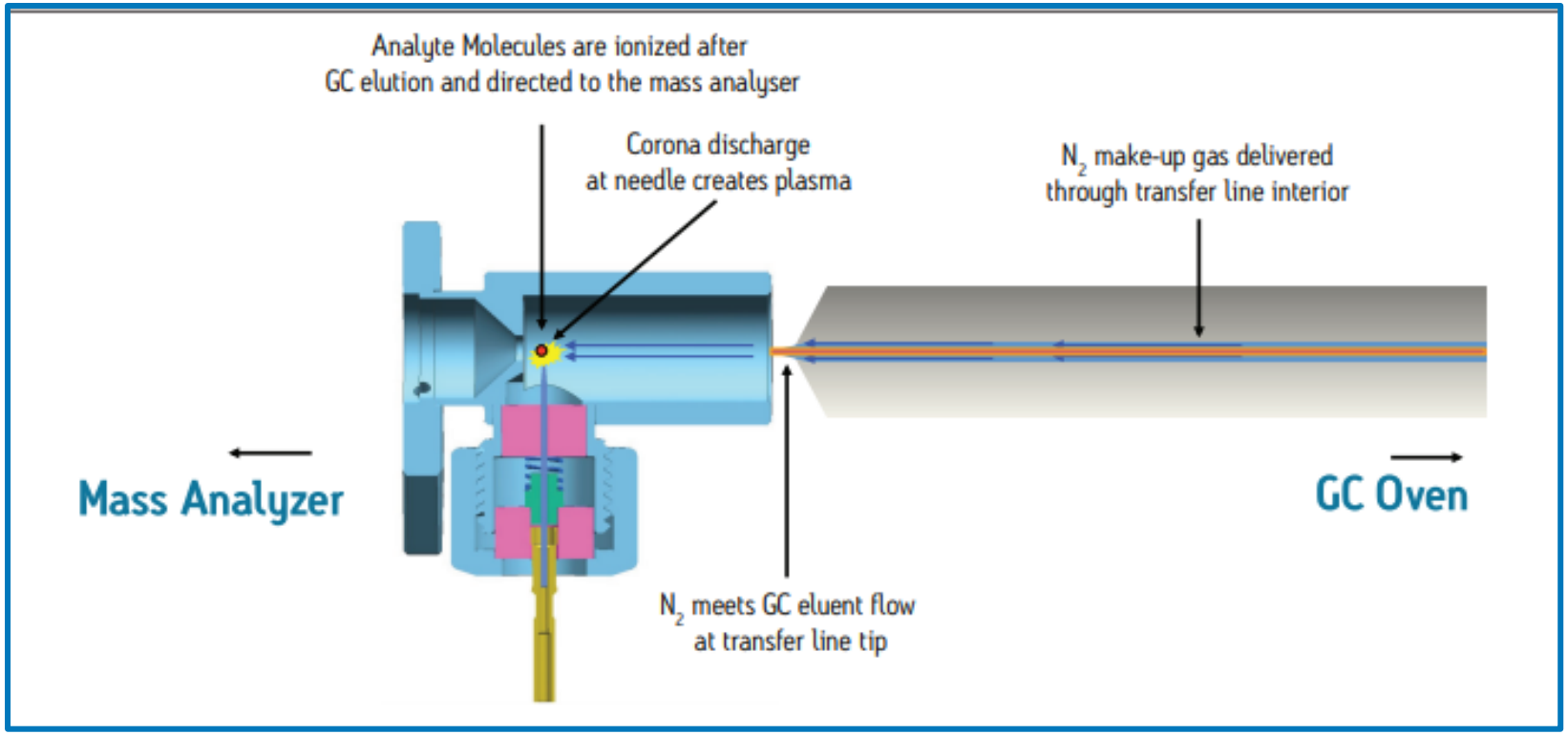


Pyrolysis GC-MS and Soft Ionization

Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

APGC (Atmospheric Pressure Gas Chromatography)

