APPLICATION NOTE

Gas Chromatography/ Mass Spectrometry

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Cold EI GC/MS Enhancement of High MW Hydrocarbon Molecular Weight Information

Introduction

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. It is the single most important peak in the mass spectrum, since it is most characteristic of the target compound. Having a strong molecular ion in the spectrum helps the analyst reject many false-positive library search matches. However, many compounds, including long-chain and highly-branched hydrocarbons, do not yield a stable molecular ion under EI conditions and it is small or even absent from their spectra.

This makes analyte identification more difficult, especially at low concentrations or in complex matrices. Without the molecular ion, identification depends much more heavily upon matching unknown compounds to the chromatographic retention time of calibration standards.

Cold Electron Ionization GC/MS (Cold EI GC/MS) is an enhancement of traditional EI available as an option on the PerkinElmer AxION® iQT™ GC/MS/MS mass spectrometer. Cold EI enhances the relative molecular ion abundance of most compounds compared with conventional EI, while retaining the EI fragmentation pattern for spectral library searching. Its operation is described in the Discussion section.

Experimental and Results

Figure 1a shows the EI spectrum of *n*-decane ($C_{10}H_{22}$) found in the NIST mass spectral library database¹, a commonly used tool to match GC/MS spectra for compound identification. Note the abundance of the molecular ion, indicated by the arrow. Figure 1b shows the Cold EI mass spectrum for the same compound, and demonstrates significantly enhanced molecular ion intensity relative to the other ions in the spectrum.

