# Enhanced Molecular Weight Information in GC/MS by Cold EI

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For the Better

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HUMAN HEALTH • ENVIRONMENTAL HEALTH

# Topics

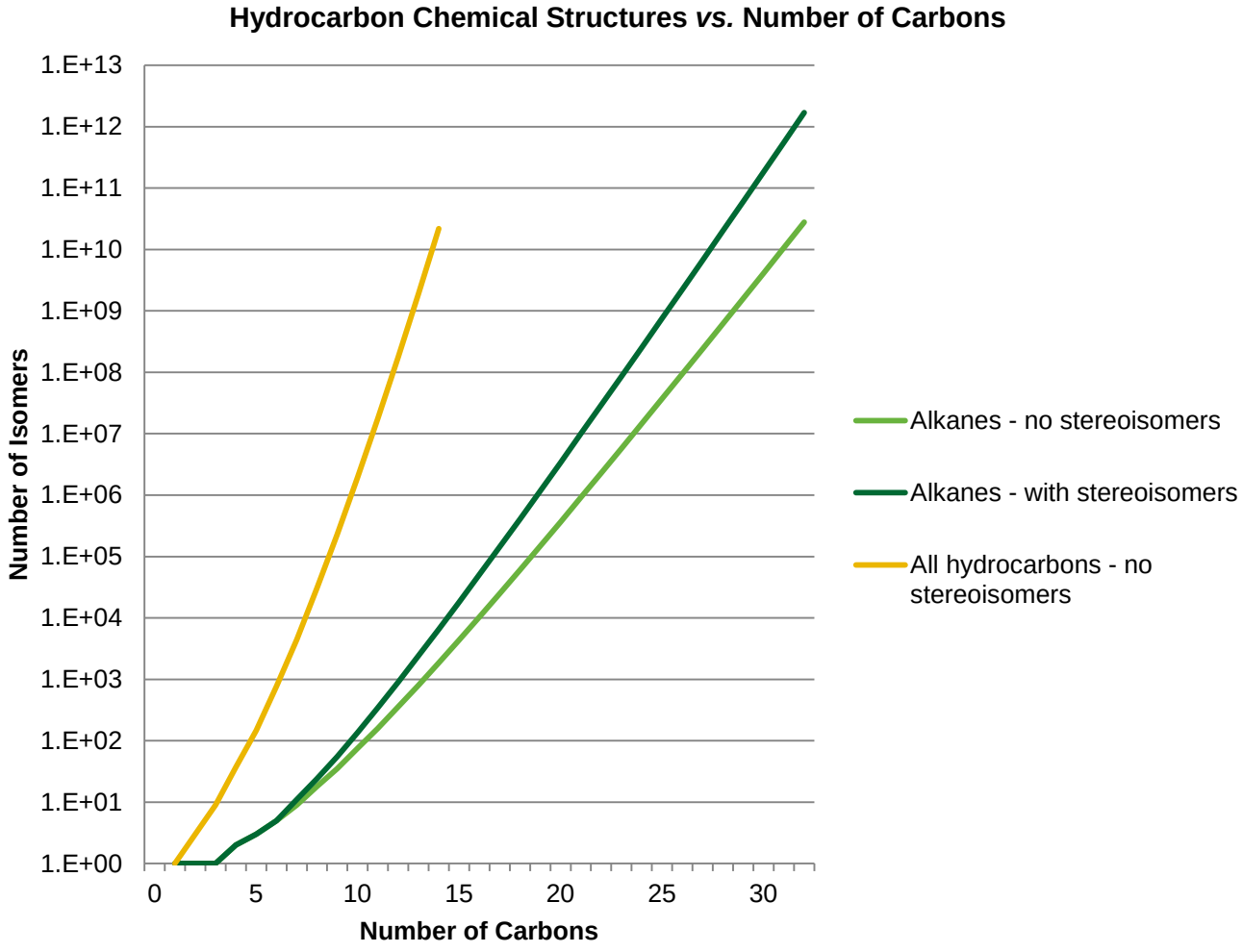
- Importance of the molecular ion for GC/MS
- Isomer Distribution Analysis for Jet Fuel characterization
- How does Cold EI GC/MS work?
- Cold EI molecular ion enhancement for hydrocarbon analysis
  - High molecular weight
  - Highly branched
- Potential petrochemical applications for Cold EI

# 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.
- One of its most valuable functions 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.

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.

# 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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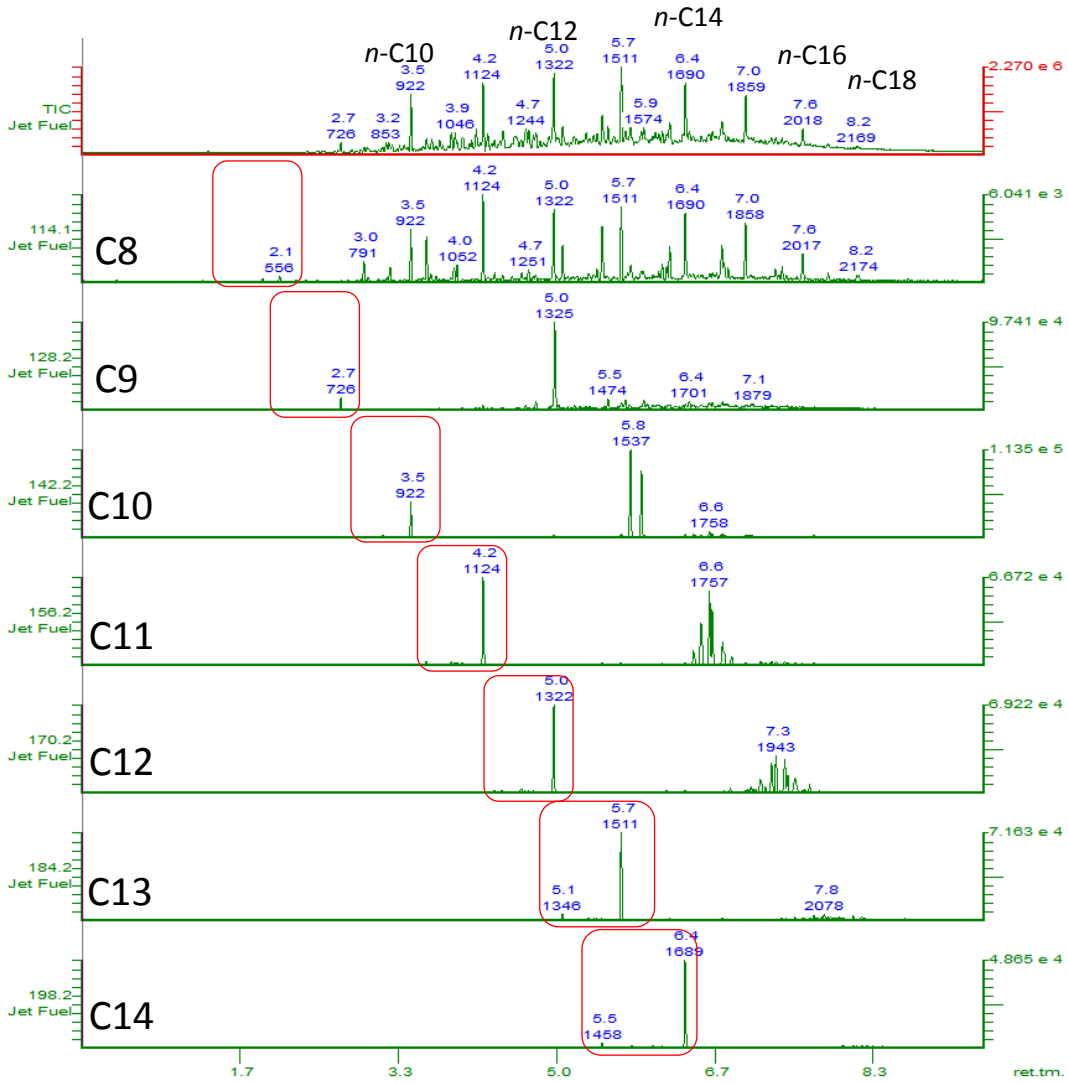
# Isomer Distribution Important for Jet Fuel Analysis

- 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 Distribution Analysis”