- Soft ionization



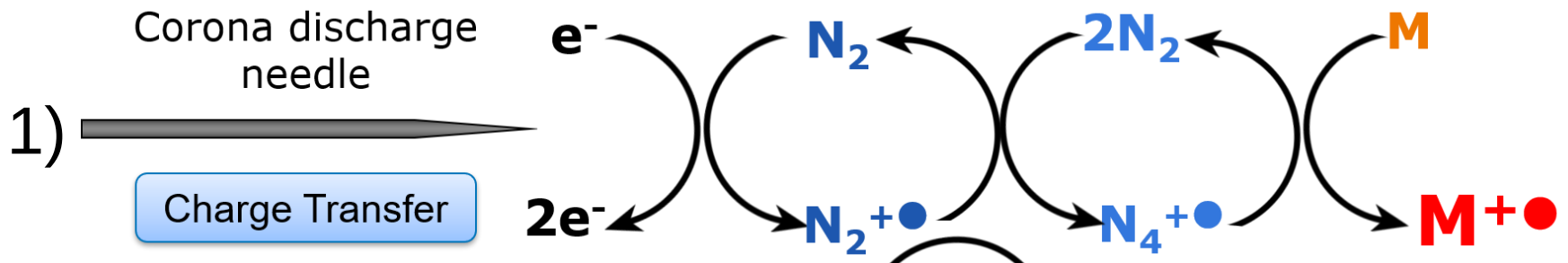
Pyrolysis GC-MS and Soft Ionization

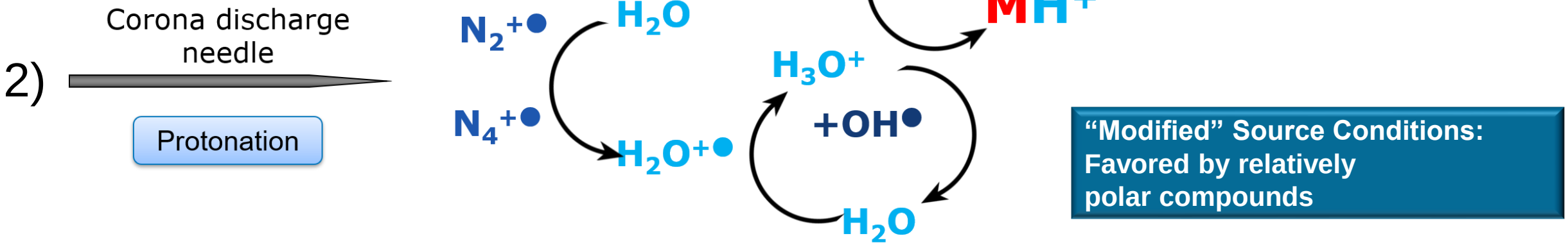
Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

APGC (Atmospheric Pressure Gas Chromatography)

- Soft ionization

"Dry" Source Conditions: Favored by relatively non-polar compounds



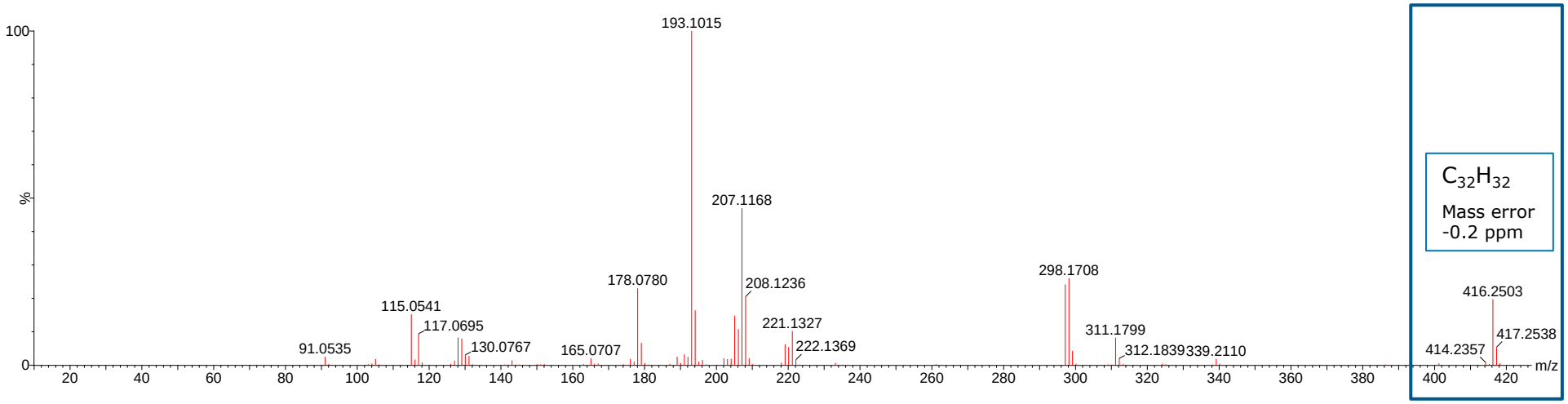


"Modified" Source Conditions: Favored by relatively polar compounds

Pyrolysis-APGC-QToF MS

Soft Ionization

- Higher masses can be seen:



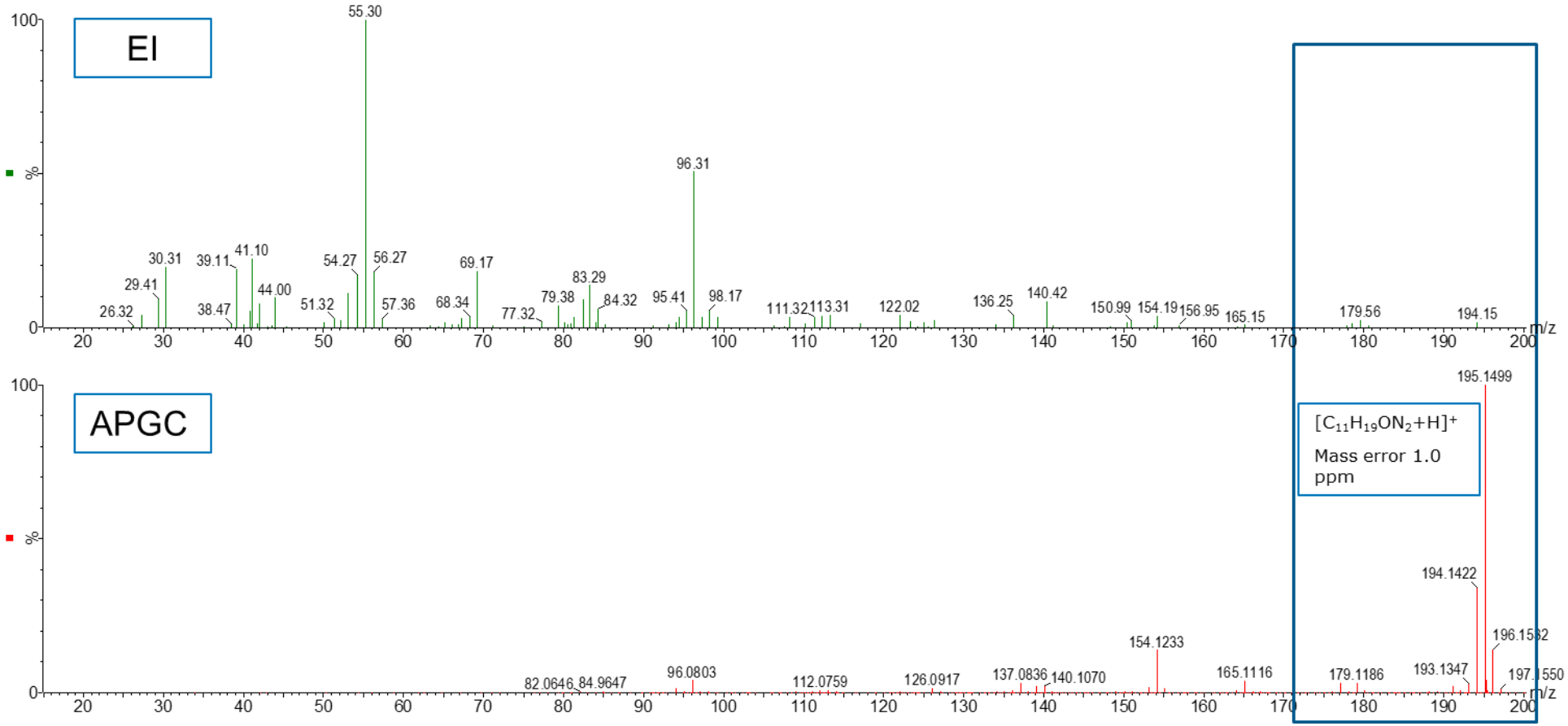
Polystyrene tetramer at m/z 416.2503 corresponding to [M+$C_{32}H_{32}$]$^+$cation

Pyrolysis-APGC-QToF MS

Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

Soft Ionization

- Presence of the molecular ion:



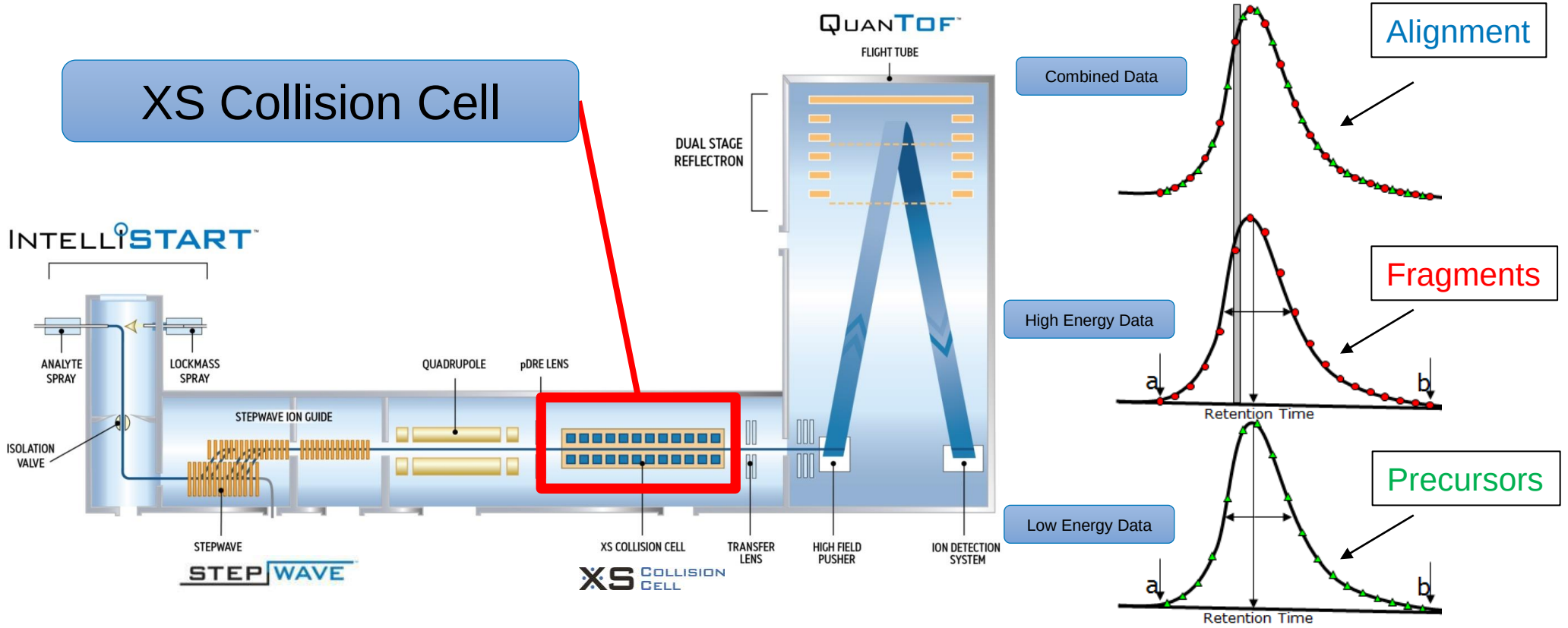
Comparison of spectra from EI and APGC highlighting the presence of the protonated molecular ion in APGC. (polycaproamide (Nylon 6))

Pyrolysis-APGC-QToF MS

Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

MS^E

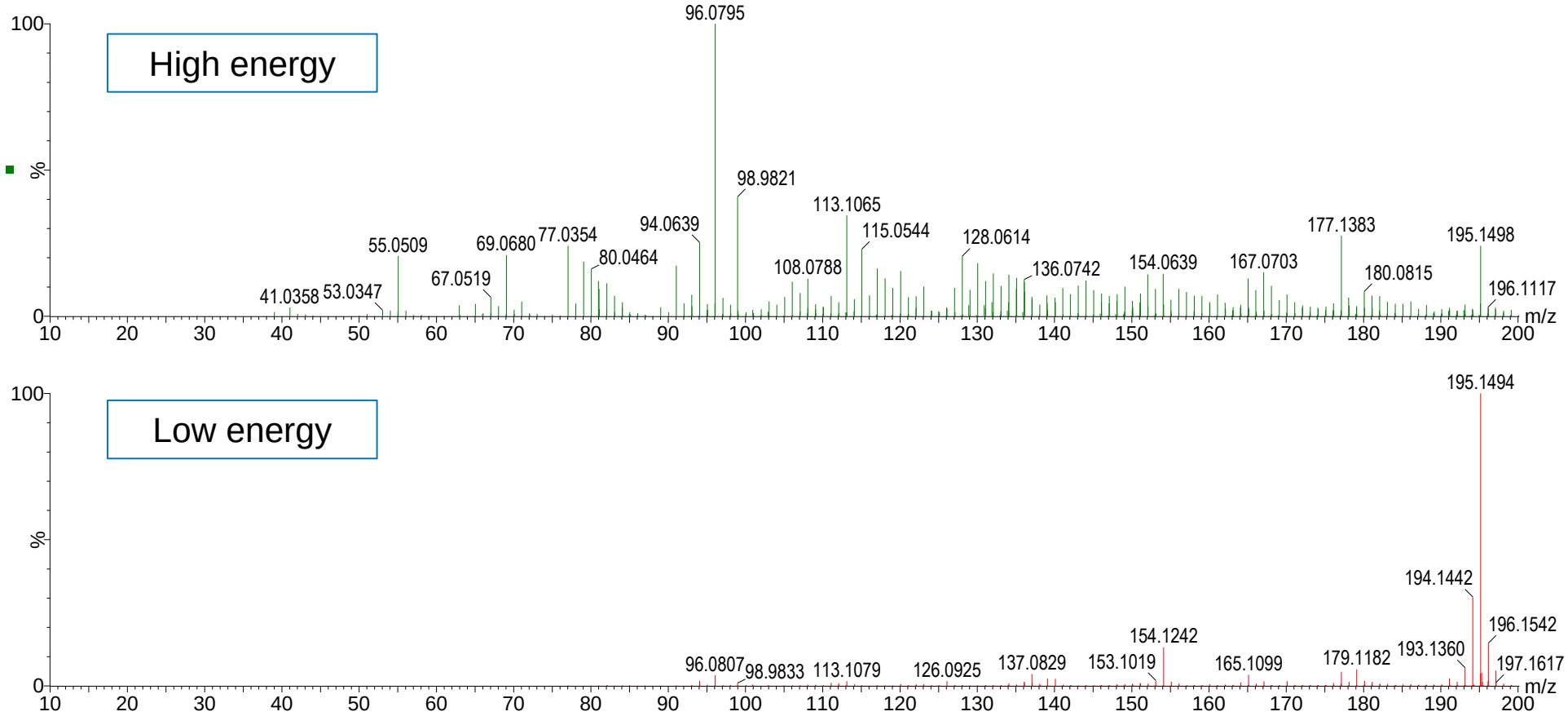
- High and low collision energies are alternated so that the accurate mass of both precursor and fragments ion can be simultaneously acquired.



