Enhanced Molecular Ion in GC/MS by Cold EI

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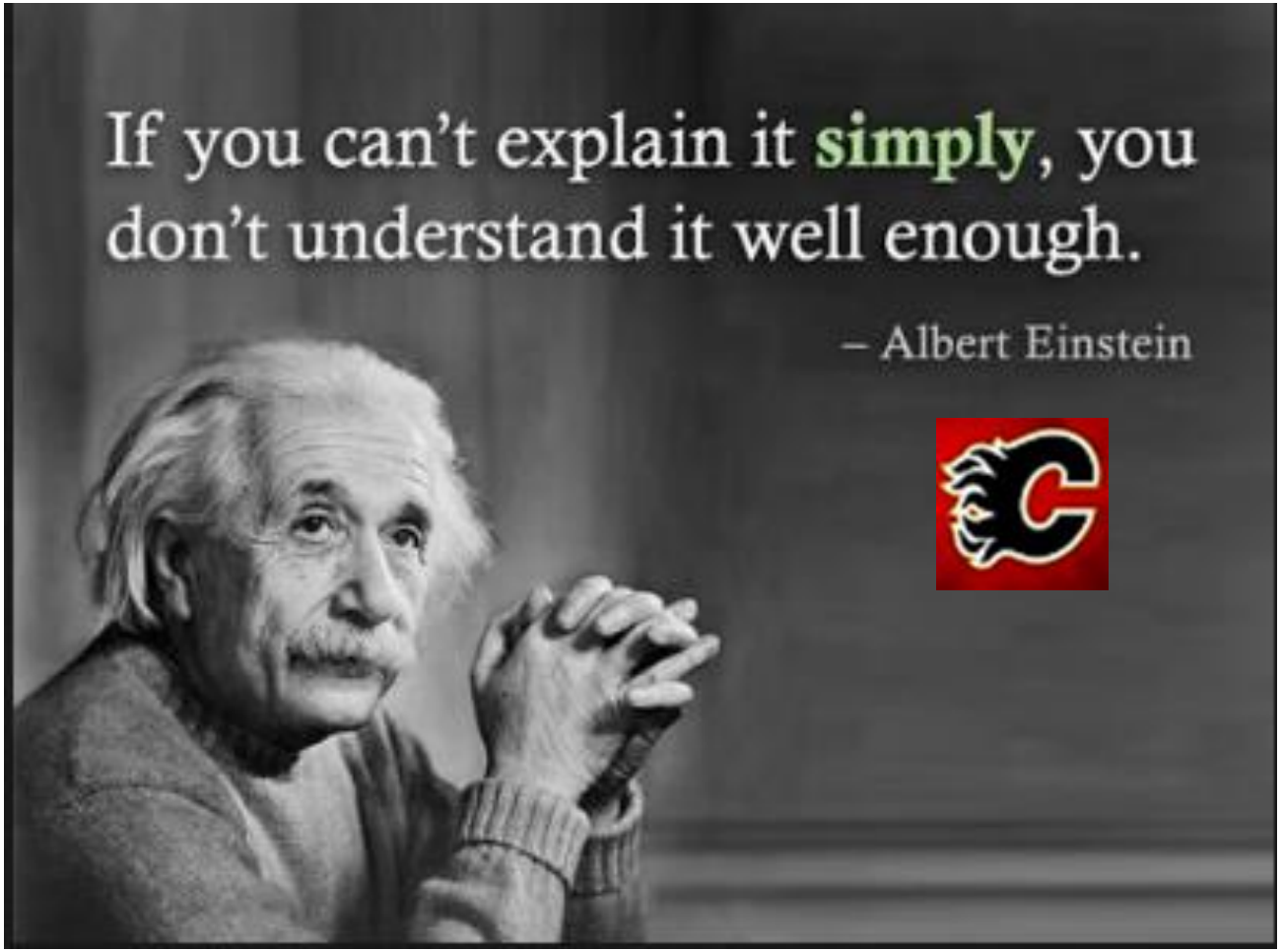
29 April 2015 WCTOW

Keep it simple



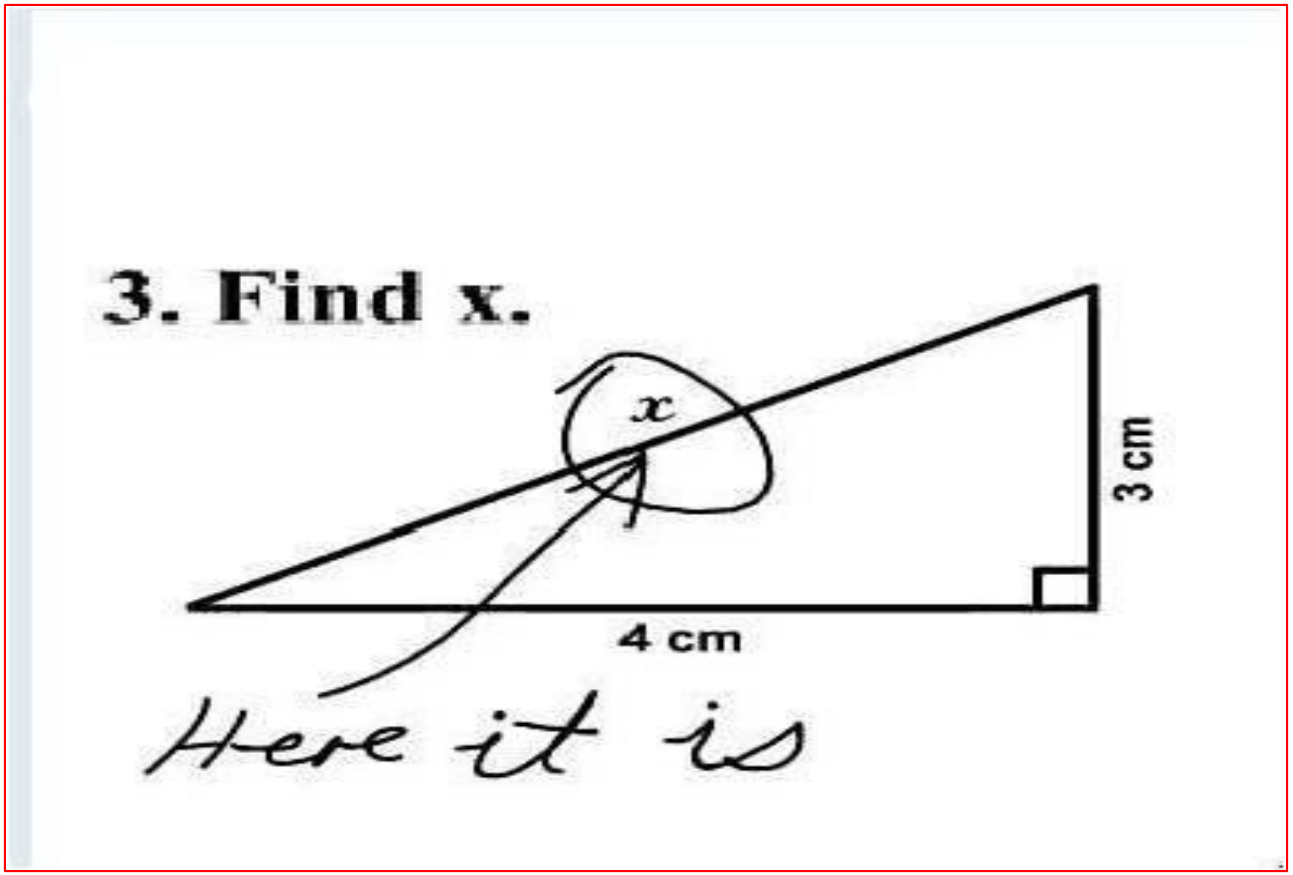
Importance of Molecular Ion for GC/MS

- Electron Ionization Gas Chromatography / Mass Spectrometry (EI GC/MS) is a powerful and information-rich technique for qualitative characterization and quantitative analysis of the compounds in a mixture.

- A very valuable function of EI GC/MS is to provide the molecular weight of a compound, often key to analyte identification.

- Many compounds, especially those with long or branched hydrocarbon chains, do not have a stable molecular ion under EI conditions - it can be small or completely absent in the spectrum.