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






… EI does not show significant alkane isomers

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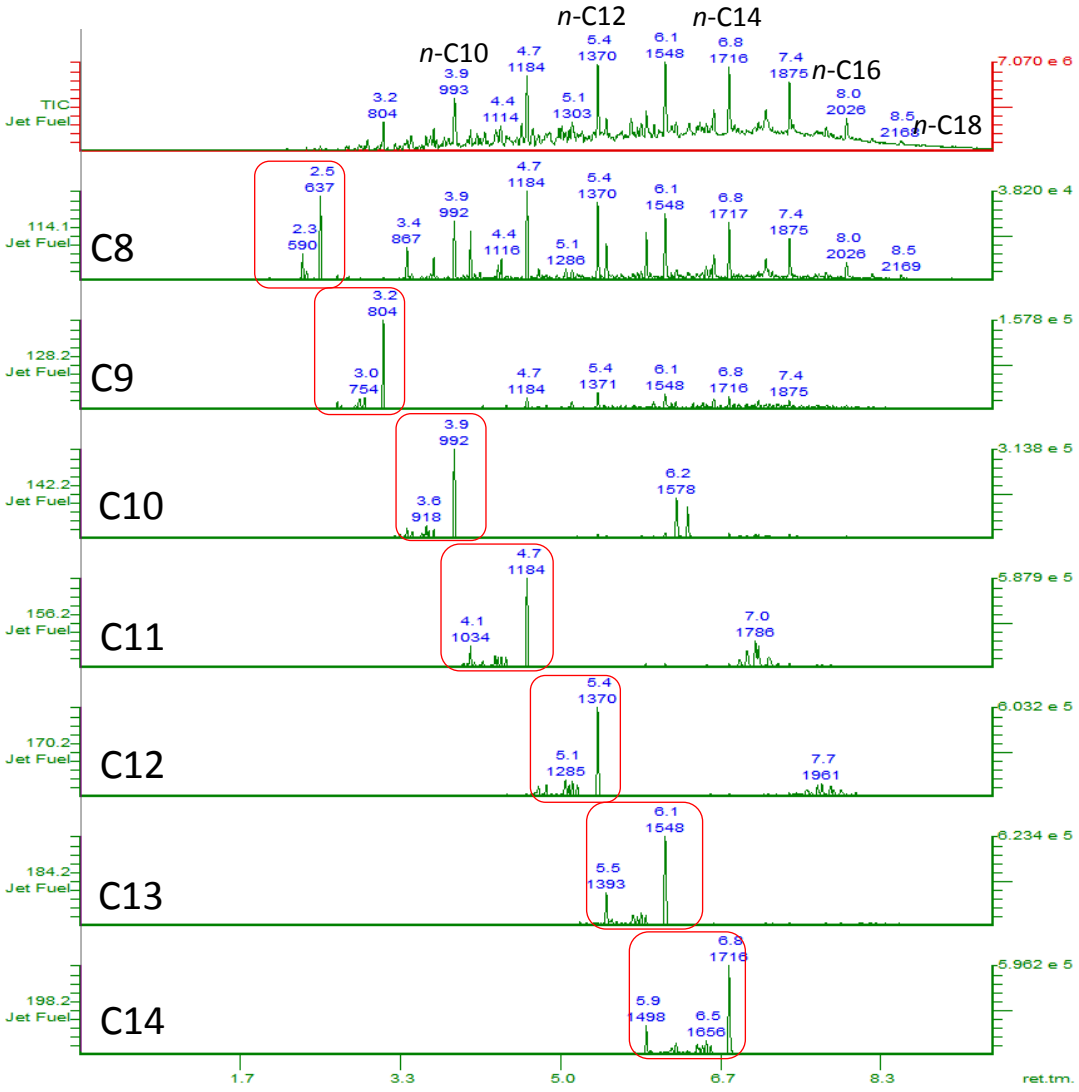
# “Jet A” Jet Fuel, $C_8$ - $C_{14}$ by *Cold EI* GC/MS






… Cold EI clearly show alkane isomers

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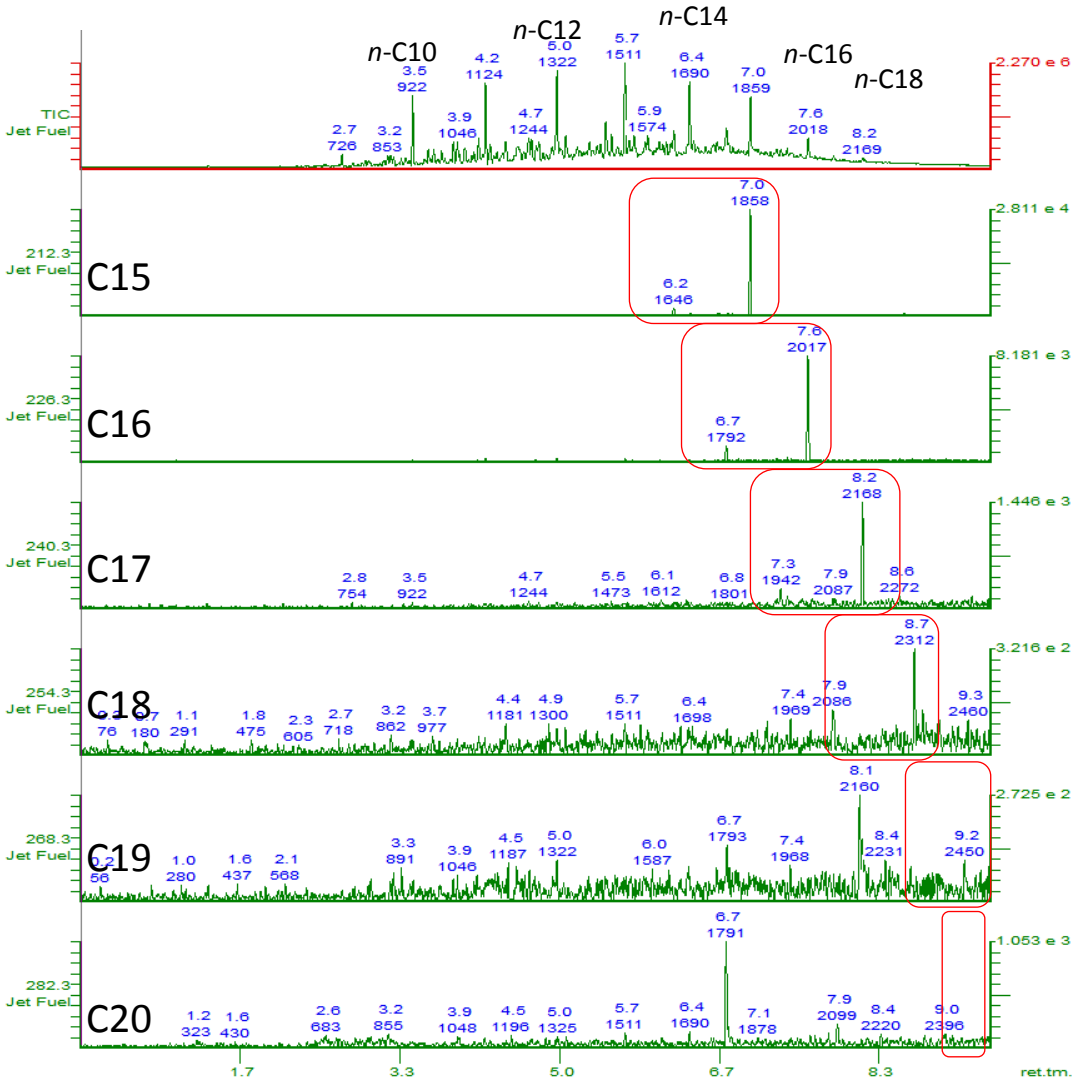
# “Jet A” Jet Fuel, $C_{15}$ – $C_{20}$ by EI GC/MS






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

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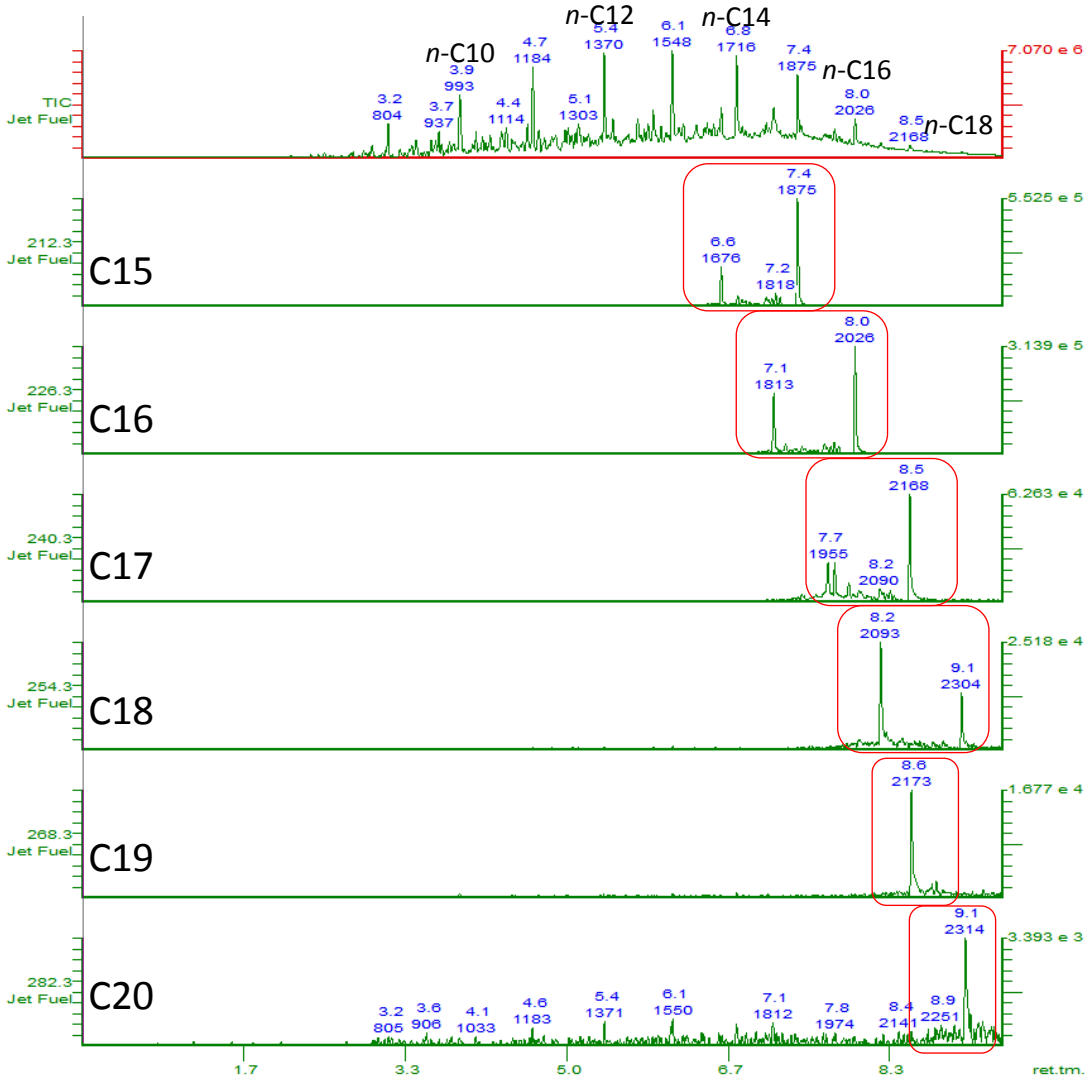
# “Jet A” Jet Fuel, $C_{15}$ – $C_{20}$ by *Cold EI* GC/MS