Pyrolysis-APGC-QToF MS

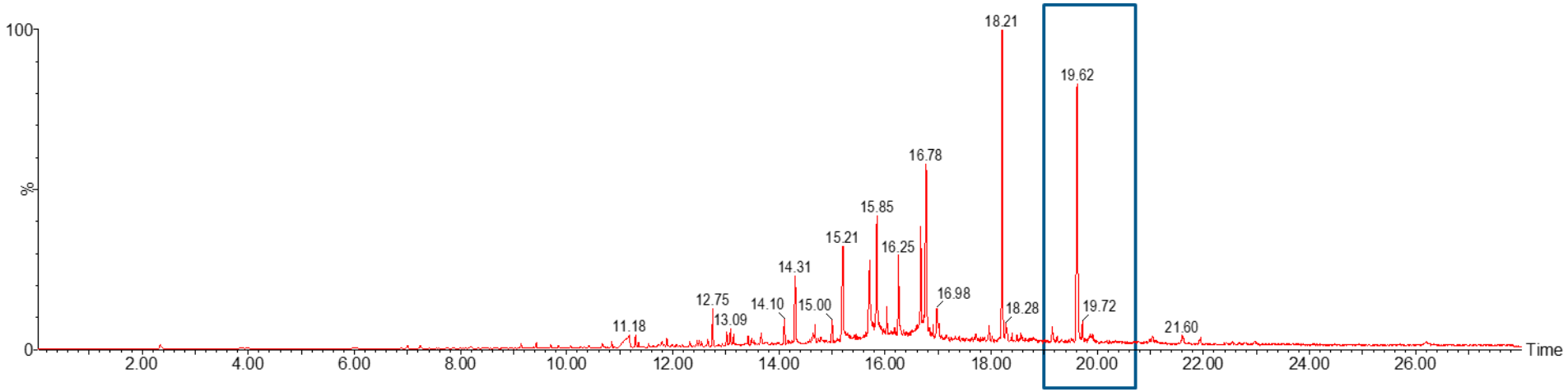
MS^E

- High and low collision energies are alternated so that the accurate mass of both precursor and fragments ion can be simultaneously acquired.



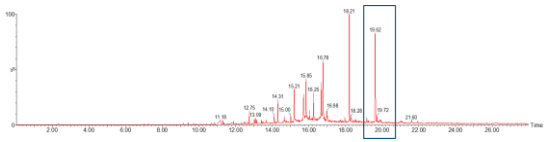
The high and low energy spectra for the pronated ion of m/z 194.2374 using MS^E .