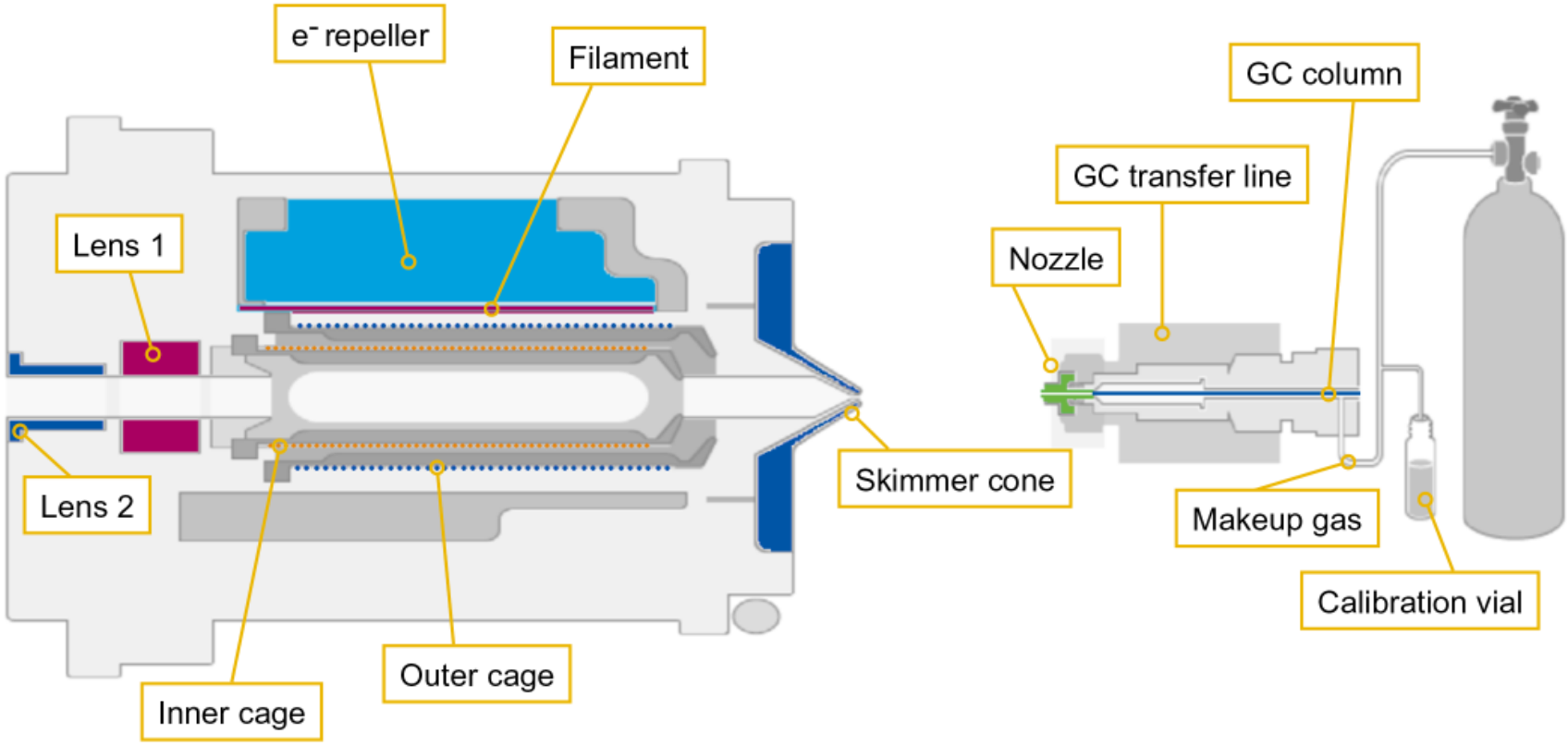
If Only It Was This Easy



Importance of Molecular Ion for GC/MS

- Cold Electron Ionization GC/MS (Cold EI GC/MS)
  - Enhances the molecular ion abundance of most compounds
  - Enhancing molecular weight determination
  - While retaining the EI fragmentation pattern for spectral library searching.

Cold EI Ion Source



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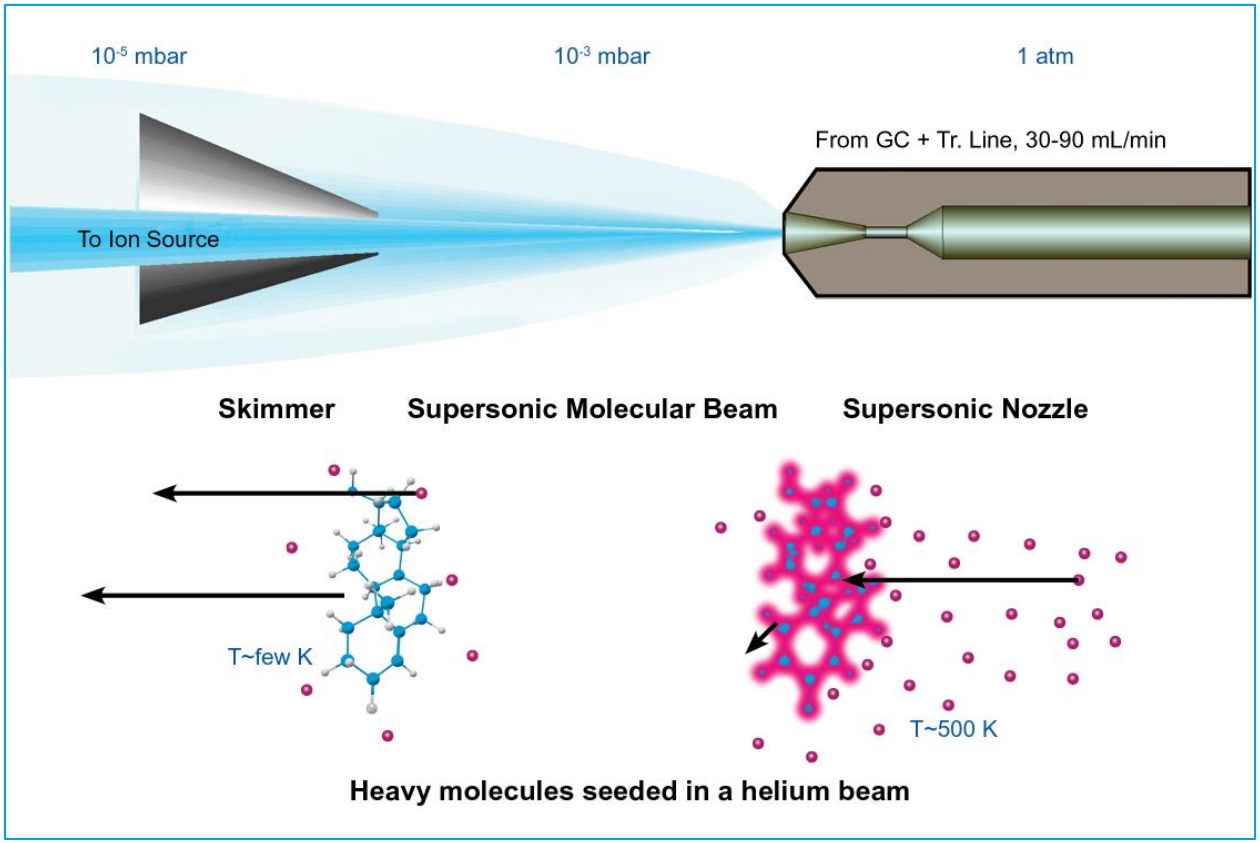
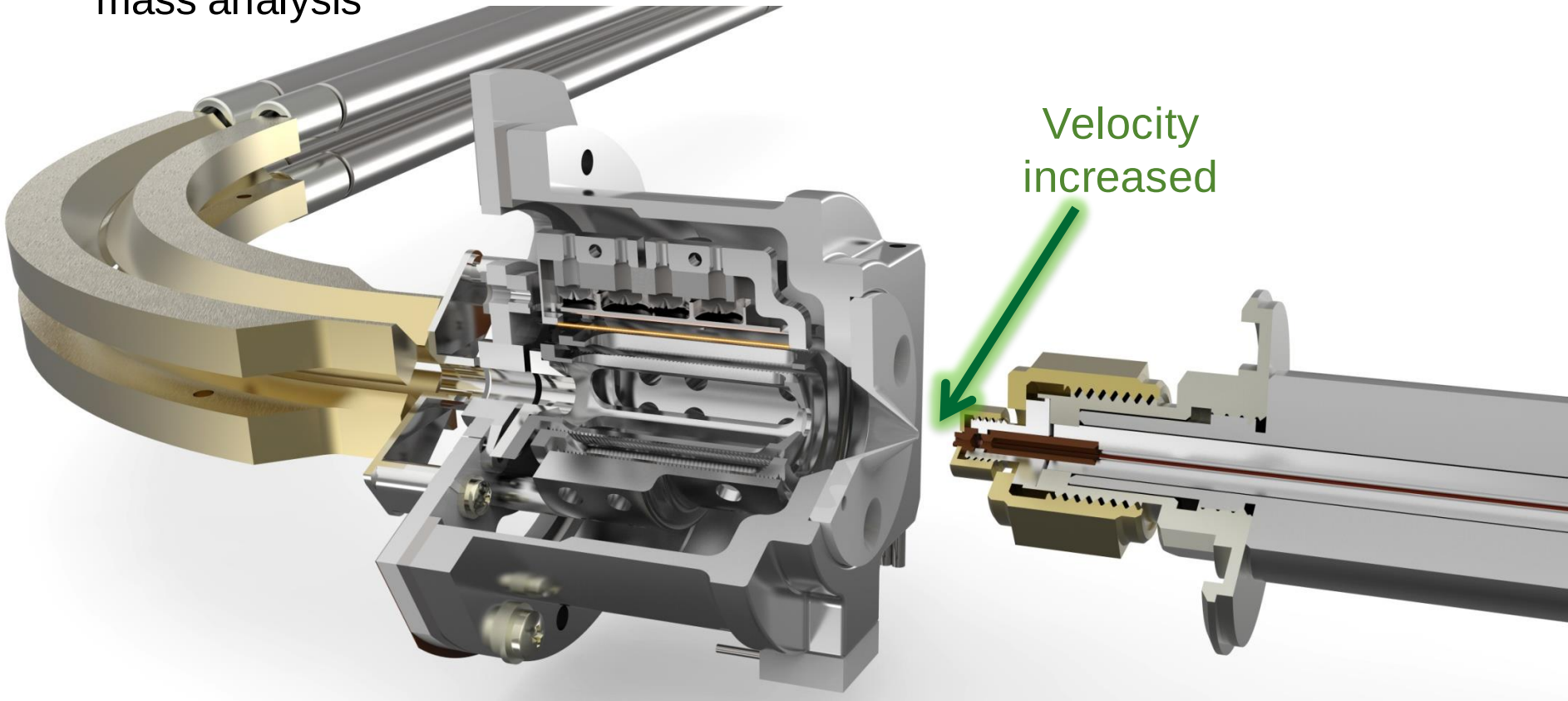
Supersonic Molecular Beam