… Cold EI clearly shows isomers

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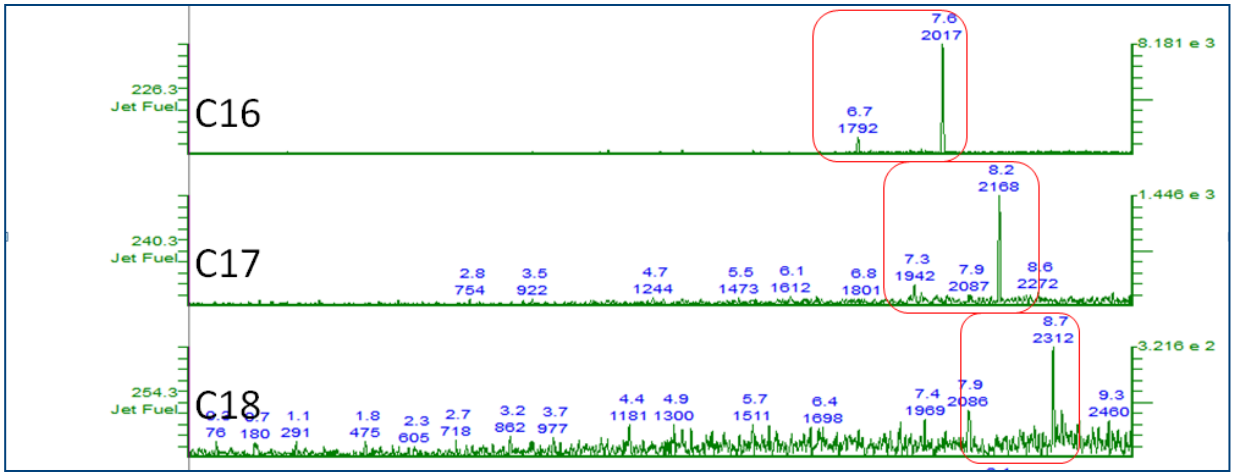
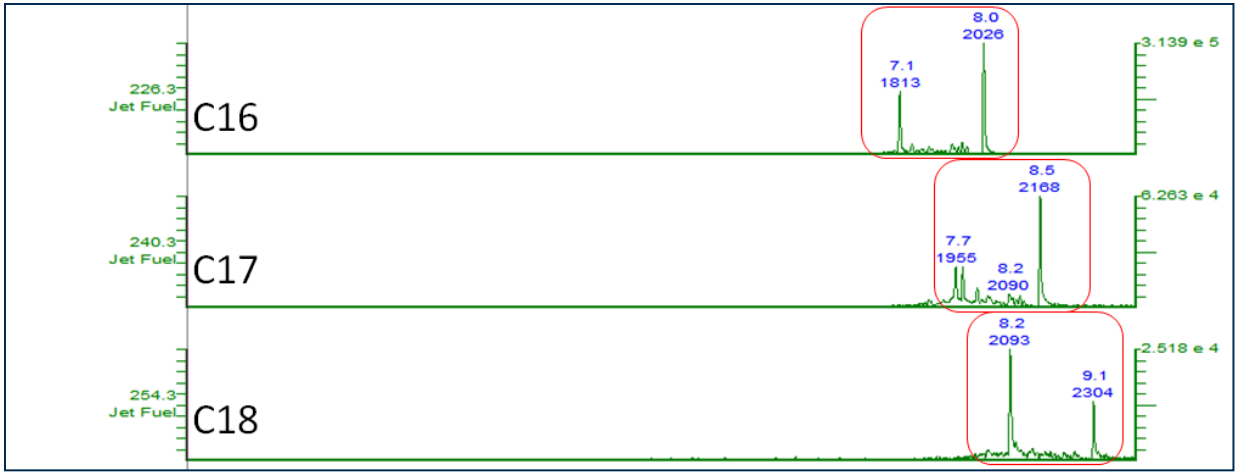
# Comparing EI and *Cold* EI GC/MS

EI




Cold EI




 Cold EI shows much stronger isomer peaks and mass chromatograms

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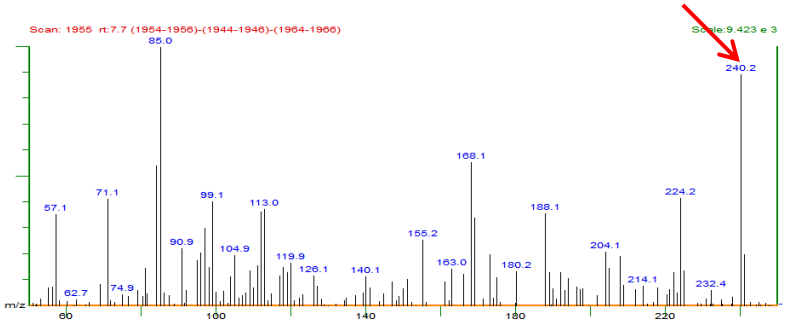
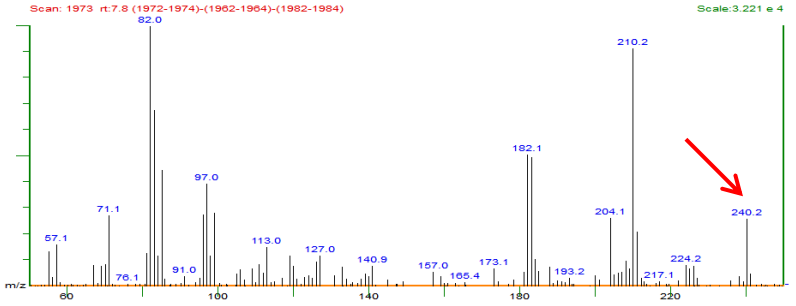
# “Jet A” Jet Fuel, $C_{17}$ isomers all show Molecular Ion in Cold EI

Isomer A



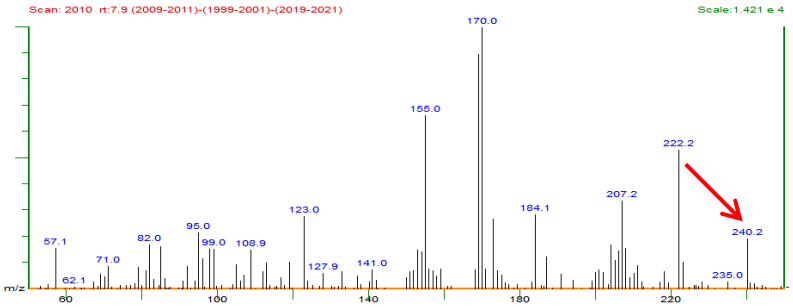

Isomer B



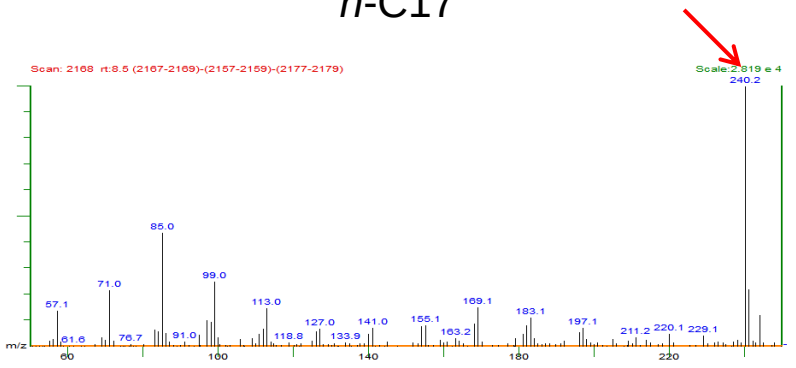

*Hydrocarbon series*

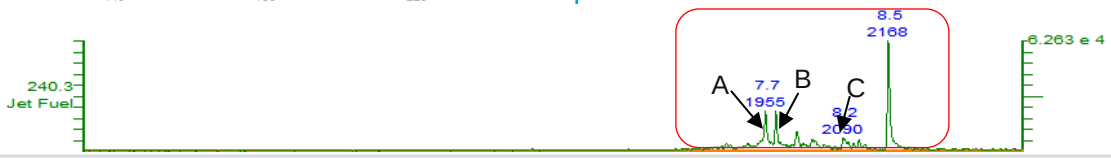
57
71
85
99
113
127
141
155
169
183
197
211
225

Isomer C




*n*-C17






… complex spectra with extraneous peaks from coeluting compounds

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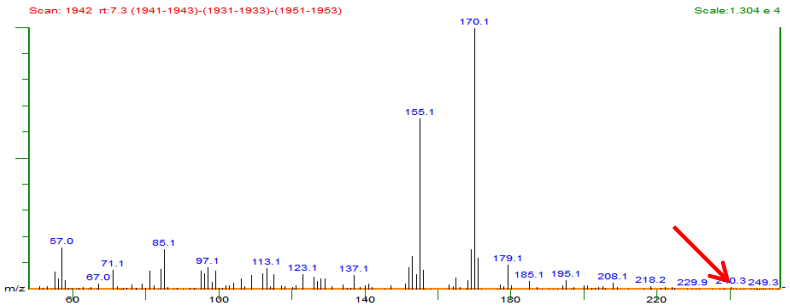
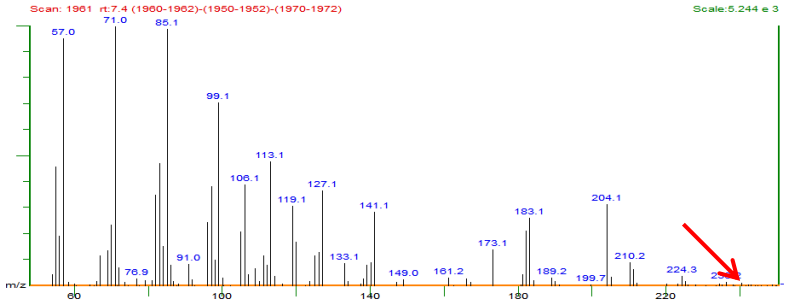
# “Jet A” Jet Fuel, $C_{17}$ isomers show small or no Molecular Ion with EI