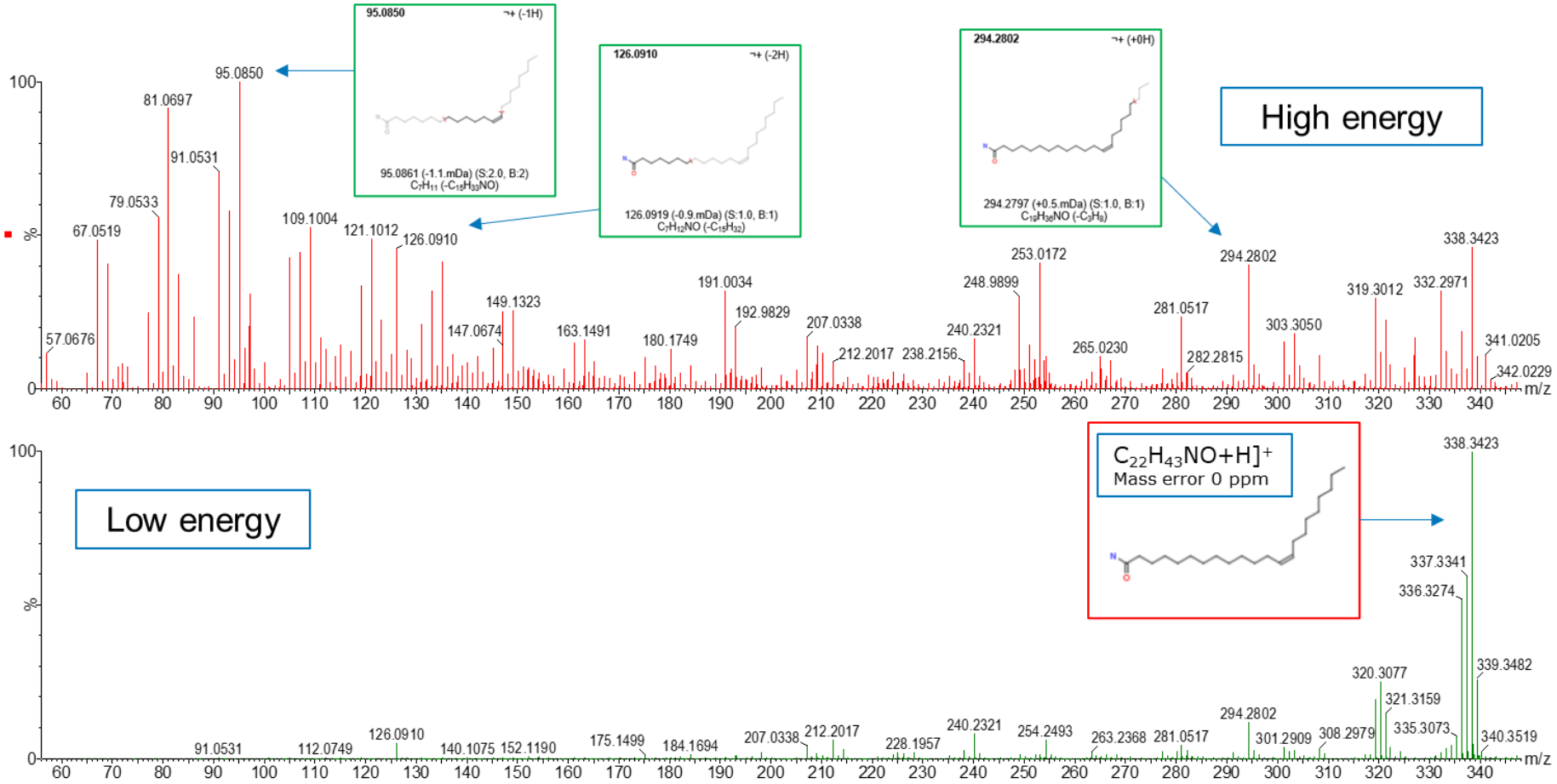
Characterization



Pyrogram of biobased plastic bag

Characterization



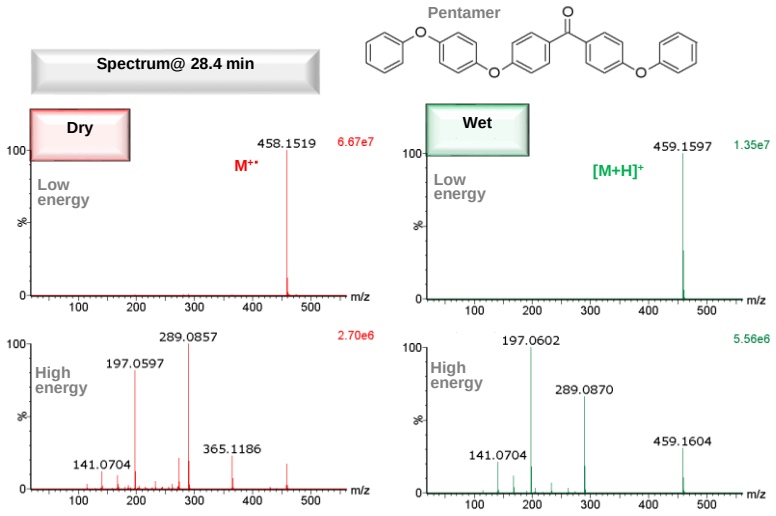


High and low energy spectra for *m/z* 337.5829 corresponding to erucamide protonated ion using MS^E. Mass fragments assigned by MassFragment.