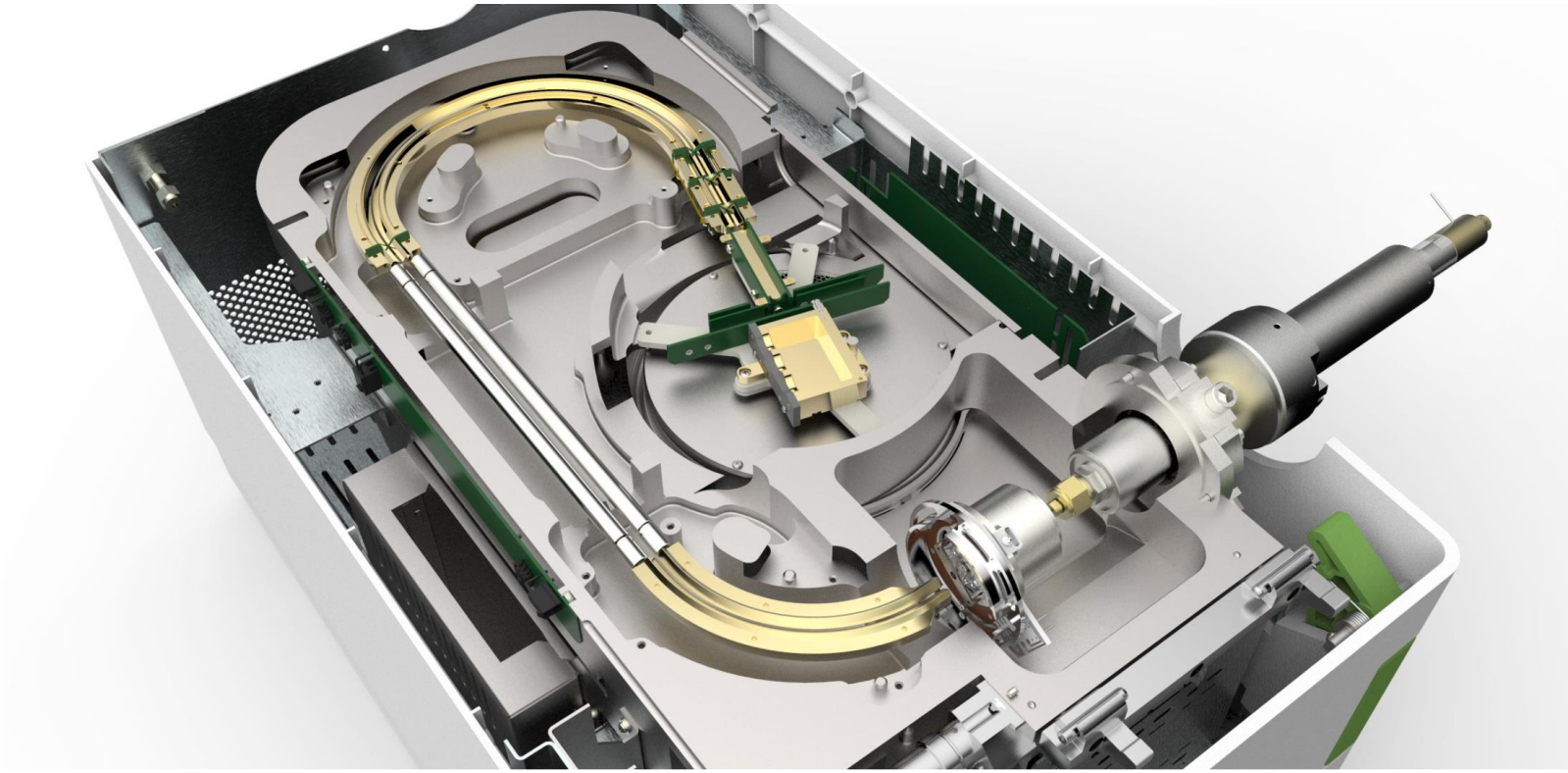
- Velocity is increased (kinetic energy in the range of 1-20 eV)
- Velocity is directed along the beam (jet separation)
- Vibrational Energy is decreased (supercooling hence “Cold EI”)
- Flow rate compatibility of 100 mL/min (x100 of standard GC-MS)

How does Cold EI work?

- Molecules exit the GC column, and are mixed with a make-up gas
- Nozzle adiabatic expansion ‘cools’ the analyte molecules in a supersonic molecular beam, reducing internal energy
- Excess carrier gas is skimmed off
- Cold molecules (~15 K) enter source for molecular ion formation and mass analysis



AxION iQT - Innovative ion optics

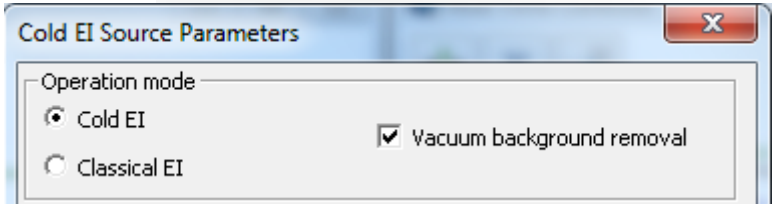


Curved ion guides to eliminate neutrals and maximize signal-to-noise

MS data at the speed of ToF

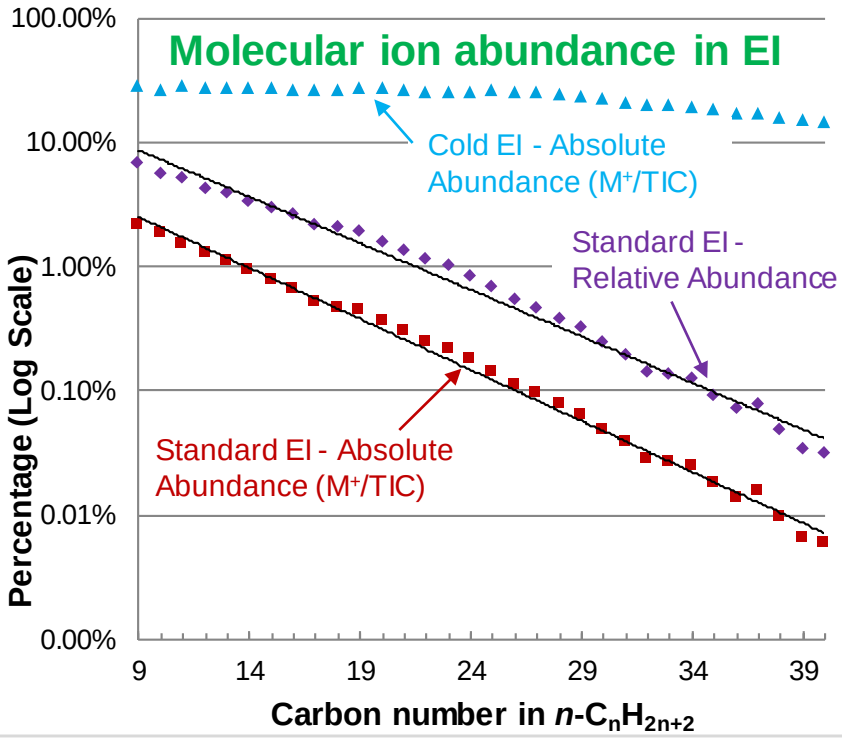
AxION iQT GC/MS/MS

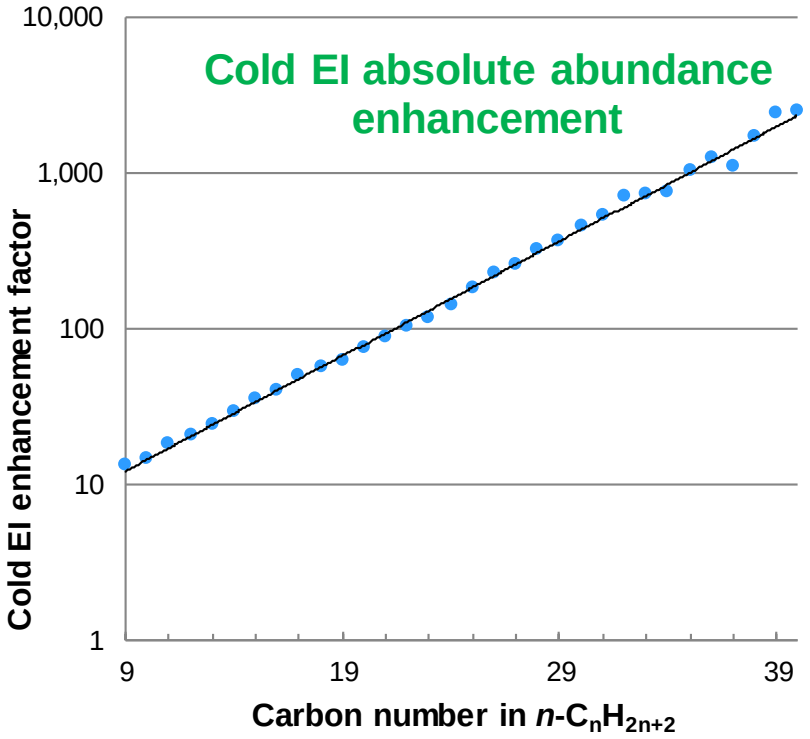
- GC/MS/MS
  - Novel GC/MS/MS configuration
  - All MS/MS fragment ions all the time
- Conventional EI and Cold EI ion sources
- Cold EI operates in four modes:
  - Cold EI with Vacuum Background Removal (VBR)
  - Cold EI without VBR
  - Classical EI
  - Low eV Cold EI
- Mass analysis can be full spectrum or MS/MS
- MS/MS shows full fragment ion spectra, not just 1 or 2 MRM ions



Molecular Ion Dependence on Carbon Number

- In Standard EI the molecular ion is reduced by ~20% per each added carbon
- In Cold EI it is approximately size independent
- The relative abundance of the molecular ion in Cold EI is significantly enhanced
- The enhancement is exponentially increased with the carbon number up to a factor of 2500 for $C_{40}H_{82}$.





