Enhanced Molecular Ion in GC/MS by Cold EI

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If you can’t explain it simply, you don’t understand it well enough.

– Albert Einstein
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

3. Find $x$.

Here it is
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
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\textsubscript{40}H\textsubscript{82}.

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
Strong Molecular Ions when EI does not have any
- Squalane C\textsubscript{30}H\textsubscript{62}

 Highly-branched chains often have low intensity molecular ion
Cold EI for molecular ions from high-boiling hydrocarbons

$n\text{-}C_{54}$ - EI (NIST)

$n\text{-}C_{70}$ - EI (NIST)

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

$n\text{-}C_{54}$ - Cold EI

$n\text{-}C_{70}$ - Cold EI

… high flow rates enable high boiling points
Jet Fuel Isomer Characterization
Many possible hydrocarbon isomers

The On-Line Encyclopedia of Integer Sequences (OEIS), A000602, A000628, A134818.
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, C₈ - C₁₄ by EI GC/MS

... EI does not show significant alkane isomers
“Jet A” Jet Fuel, C₈ - C₁₄ by *Cold EI* GC/MS

Cold EI clearly show alkane isomers n-C₁₀, n-C₁₂, n-C₁₄, n-C₁₆, and n-C₁₈.
“Jet A” Jet Fuel, C\textsubscript{15} – C\textsubscript{20} by EI GC/MS

EI begins to show weak isomers, then drops into the noise.
“Jet A” Jet Fuel, C$_{15}$ – C$_{20}$ by Cold EI GC/MS

Cold EI clearly shows isomers.
Comparing EI and Cold EI GC/MS

Cold EI shows much stronger isomer peaks and mass chromatograms.
“Jet A” Jet Fuel, C$_{17}$ isomers all show Molecular Ion in Cold EI
"Jet A" Jet Fuel, C\textsubscript{17} isomers show small or no Molecular Ion with EI

Isomer A

Isomer B

Isomer C

Not detected

n-C17
“Jet A” Jet Fuel, EI vs. Cold EI

EI Isomer A

Scan: 1942 n:7.3 (1941-1943)-(1951-1953)

Scale: 1.304 e - 4

EI n-C17

Scan: 2168 n:8.2 (2157-2169)-(2177-2179)

Scale: 4.205 e - 3

Cold EI Isomer A


Scale: 4.223 e - 3

Cold EI n-C17

Scan: 2168 n:8.5 (2157-2169)-(2177-2179)

Scale: 319 e - 4

... much larger Molecular Ion with Cold EI for isomer identification
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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