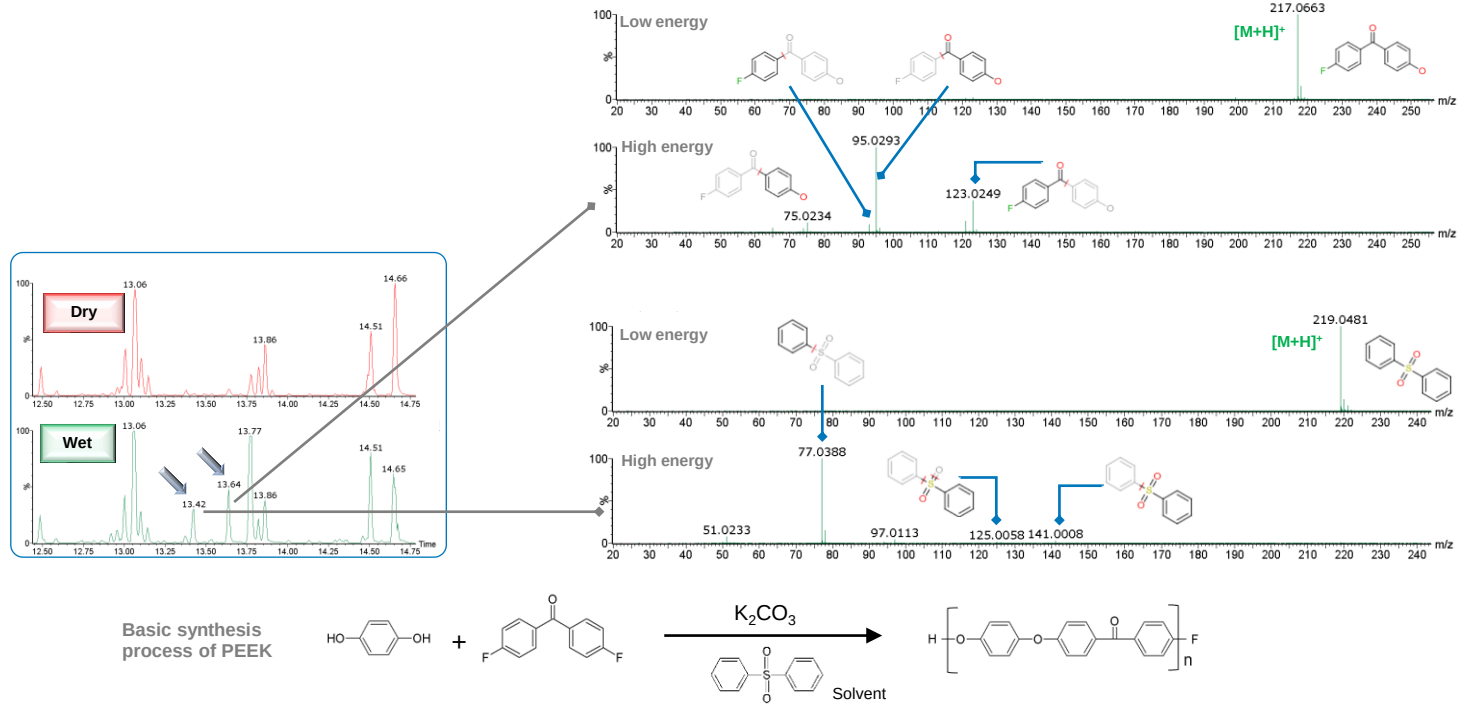
Applications

Characterization of Engineering plastic (PEEK)

- Wet and dry source conditions to understand the polarity of the PEEK pyrolyzates



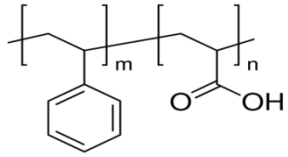
- Elucidation of polar end groups and components