Aviv Amirav, *http://blog.avivanalytical.com/2012/09/how-much-is-molecular-ion-enhanced-in.html*

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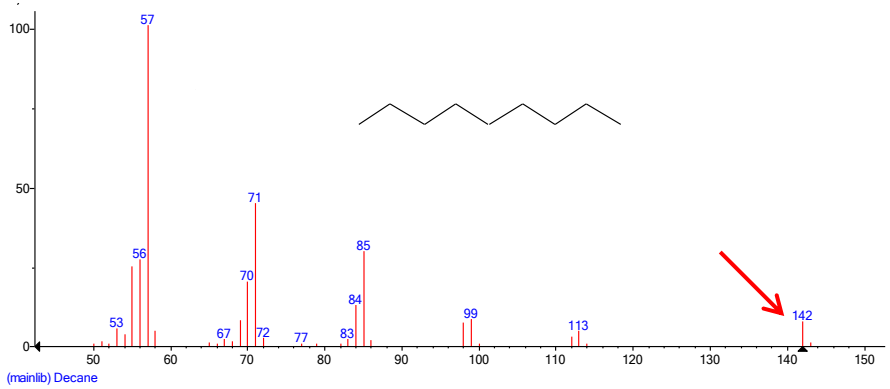
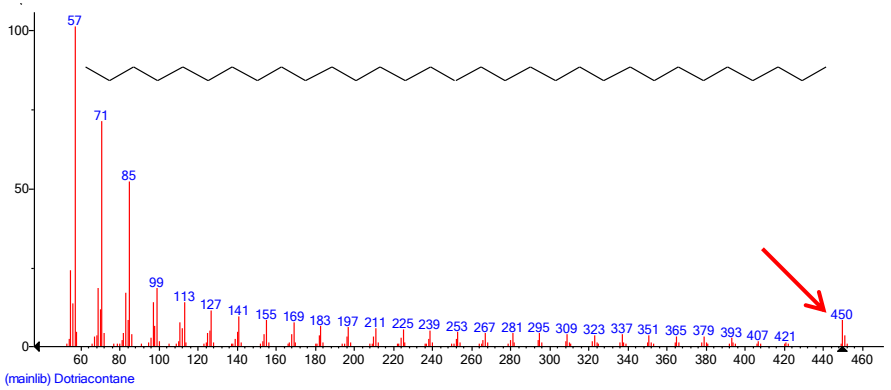
Cold EI Enhances Molecular Ion for Hydrocarbons as Carbon Number Increases

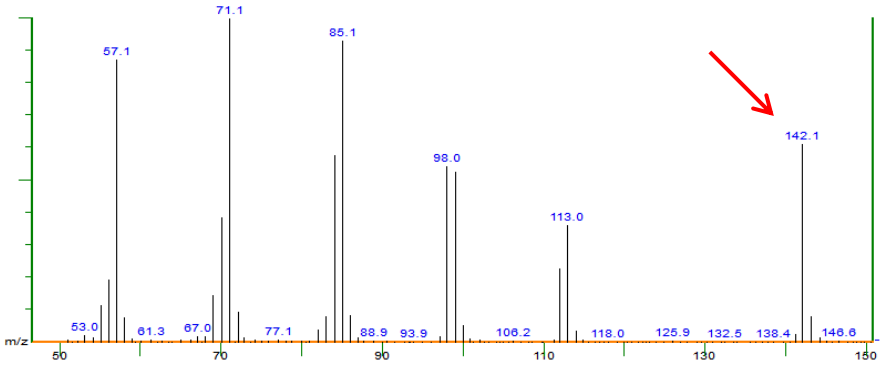
n-C_{10} - EI (NIST)



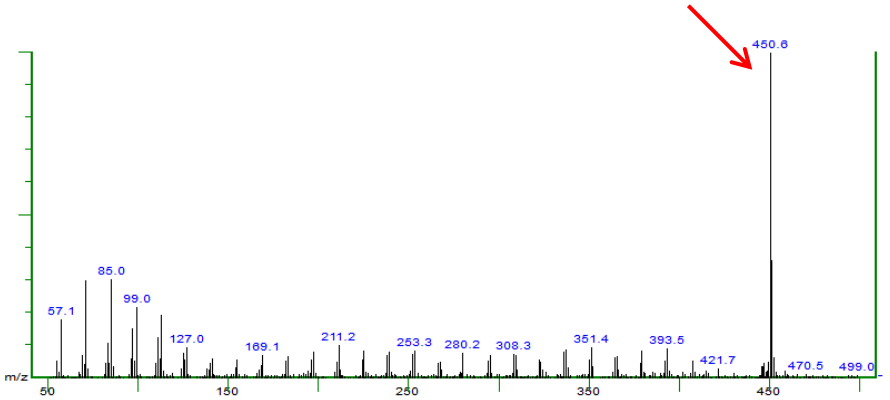
n-C_{32} - EI (NIST)



n-C_{10} - Cold EI



n-C_{32} - Cold EI



… molecular ion increases with carbon number

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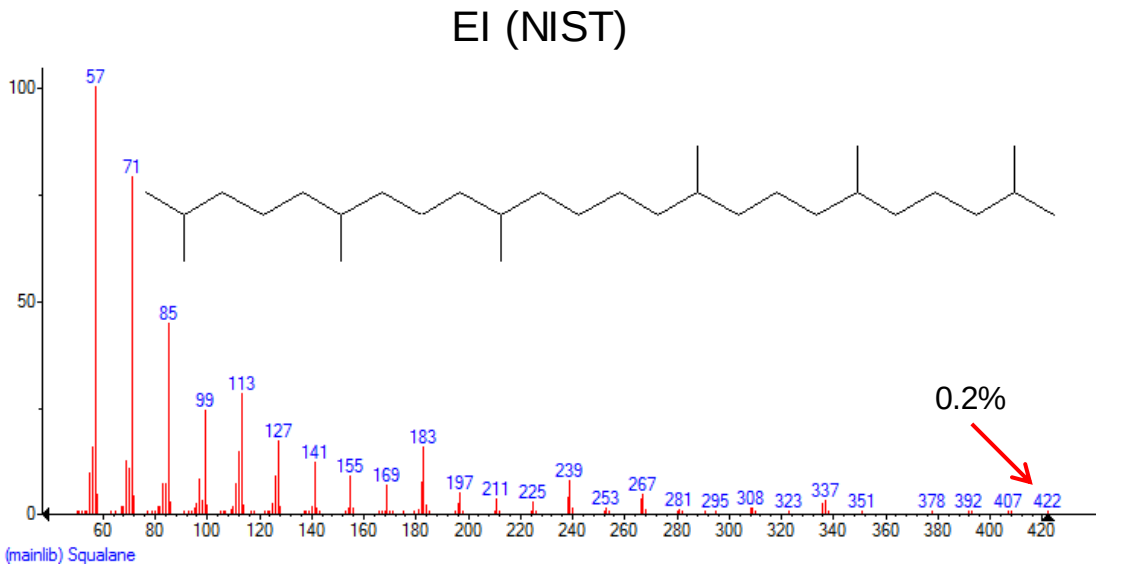
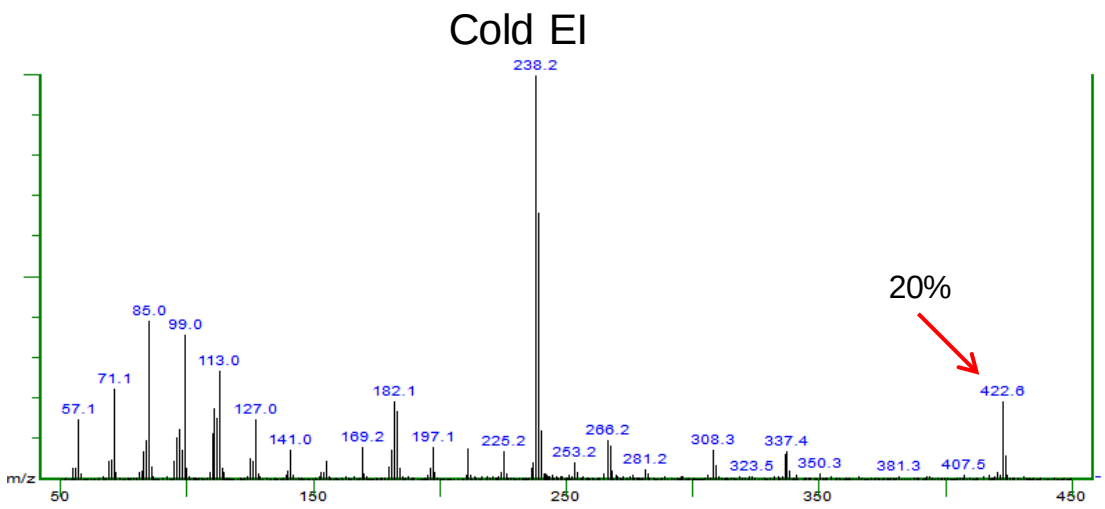
Strong Molecular Ions when EI does not have any - Squalane $C_{30}H_{62}$





… Highly-branched chains often have low intensity molecular ion

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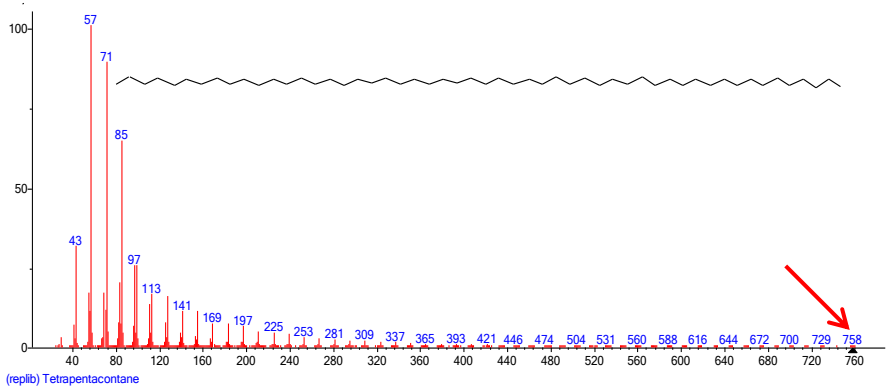
Cold EI for molecular ions from high-boiling hydrocarbons

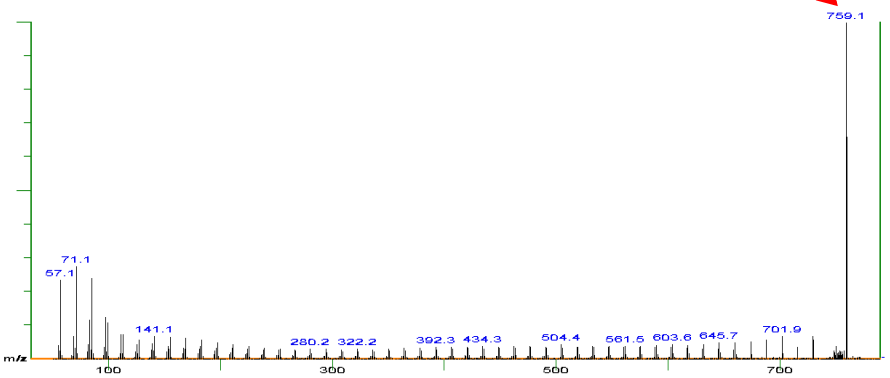
n-C_{54} - EI (NIST)