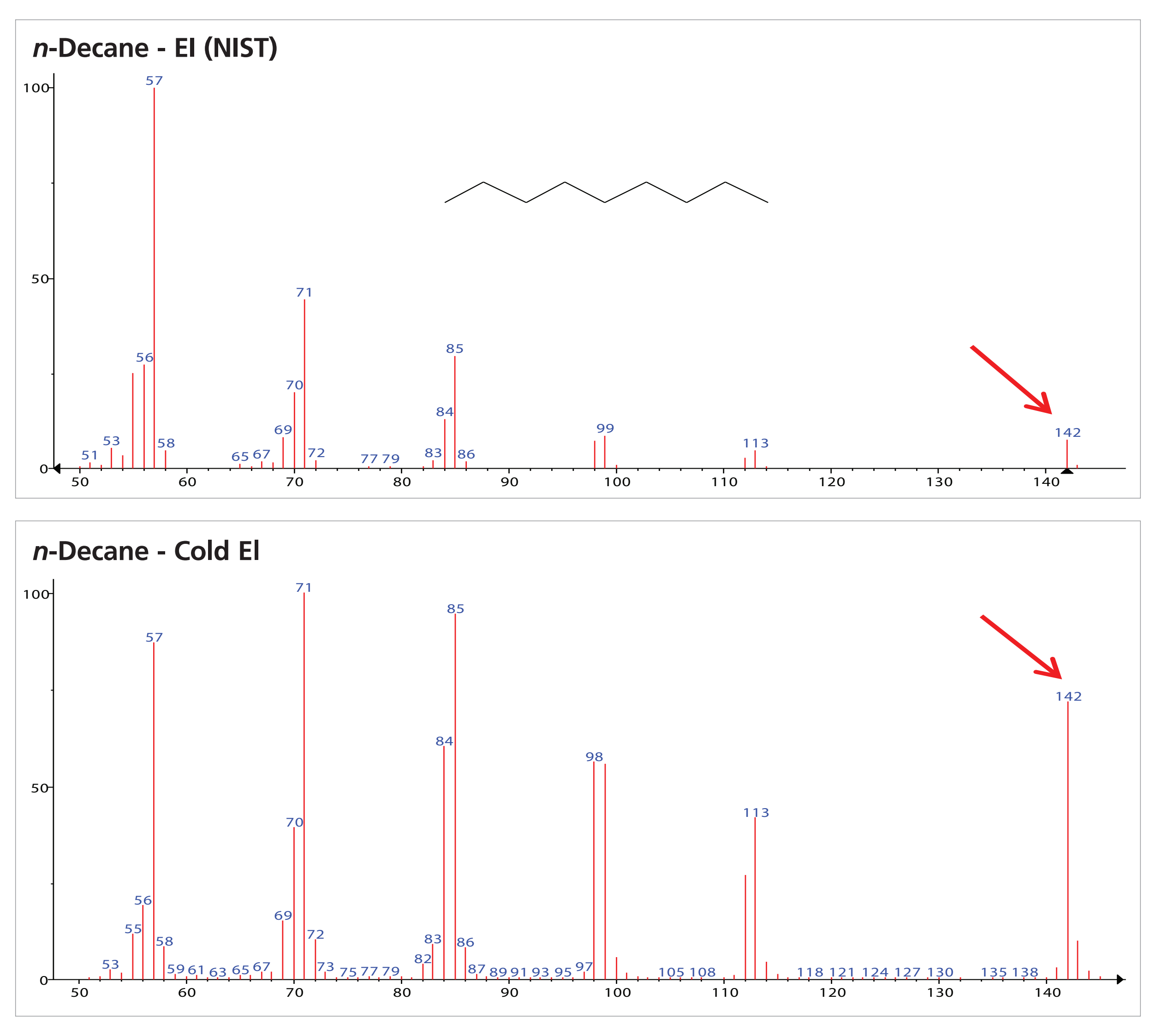
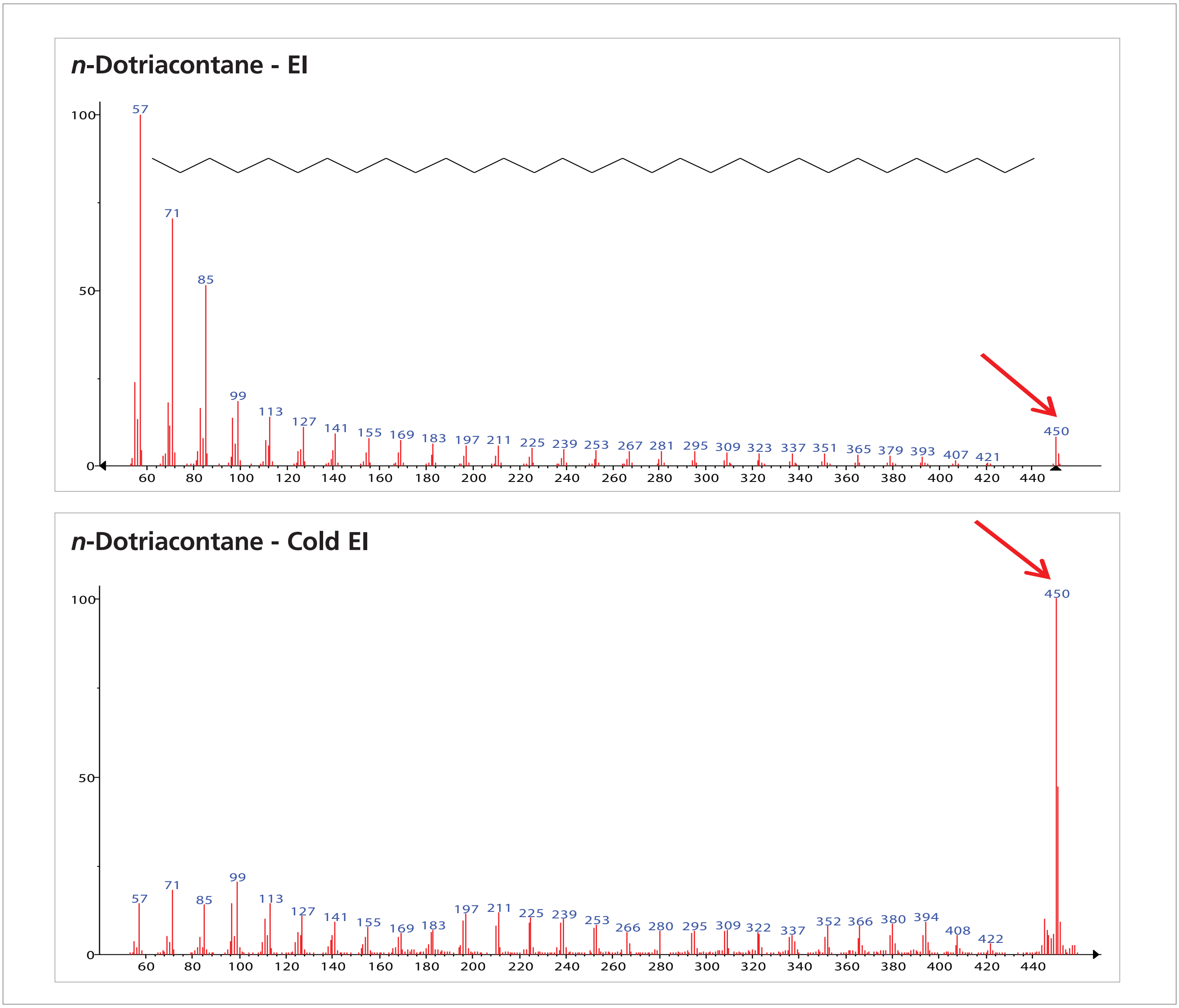


Figure 1 a, b. *n*-Decane ($C_{10}H_{22}$) EI and Cold EI Spectra.

Figure 2a shows the increasing advantage of Cold EI as the hydrocarbon molecular weight increases. Here the NIST spectrum of *n*-dotriacontane ($C_{32}H_{66}$) demonstrates that the relative intensity of a molecular ion in a long chain hydrocarbon can be quite small, while Figure 2b shows the strong enhancement to this molecular ion by Cold EI. The molecular weight of the compound is unambiguous.