Isomer A



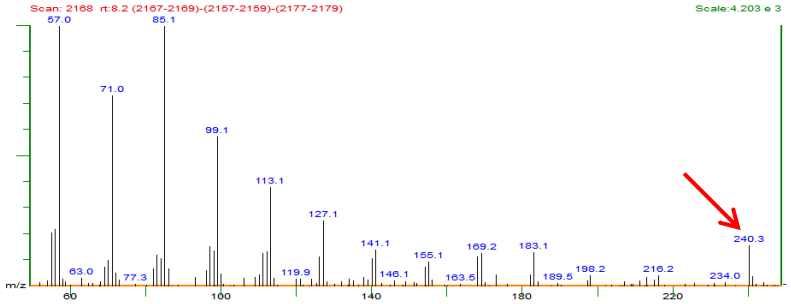

Isomer B

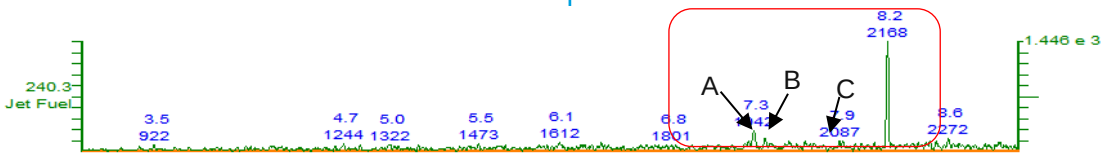



Isomer C

*Not detected*

*n*-C17



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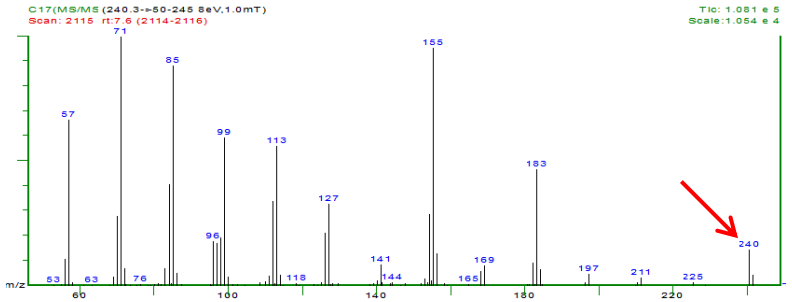
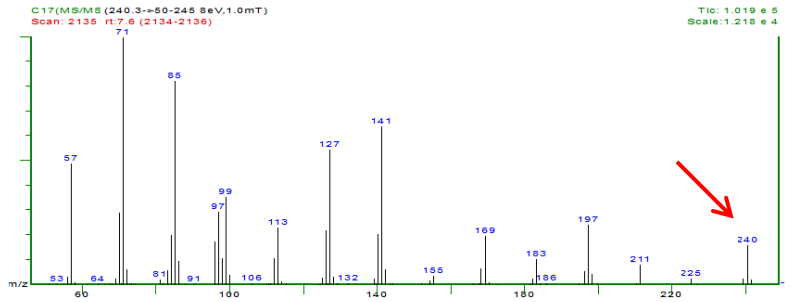
# "Jet A" Jet Fuel, $C_{17}$ isomers confirmed by Cold EI with MS/MS detection (240 → 50-300)

Isomer A




Isomer B




*Hydrocarbon series*

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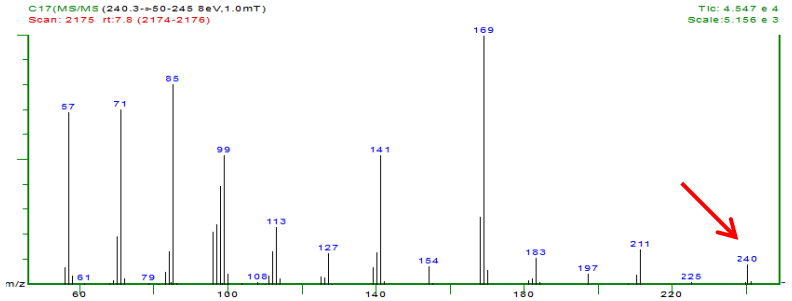
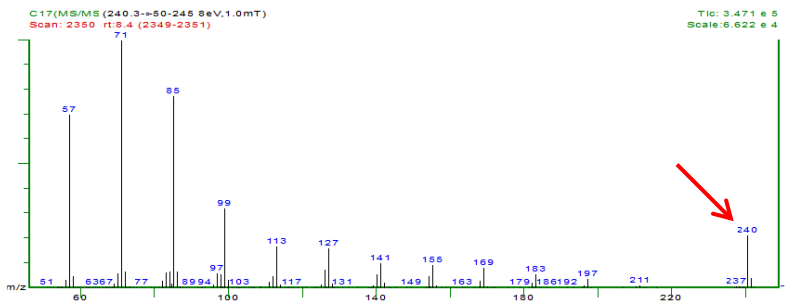
Isomer C




*n*-C17




240 → 50-300


 … all show hydrocarbon fragment ion series

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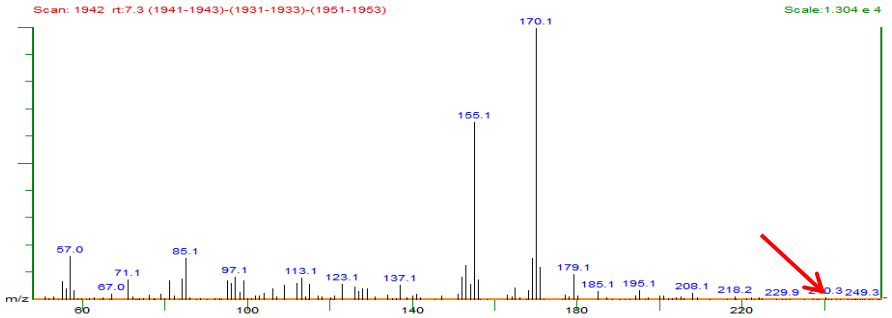
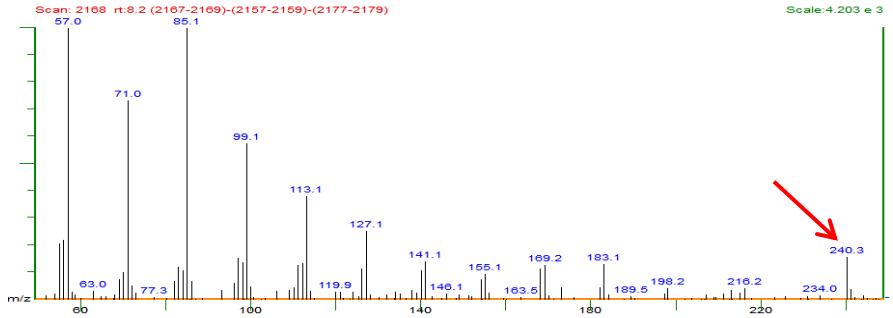
# “Jet A” Jet Fuel, EI *vs.* Cold EI