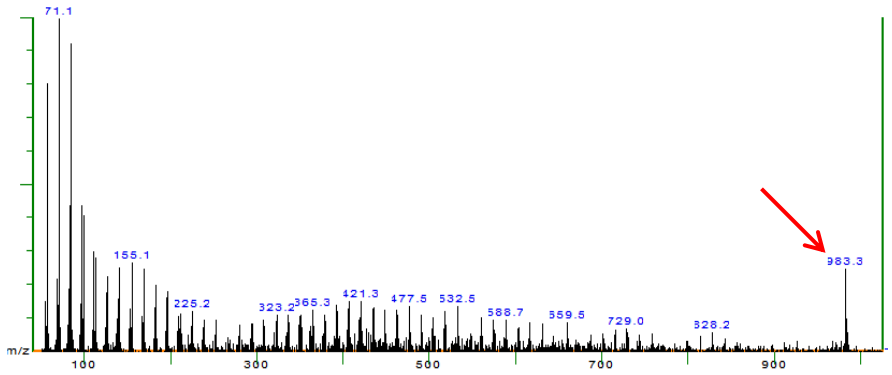
n-C_{70} - EI (NIST)

Not available in NIST 2014 or Wiley 10th mass spectral databases

n-C_{54} - Cold EI



n-C_{70} - Cold EI



… high flow rates enable high boiling points

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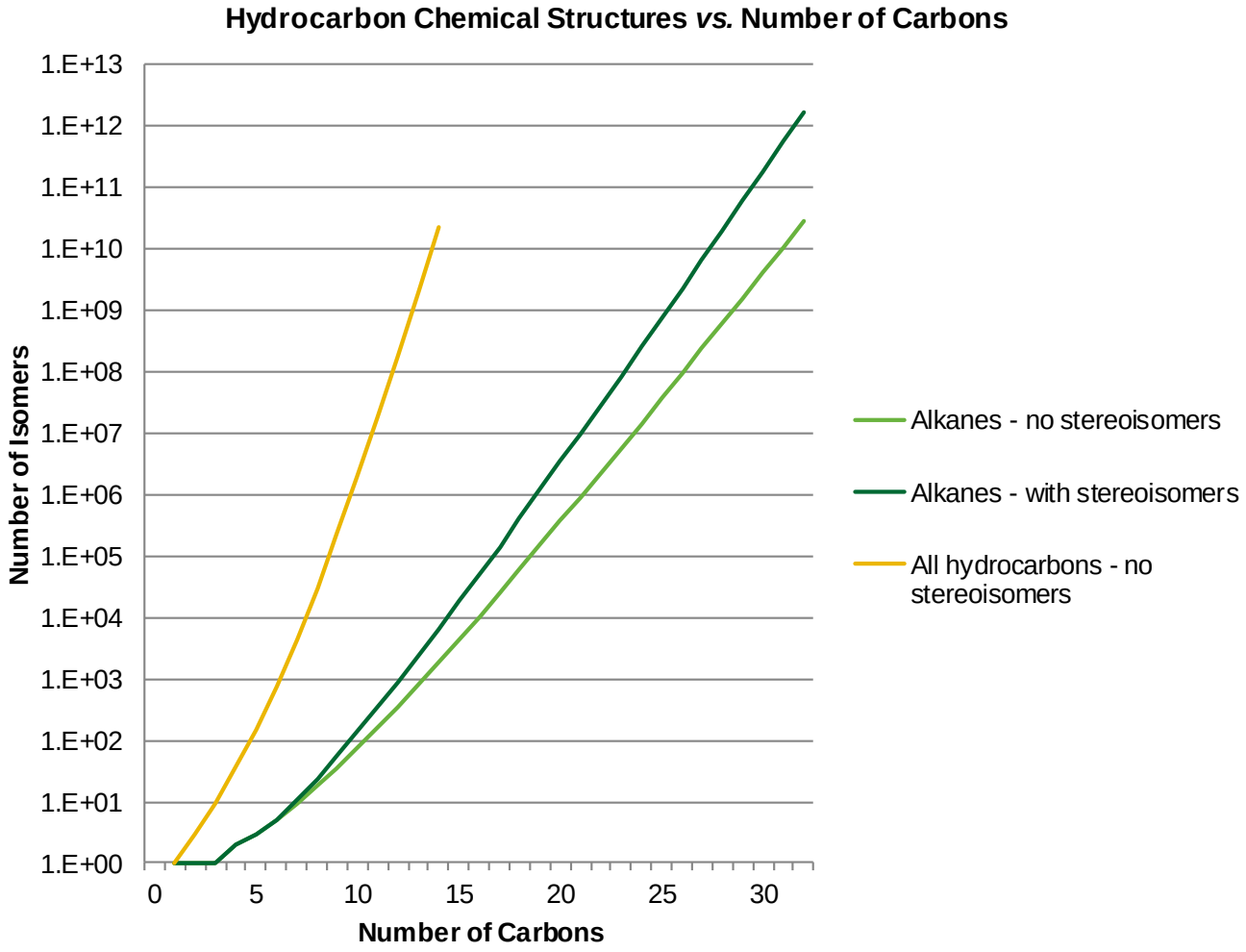
Jet Fuel Isomer Characterization

Many possible hydrocarbon isomers



# Carbons	Number of Alkanes, no stereoisomers
1	1
2	1
3	1
4	2
5	3
6	5
7	11
8	24
9	55
10	136
11	345
12	900
13	2412
14	6563

The On-Line Encyclopedia of Integer Sequences (OEIS), #A000602, A000628, A134818.

… increase exponentially

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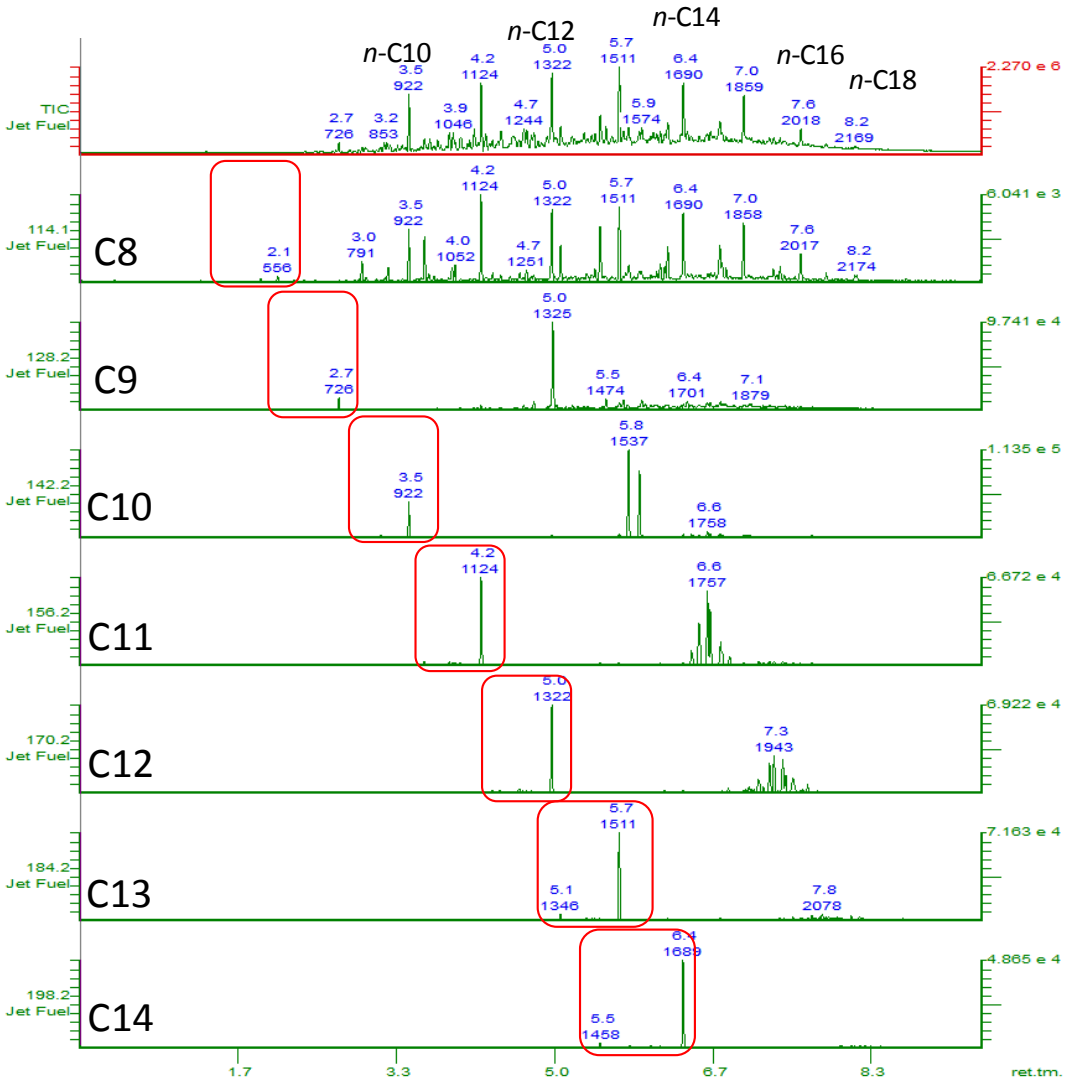
Isomer Distribution Important for Jet Fuel Analysis