Basic synthesis process of PEEK

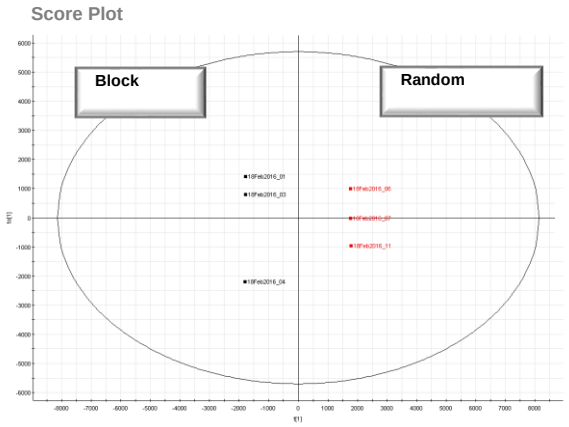
Applications

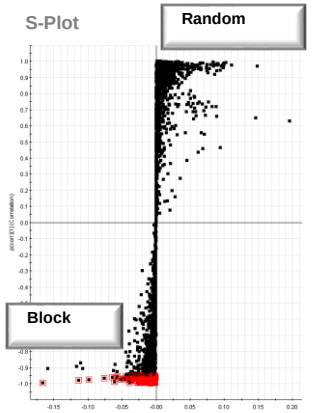
Comparison of Block and Random Copolymer

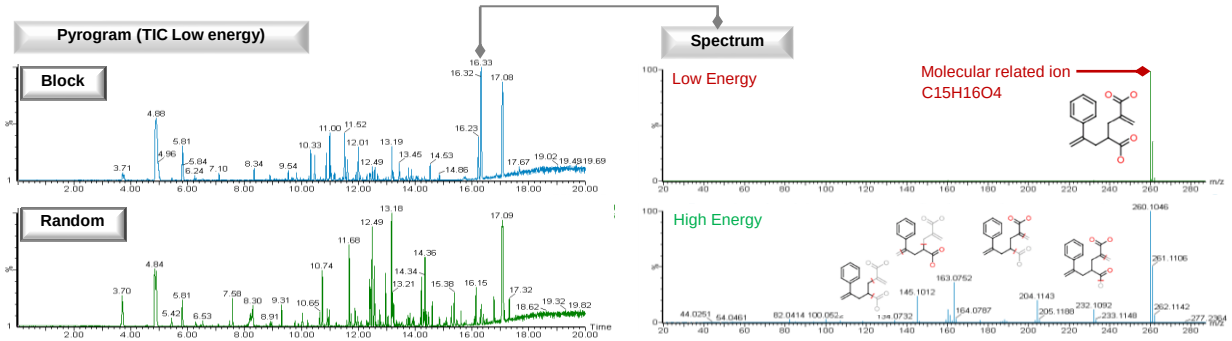


Styrene (Sty) Acrylic Acid (AA)

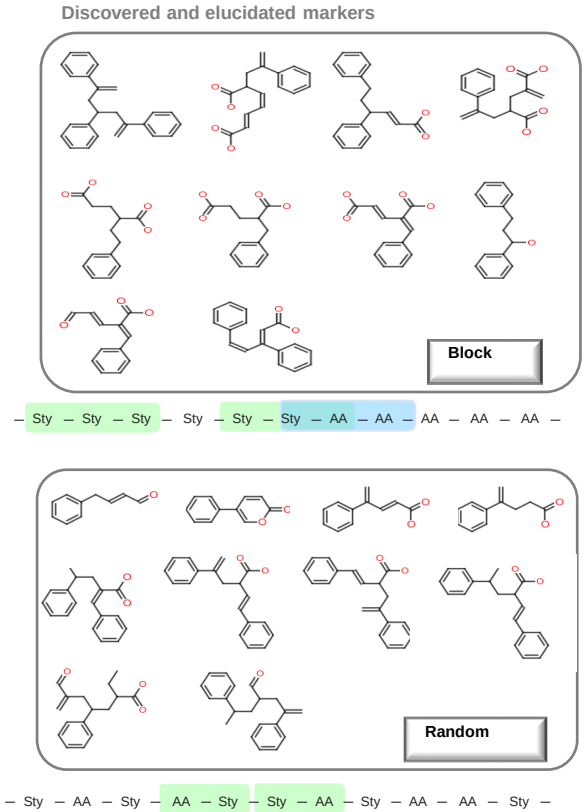
- Specific pyrolyzates (markers) were extracted with multivariate analysis







- Elucidation of pyrolyzates to understand polymer connectivity



Advantages of the Approach

Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

- Analytical pyrolysis-GC-MS for the characterization of complex materials
  - Ongoing project: Recycled materials
- Soft ionization
  - Higher masses
  - Presence of the molecular ion assisting with the identification of unknowns
- MS^E
  - Collection of both the accurate mass of precursor and fragment ions which is key for the structural elucidation of unknowns within a sample. (all of the data, all of the time)
- In house library search/development in addition to existing commercial libraries for putative compound ID
  (Poster - TP 138 Combined approach for the characterization of plastics using spectral libraries created from both pyrolysis-GC-MS and pyrolysis-APGC-ToF-MS)