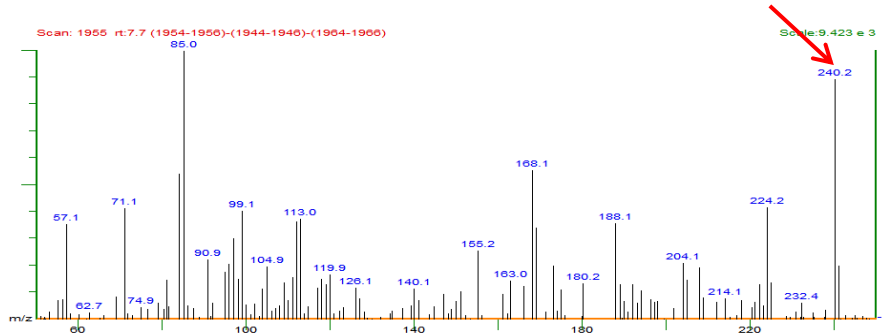
EI Isomer A



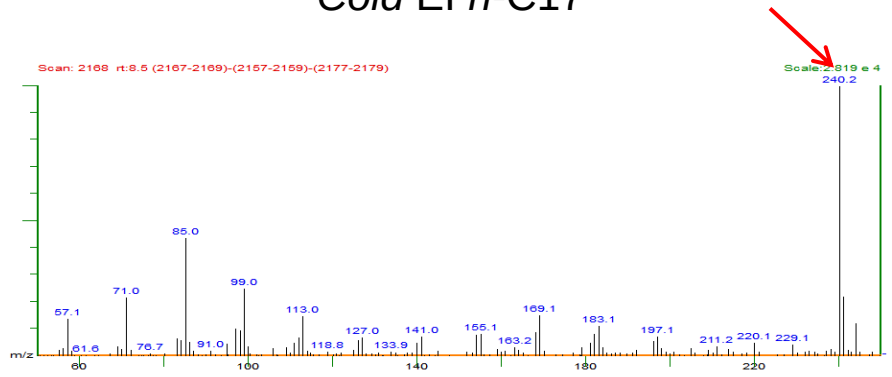

EI *n*-C17




*Cold EI* Isomer A




*Cold* EI *n*-C17




 … much larger Molecular Ion with Cold EI for isomer identification

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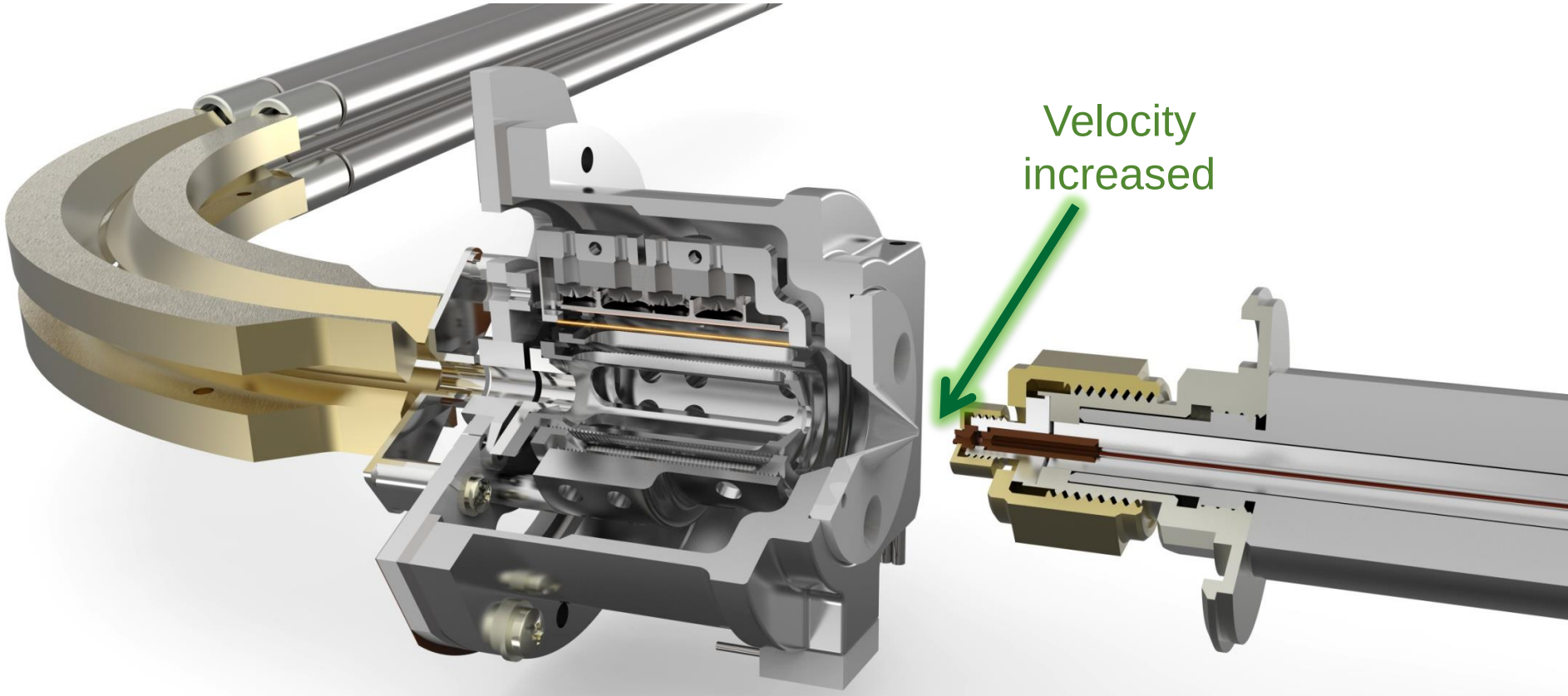
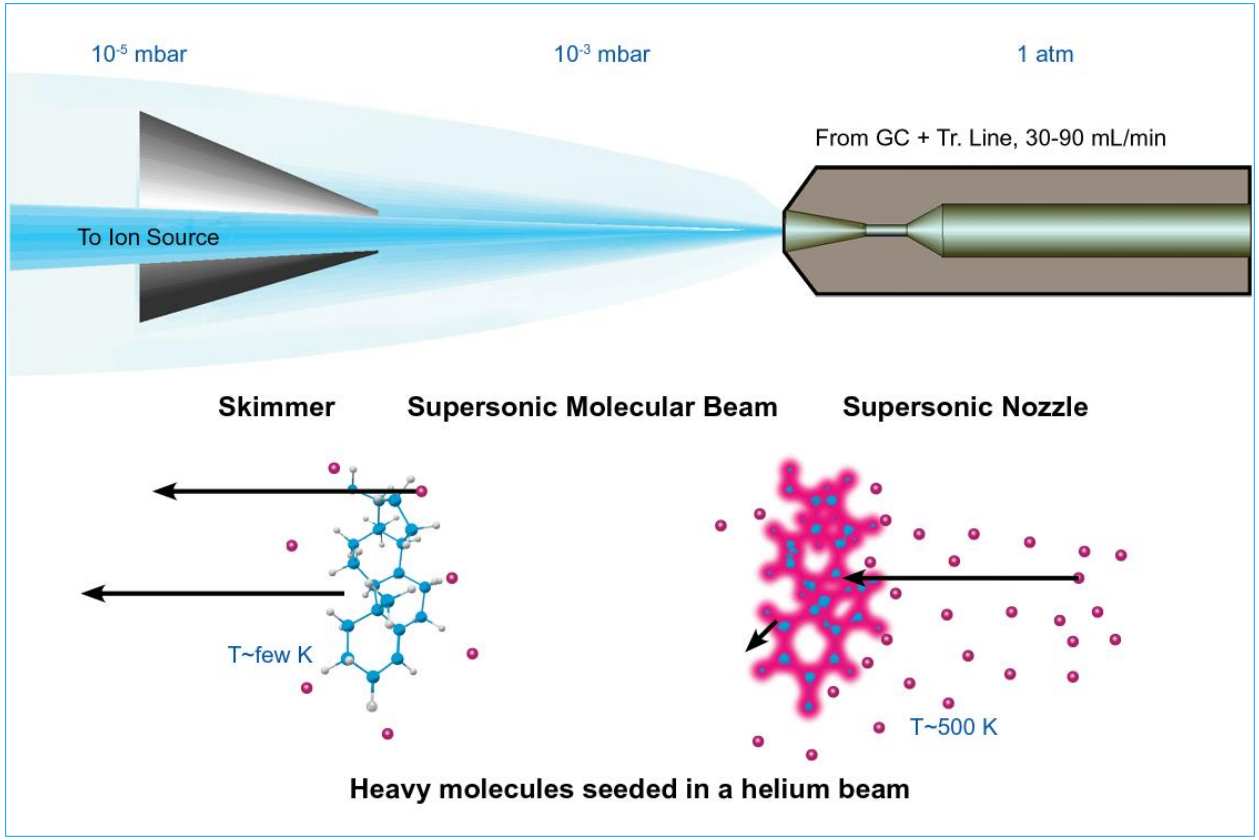
# How does Cold EI work?

- Molecules exit the GC column at ~+250 ºC , and are mixed with a make-up gas
- Nozzle adiabatic expansion ‘cools’ the analyte molecules in a supersonic molecular beam, reducing internal vibrational energy (“temperature”)
- Excess carrier gas is skimmed off
- Cold molecules (~15 K, ~-260 ºC) enter source for molecular ion formation and mass analysis

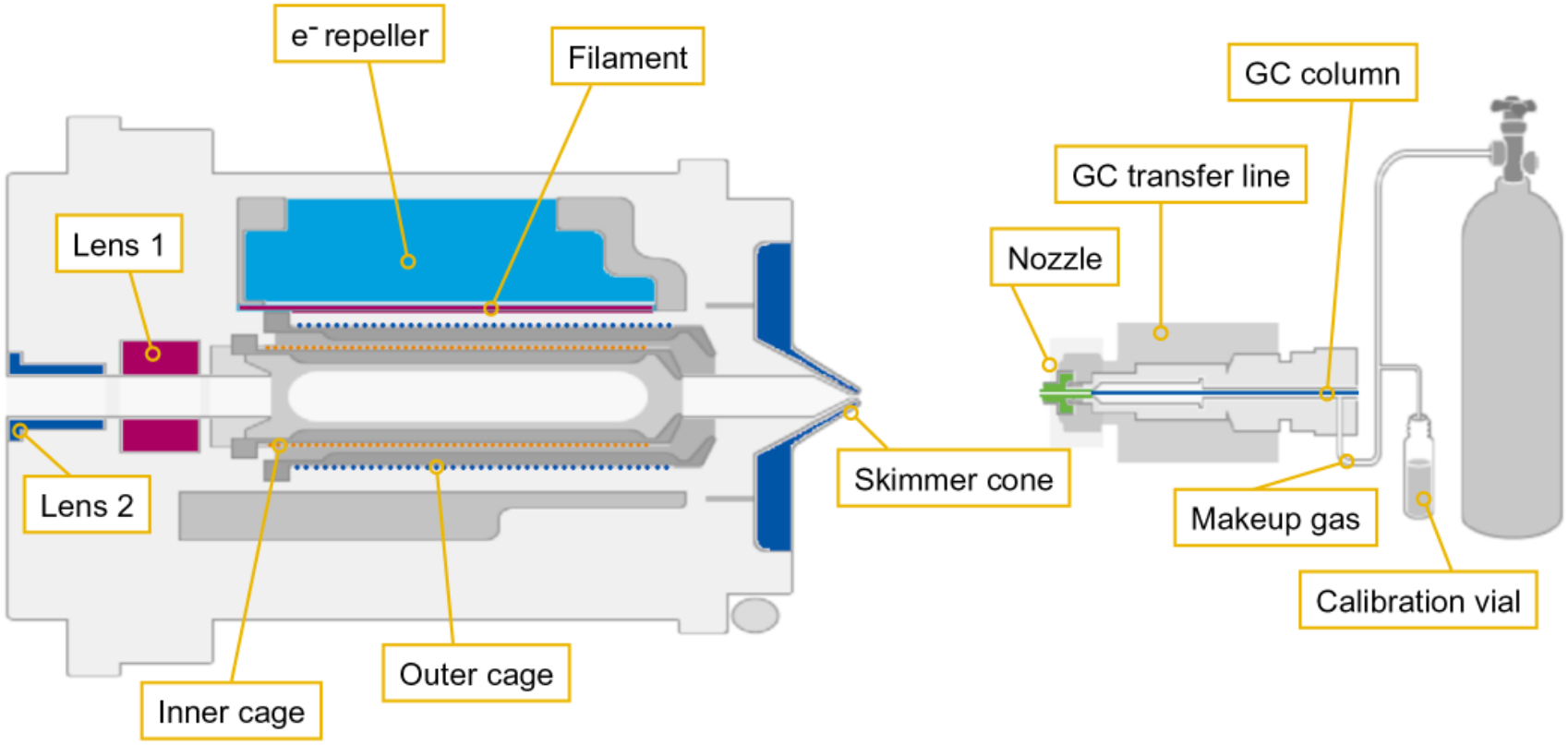


# Supersonic Molecular Beam




- 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)