- Hydrocarbon isomer distribution contributes to important fuel characteristics
  - Boiling and melting points, octane number, combustion efficiency, flash point, viscosity, lubricity, solubility, and solvation power
  - Strongly influenced by hydrocarbon chain branching
  - Helpful to monitor blending & refining process, catalysts, and the product
- If these are not to specification, jet fuel lines can freeze up or engines malfunction
- Without knowing component molecular weights, difficult to figure out the composition
  - High mass accuracy does not help without a molecular ion
- Cold EI provides the molecular ion
  - Can use this to help determine fuel composition
- “Isomer analysis”

“Jet A” Jet Fuel, C_8 - C_{14} by EI GC/MS



 … EI does not show significant alkane isomers

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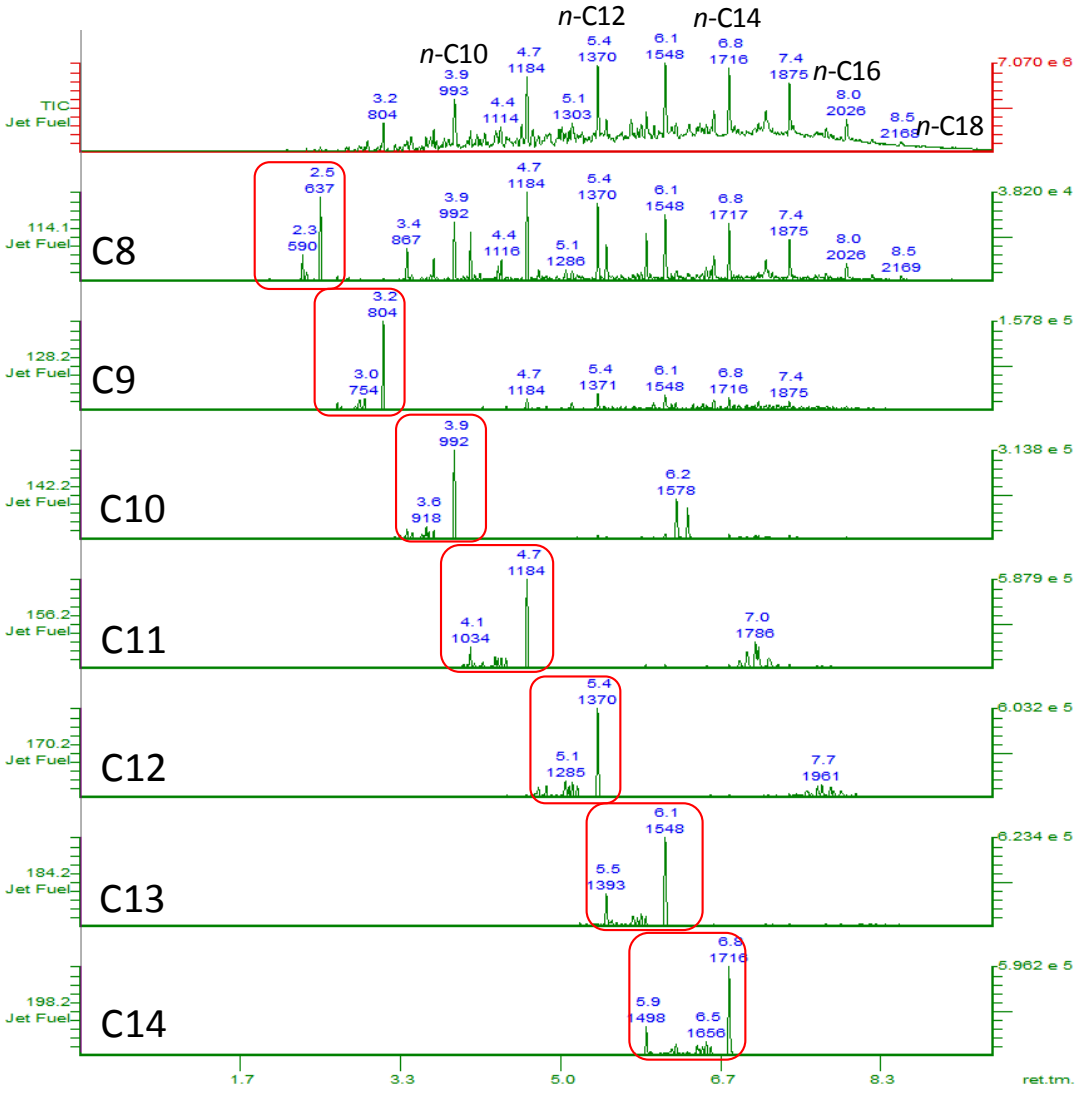
"Jet A" Jet Fuel, C_8 - C_{14} by *Cold EI* GC/MS



… Cold EI clearly show alkane isomers

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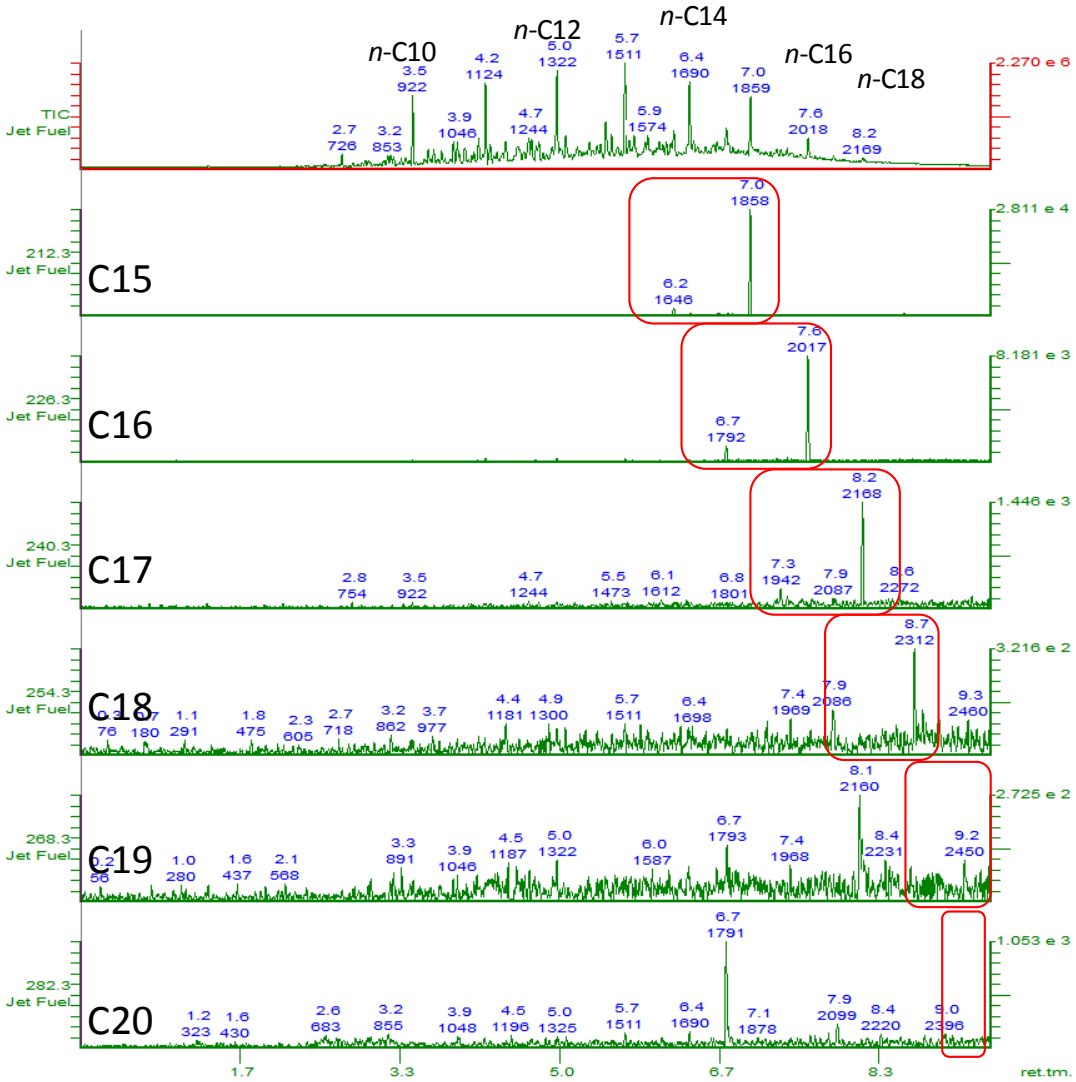
“Jet A” Jet Fuel, C_{15} – C_{20} by EI GC/MS