# Cold EI Ion Source



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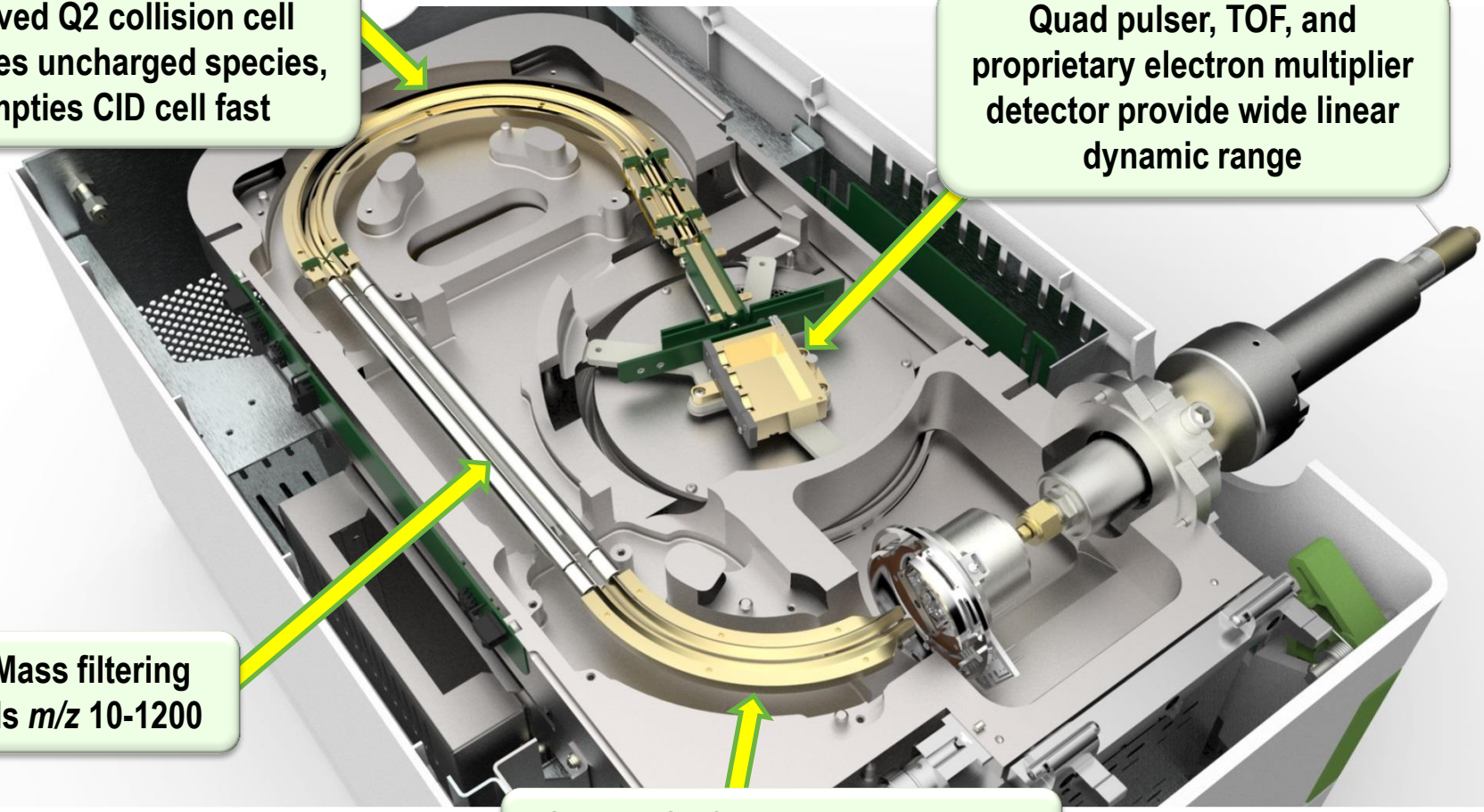
# AxION iQT MS/MS Ion Optics



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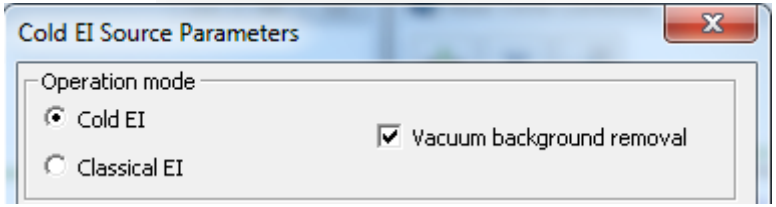
# PerkinElmer AxION iQT™ GC/MS/MS system

- AxION iQT shows excellent MS mode sensitivity with fast data acquisition speeds.
- AxION-iQT offers full mass range spectra, and excellent matching of analyte spectra with NIST & Wiley spectra libraries
- Includes software tools for deconvolution of chromatograms to identify components in complex samples.
- Data can be imported into TIBCO Spotfire® Software for Principle Component Analysis (PCA)

# AxION iQT GC/MS/MS

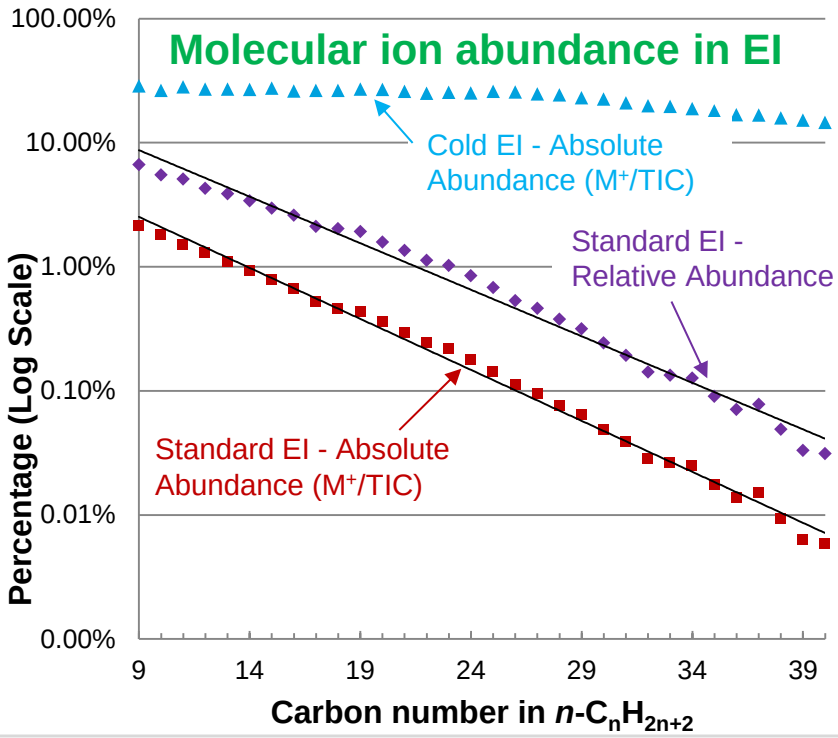
- GC/MS/MS
  - Novel GC/MS/MS configuration
  - All MS/MS fragment ions all the time
- Conventional EI and Cold EI ion sources
- Cold EI operates in four modes:
  - Cold EI with Vacuum Background Removal (VBR)
  - Cold EI without VBR
  - Classical EI
  - Low eV Cold EI