 … EI begins to show weak isomers, then drops into the noise

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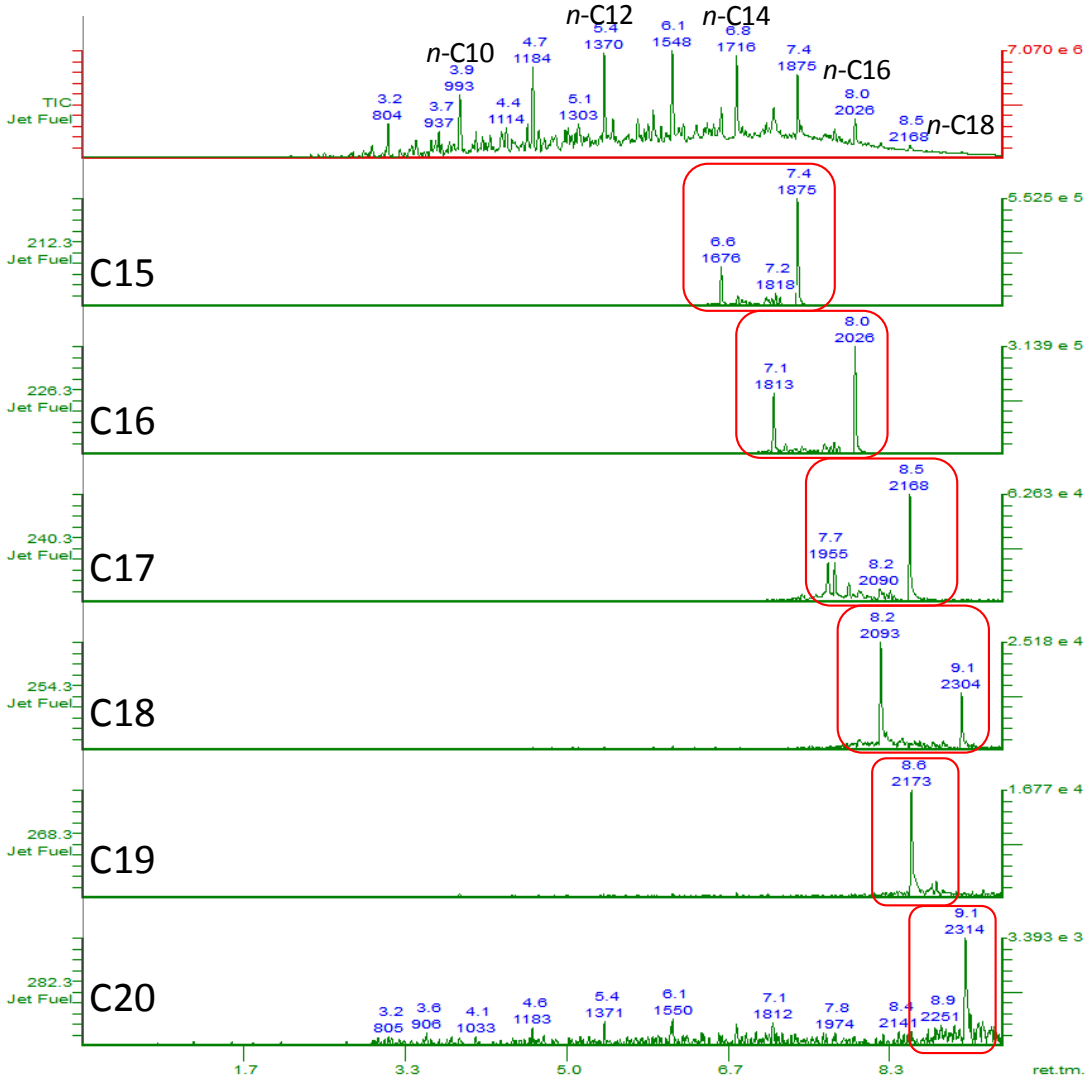
“Jet A” Jet Fuel, C_{15} – C_{20} by *Cold EI* GC/MS



 … Cold EI clearly shows isomers

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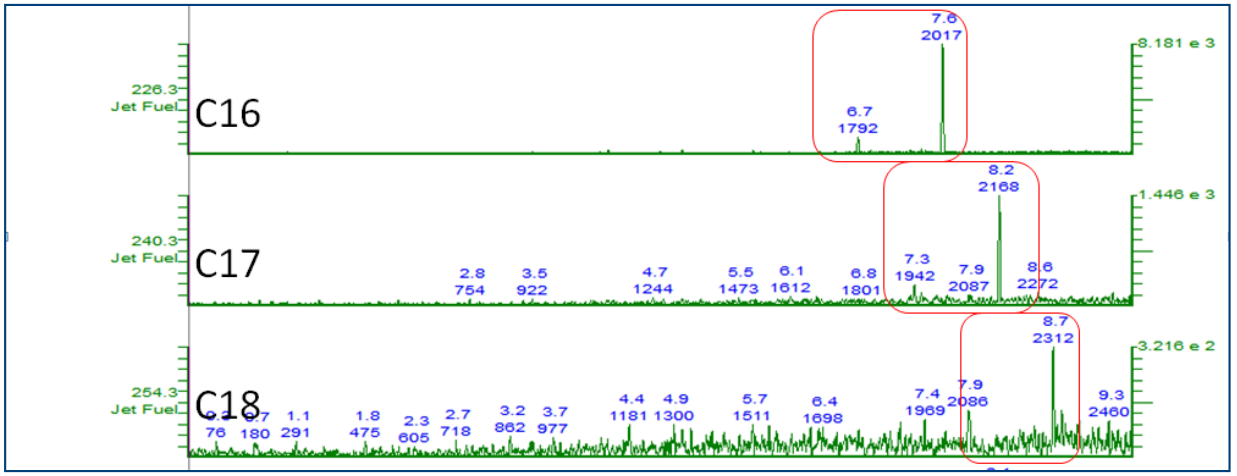
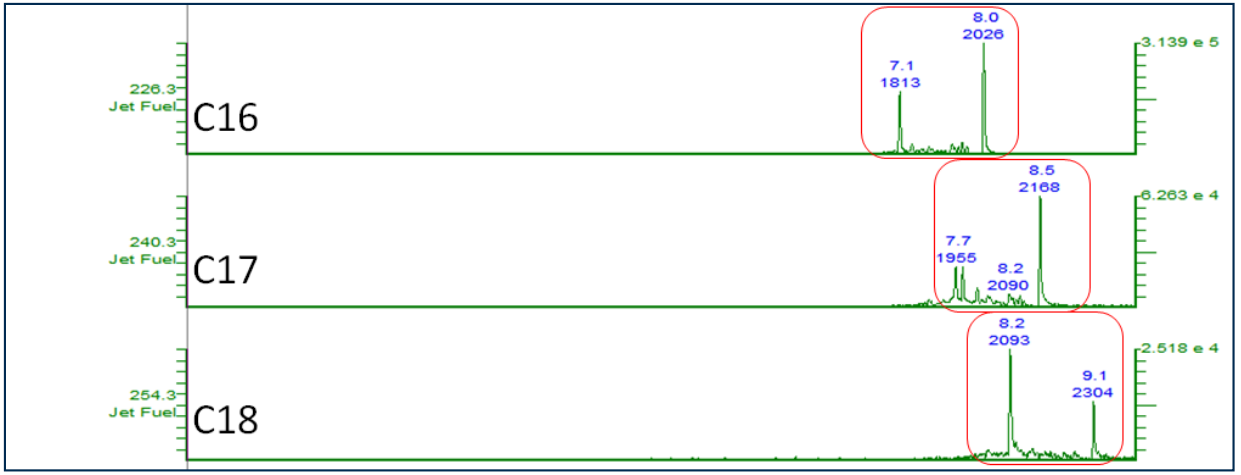
Comparing EI and *Cold* EI GC/MS

EI



Cold EI



 Cold EI shows much stronger isomer peaks and mass chromatograms

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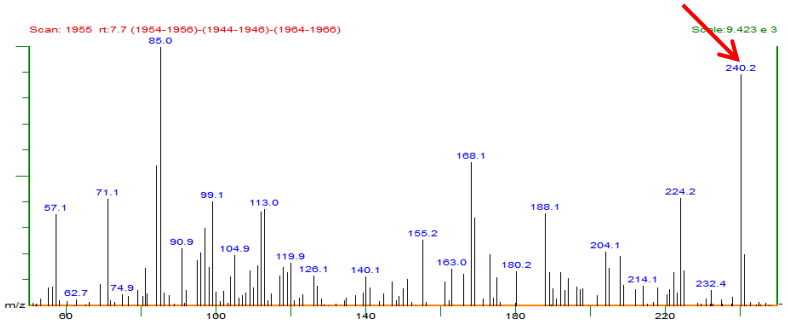
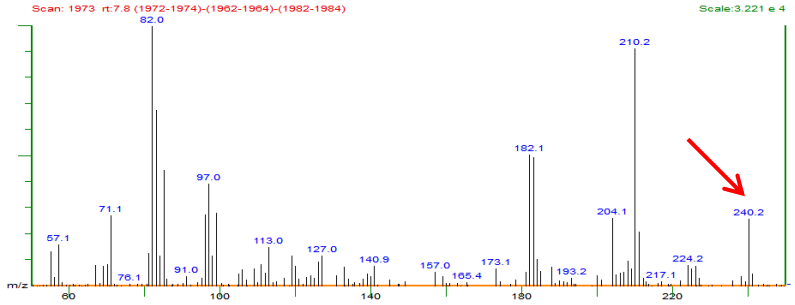
“Jet A” Jet Fuel, C_{17} isomers all show Molecular Ion in Cold EI

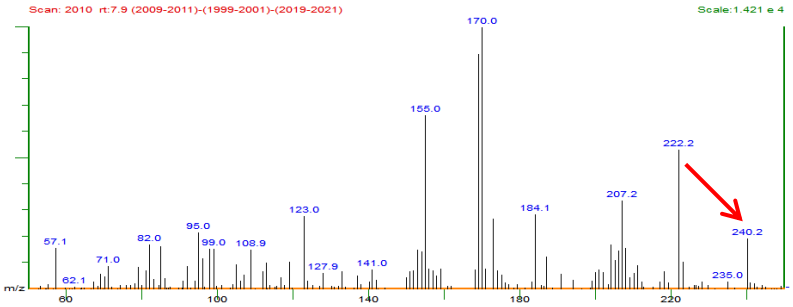
Isomer A



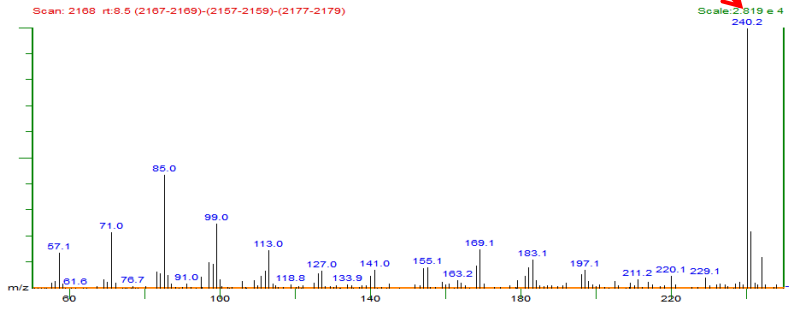
Isomer B

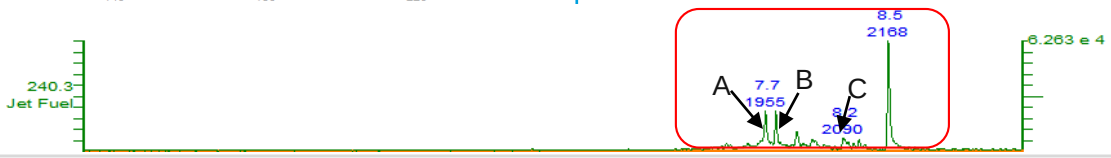


Isomer C



n-C17





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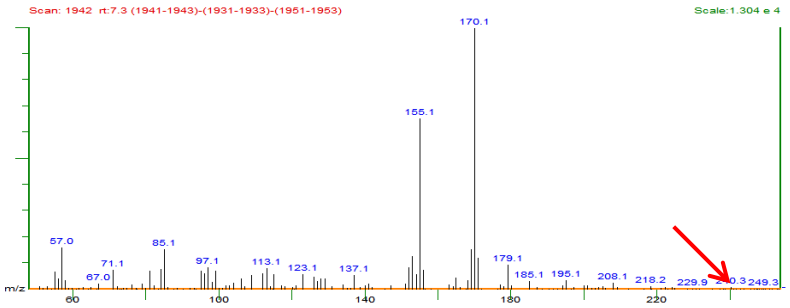
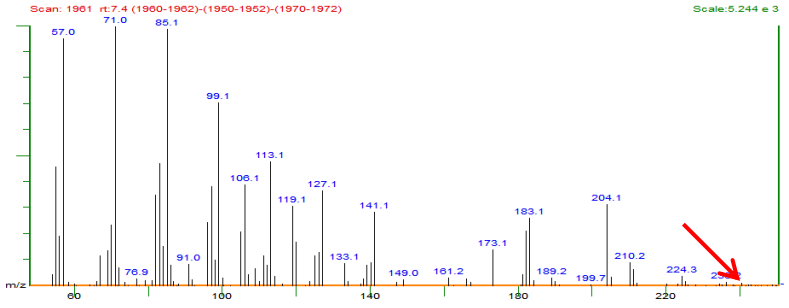
“Jet A” Jet Fuel, C_{17} isomers show small or no Molecular Ion with EI

Isomer A



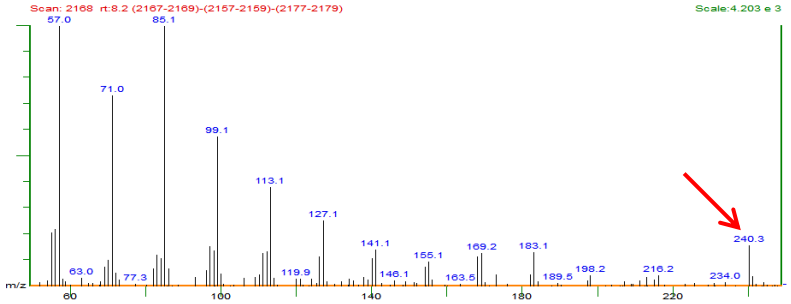
Isomer B

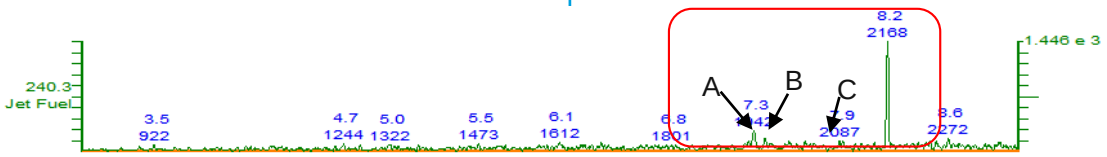


Isomer C

Not detected

n-C17





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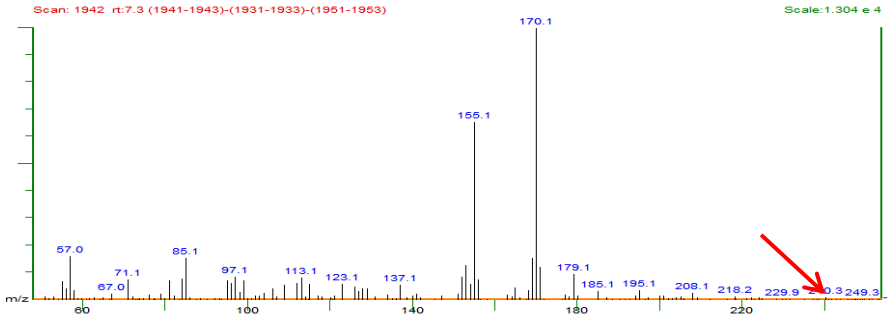
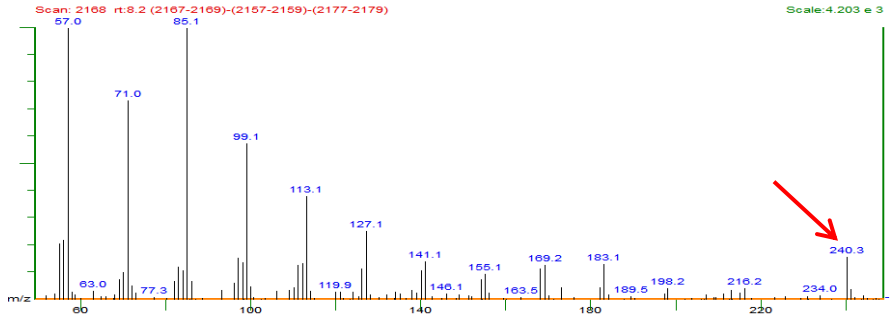
“Jet A” Jet Fuel, EI *vs.* Cold EI

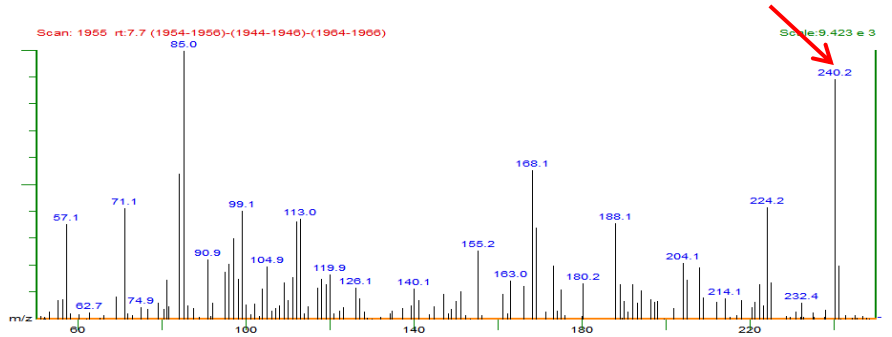
EI Isomer A



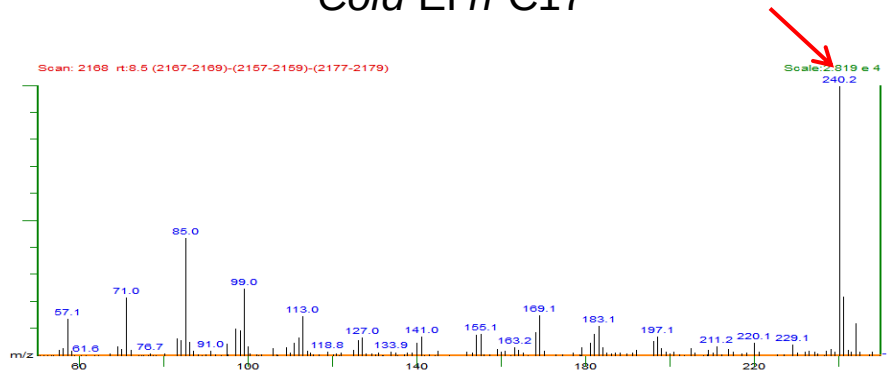
EI *n*-C17



Cold EI Isomer A



Cold EI *n*-C17



 … much larger Molecular Ion with Cold EI for isomer identification

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Potential Petro Applications for Cold EI

- Isomer analysis
- Petrochemicals and fuels development
- Fuel adulteration
- Arson & Forensic
- Motor oil analysis
- Transformer oil analysis
- Environmental oil spills
- Biodiesel analysis
- Organic Geochemistry
- Hydrocarbon polymers

Cold EI Advantages

- Selectivity and inertness
  - Stronger molecular ion than EI, or a molecular ion when EI does not yield one
  - Molecular ion gives better selectivity (uniqueness) than fragment ions
  - Elimination of neutral mass independent noise
- Extended GC compound range
  - High column flow rates (up to 100 mL/min) reduce analyte elution temperatures
  - Extended range of low volatility (e.g. *n*-C_{70}) and thermally labile compounds (e.g. Reserpine)
  - High molecular weight polar and non-polar compounds
- Uniform compound response
  - Improved “standardless” semi-quantitation – e.g. experimental reaction yields
- Isomer analysis for petrochemical

Cold EI *vs.* EI or CI MS Techniques

- AxION iQT Cold EI *vs.* Chemical Ionization GC/MS
  - Molecular ion enhanced, rather than M-1, M+1, M+15, etc.
  - EI fragmentation remains, for library searchable spectra
  - Fly-through ion source does not need cleaning, vs. daily or weekly cleaning for CI

- AxION iQT Cold EI-GC/MS/MS *vs.* EI-GC/MS/MS
  - Enhanced molecular ion for better
    - Molecular weight confidence
    - Selectivity
    - Easier method development
    - Structural assignment

Summary

- Long-chain hydrocarbons and branched isomers can have small or no molecular ions
- Cold EI typically gives a significantly stronger molecular ion than EI, and can show one even when EI does not
- Cold EI enables visualization of isomers in Jet Fuel by molecular ion mass chromatograms
- Isomer characterization aids in determination of
  - Fuel properties
  - Economic value
  - Catalyst performance
  - Process yield optimization

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Donald Hellerman
Dana Hostetler
Jay Ives
Yan Jiang
Leon Johnson
Charlie Mangarella
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Michael Pawlyk
Sharanya Reddy
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Kathy Rowberry
Jack Sanga
Jamie Saulnier
Paul Schallis
Urs Steiner
Leslie Sullivan
Ramesh Sureja
Andrew Tyler
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Rob Valley Sr.
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Dave Welkie
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Bryan Whittington
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THANK YOU!