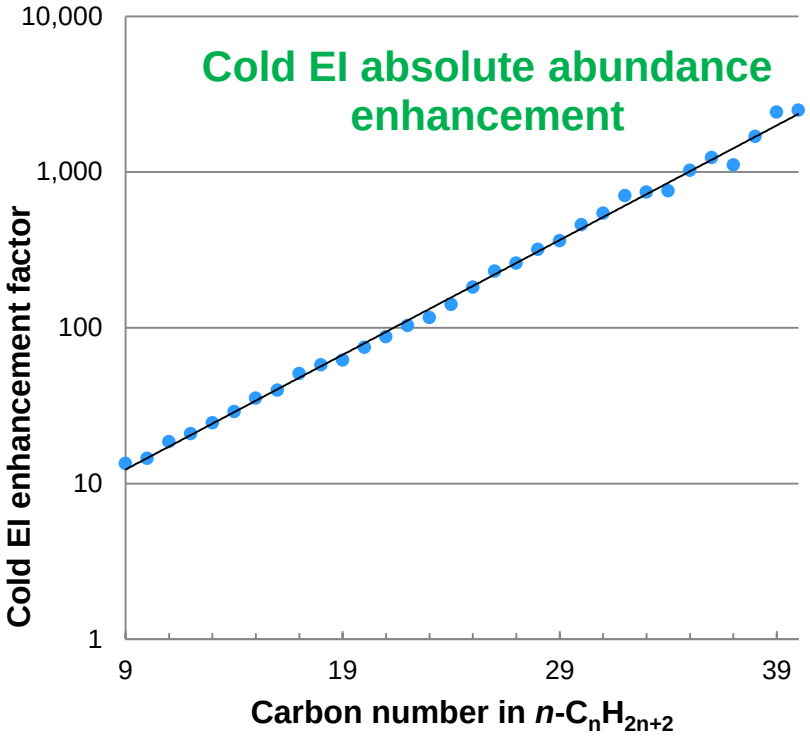



- Mass analysis can be full spectrum or MS/MS
- MS/MS shows full fragment ion spectra, not just 1 or 2 MRM ions
- Fastest heating and cooling conventional Clarus 680 GC oven

# 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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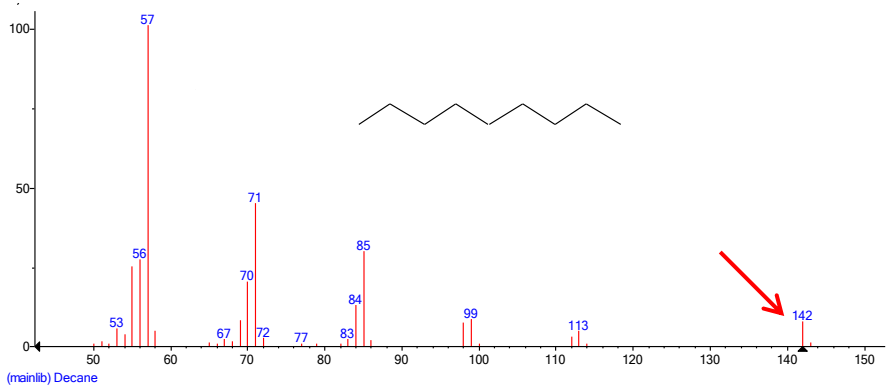
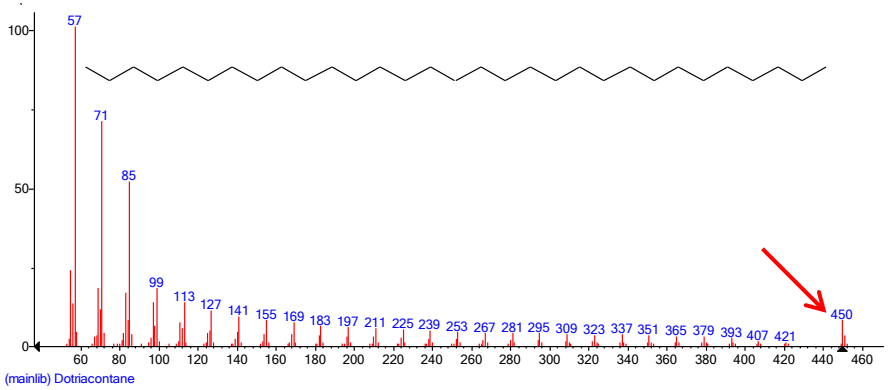
# Cold EI Enhances Molecular Ion for Hydrocarbons as Carbon Number Increases

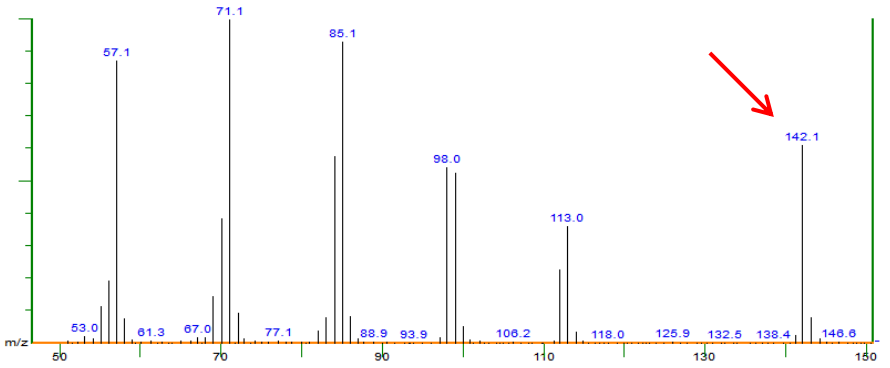
*n*-$C_{10}$ - EI (NIST)



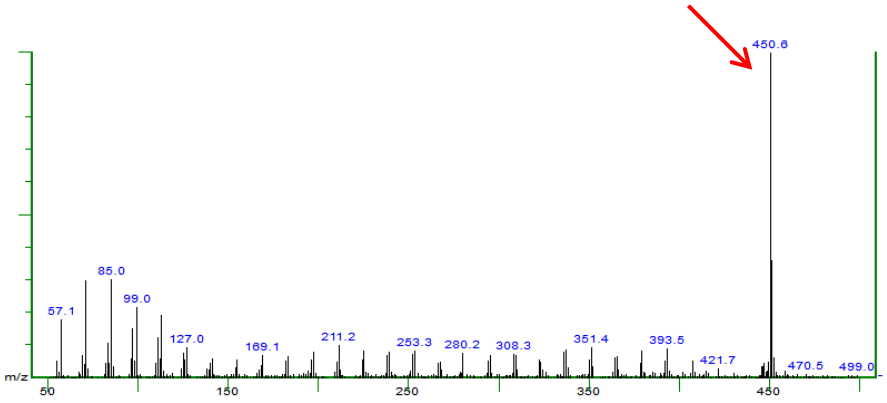

*n*-$C_{32}$ - EI (NIST)




*n*-$C_{10}$ - Cold EI




*n*-$C_{32}$ - Cold EI






… molecular ion increases with carbon number

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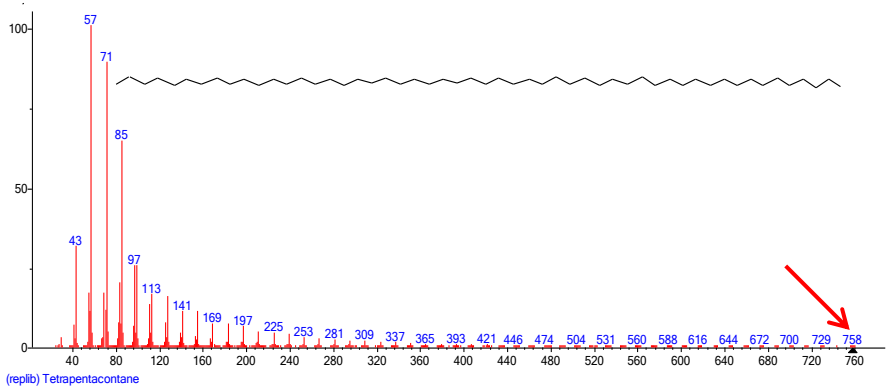
# Cold EI for molecular ions from high-boiling hydrocarbons

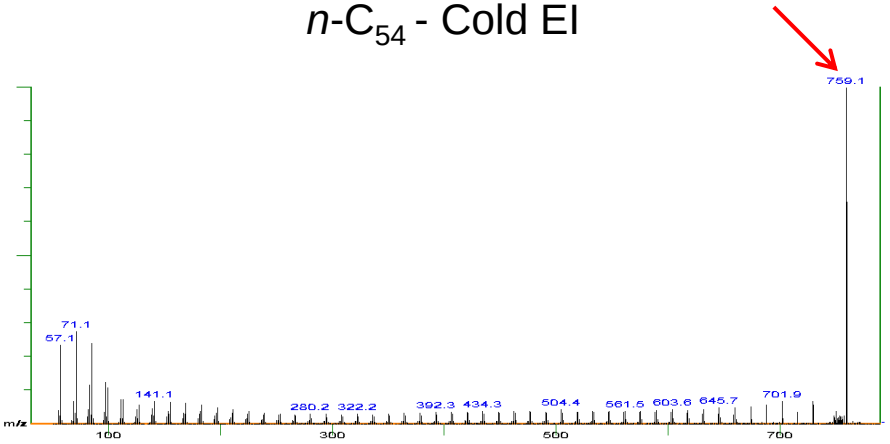
*n*-$C_{54}$ (MW=758.9) - EI (NIST)



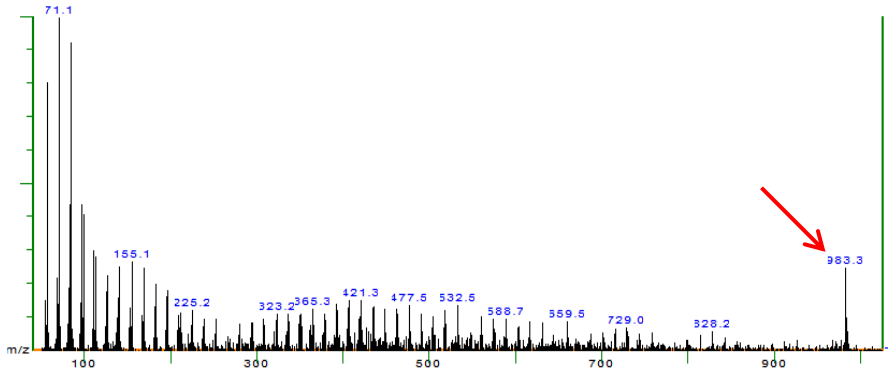

*n*-$C_{70}$ (MW=983.1) - EI (NIST)

*Not available in*
*NIST 2014 or Wiley 10th*
*mass spectral databases of*
*~1,000,000 GC/MS spectra*

*n*-$C_{54}$ - Cold EI




*n*-$C_{70}$ - Cold EI






… high flow rates enable high boiling points

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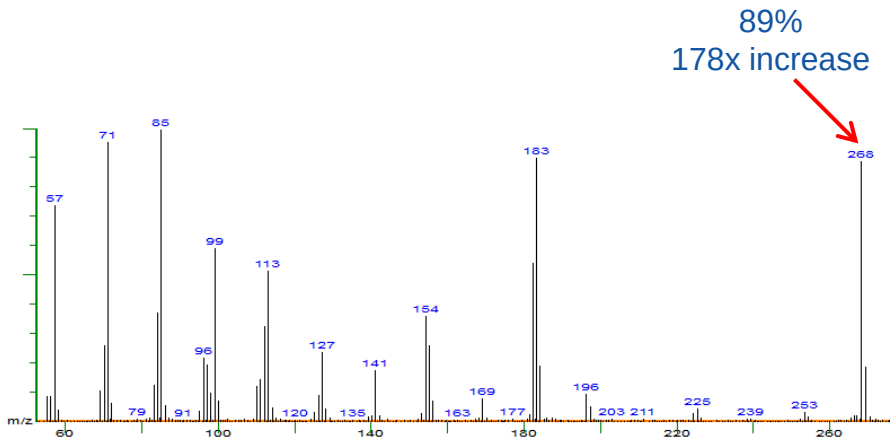
# Pristane/Phytane Ratio – Geochemistry Biomarkers

- Often used as biomarkers to help determine the origin of oil deposits and sources of oil spills
- Indicator of oil “maturity”
- Most widely used biomarker parameter for the assessment of redox conditions during sediment accumulation
- Indicator for degree of oxygen depletion in the water column
- Indicator for the biodegradation of oil
- Pristane/phytane ratios of >1 indicated oxic conditions of sedimentation, values of <1 reflected anoxic conditions
- These isoprenoids are primarily derived from the phytol side chain of the chlorophyll molecule
- Can be used as biomarkers for phytoplankton.
- Other primary sources, such as archaebacterial ether lipids, or tocopherols could complicate the source pristane-phytane interpretation.
- Highly branched, so very small molecular ions
  - Difficult to identify in the complex mixture of crude oil

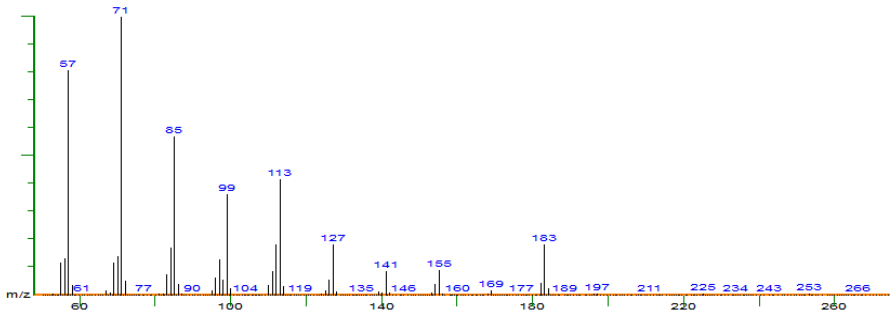
# Pristane, $C_{19}H_{40}$, MW=268

NIST

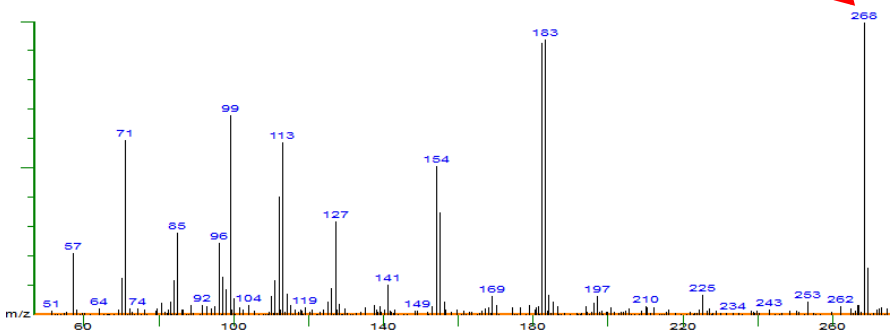

Cold EI – 70 eV




EI – 70 eV



Cold EI – 18 eV






… Cold EI → 178x increase, 18 eV → 212x increase

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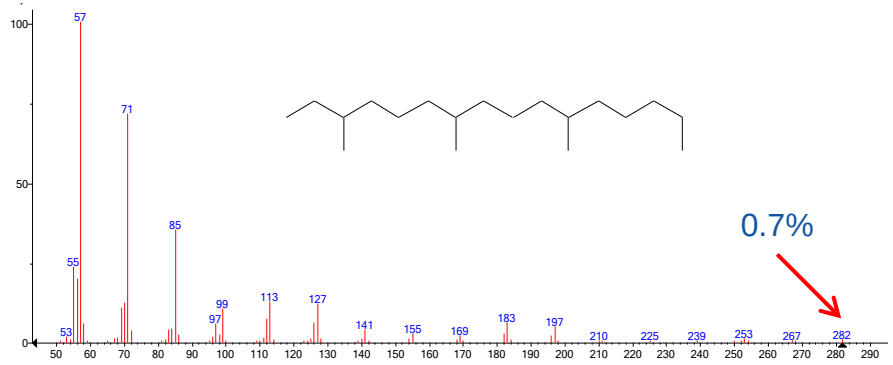
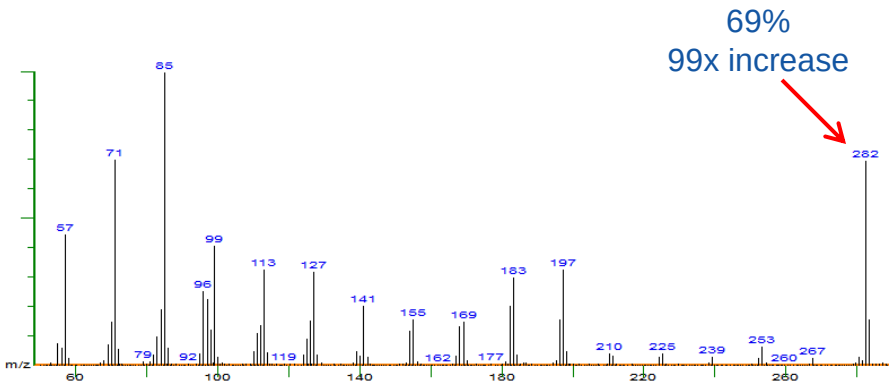
# Phytane, $C_{20}H_{42}$, MW=282

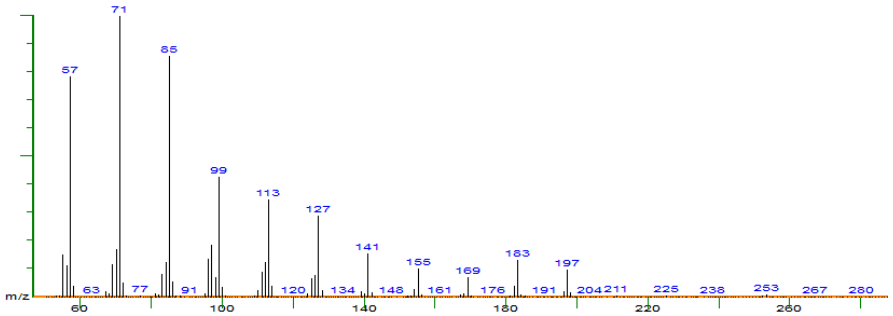
NIST



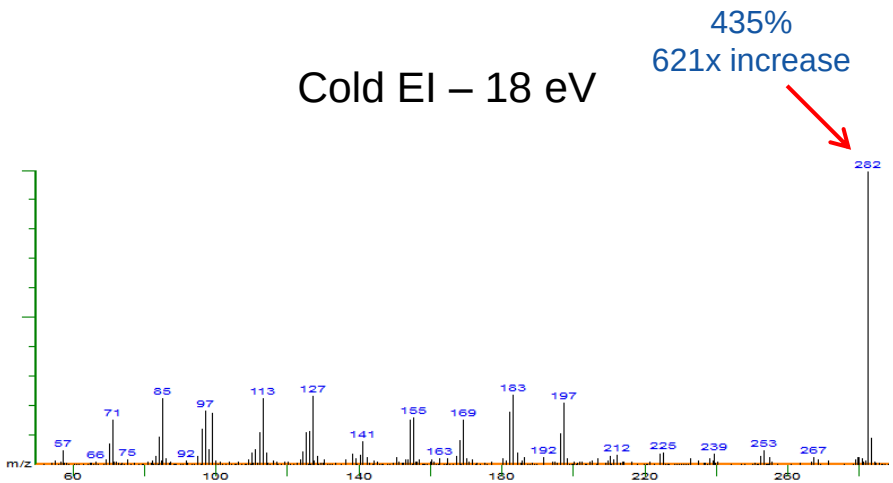

Cold EI – 70 eV




EI – 70 eV



Cold EI – 18 eV






… Cold EI → 99x increase, 18 eV → 621x increase

PerkinElmer

# 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
  - Molecular beam eliminates residual vacuum background ions
  - Ion source tailing eliminated by open source design
  - No ion suppression or enhancement effects
  - 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
- Method-based switching to Classical and “Low eV” EI

# Summary

- Long-chain hydrocarbons and branched isomers can have small or no molecular ions using EI
- Cold EI typically gives a significantly stronger molecular ion than EI, and can show one even when EI does not
- Low eV ionization can improve molecular ion with Cold EI
- 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

## Thank you for your attendance