***n*-Dotriacontane - EI**

***n*-Dotriacontane - Cold EI**

Figure 2 a, b. *n*-Dotriacontane ($C_{32}H_{66}$) EI and Cold EI Spectra.

Hydrocarbon mixtures such as crude oil may contain high molecular weight compounds which may not be easily analyzed by conventional GC/MS. Figure 3a displays the NIST spectrum of *n*-tetrapentacontane ($C_{54}H_{110}$) with a small molecular ion, while Figure 3b shows the much larger Cold EI-enhanced molecular ion.

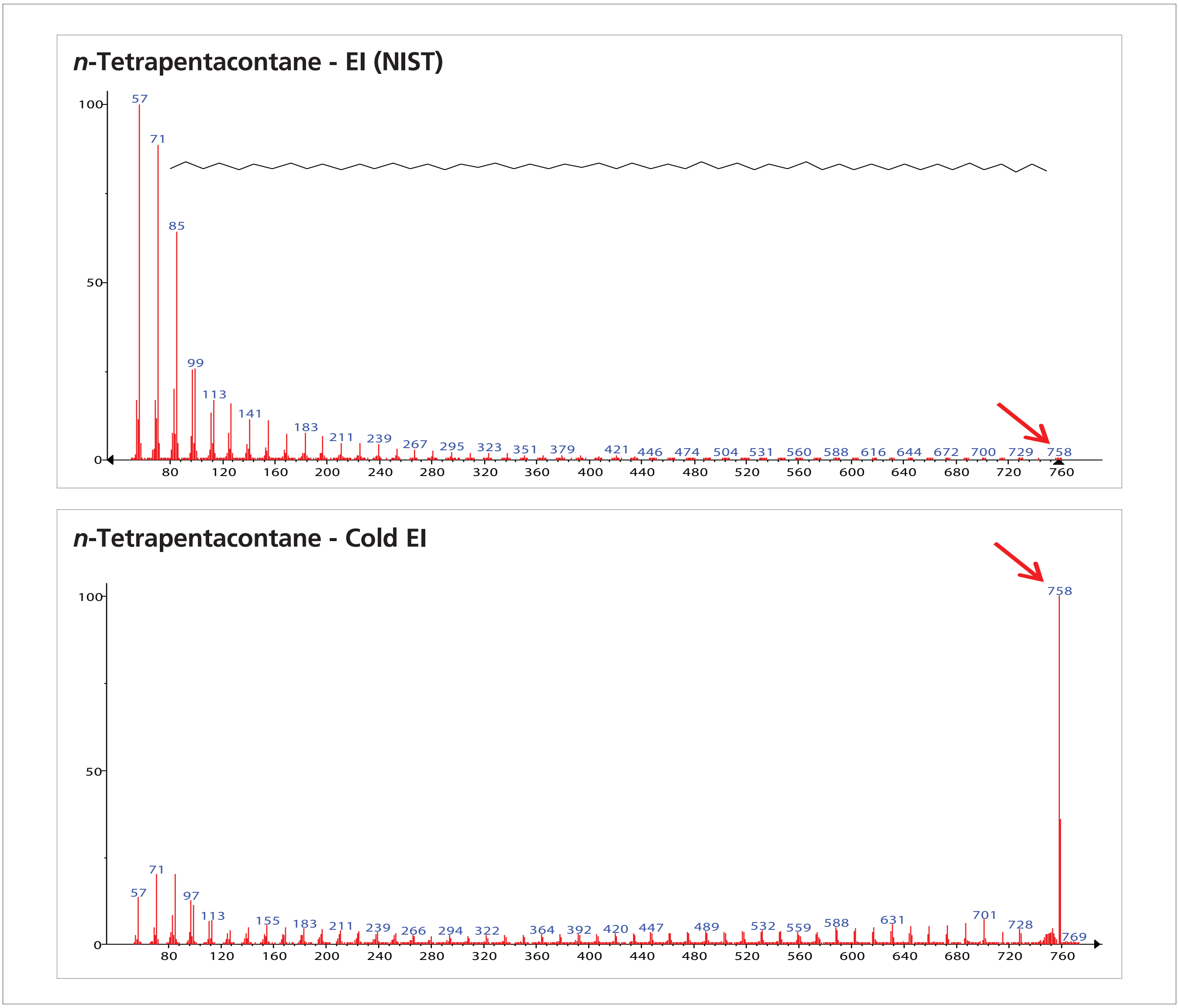
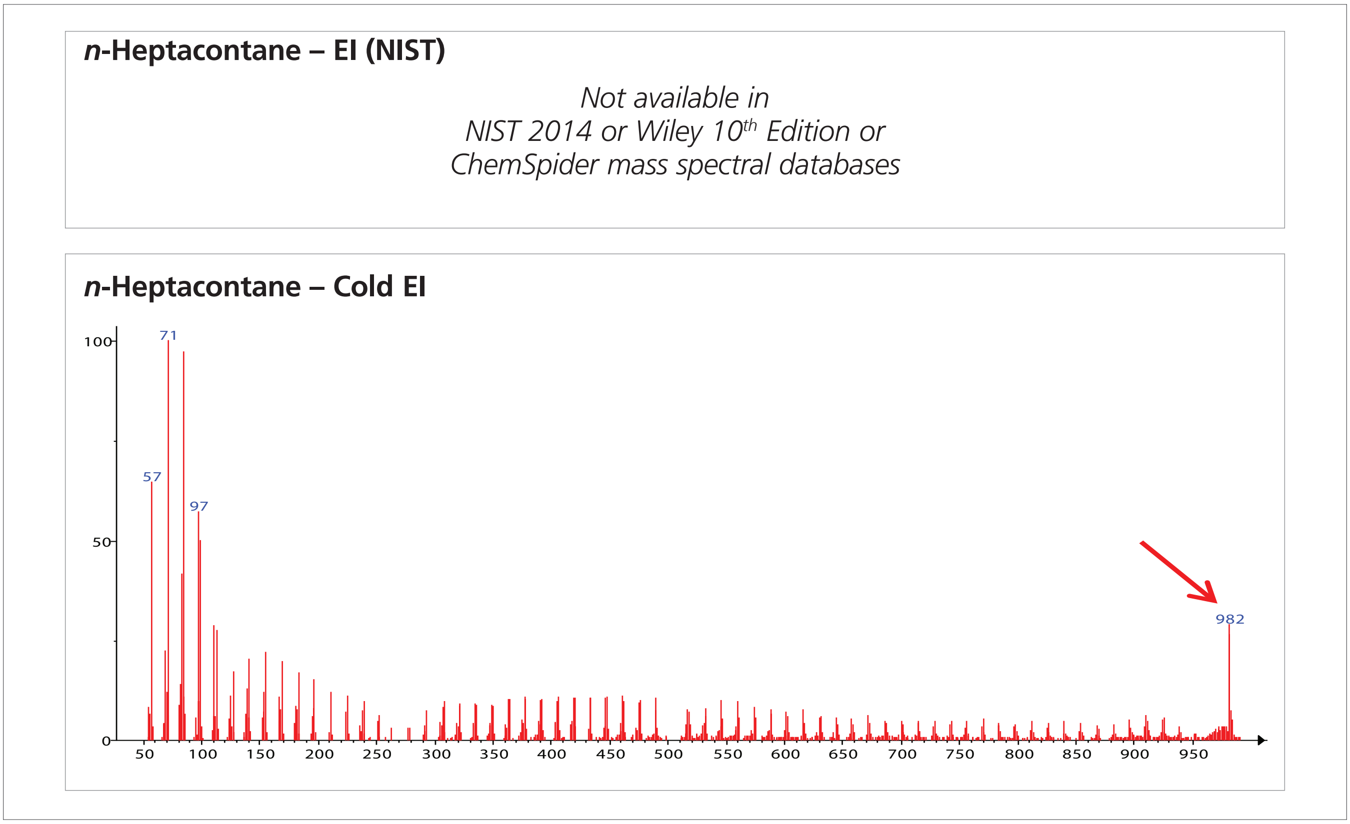


Figure 3 a, b. *n*-Tetrapentacontane ($C_{54}H_{110}$) EI and Cold EI Spectra.

Finally, Figure 4b shows the Cold EI spectrum of *n*-heptacontane ($C_{70}H_{142}$). Although lower in relative intensity, it still shows a very strong molecular ion enhancement, making compound identification easy. Its spectrum is not found in the NIST, Wiley², or ChemSpider³ mass spectral libraries, indicating the difficulty in obtaining conventional EI GC/MS spectra of such a low-volatility compound.



***n*-Heptacontane – EI (NIST)**

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

***n*-Heptacontane – Cold EI**

Figure 4 a ,b. n-Heptacontane ($C_{70}H_{142}$) Cold EI Spectrum.

It is not only linear high molecular weight hydrocarbons which may lack a significant molecular ion peak. The molecular ion abundance for branched compounds drops even faster with molecular weight then for linear compounds. Squalane ($C_{30}H_{62}$) is a triterpene compound often used in cosmetics as a moisturizer and emollient because of its low cost and resistance to oxidation. However, the high degree of branching leads to an unstable molecular ion, with a very low relative intensity in EI (0.2%) as shown in Figure 5a, but a clearly identifiable Cold EI (20%) molecular ion, as shown in Figure 5b.

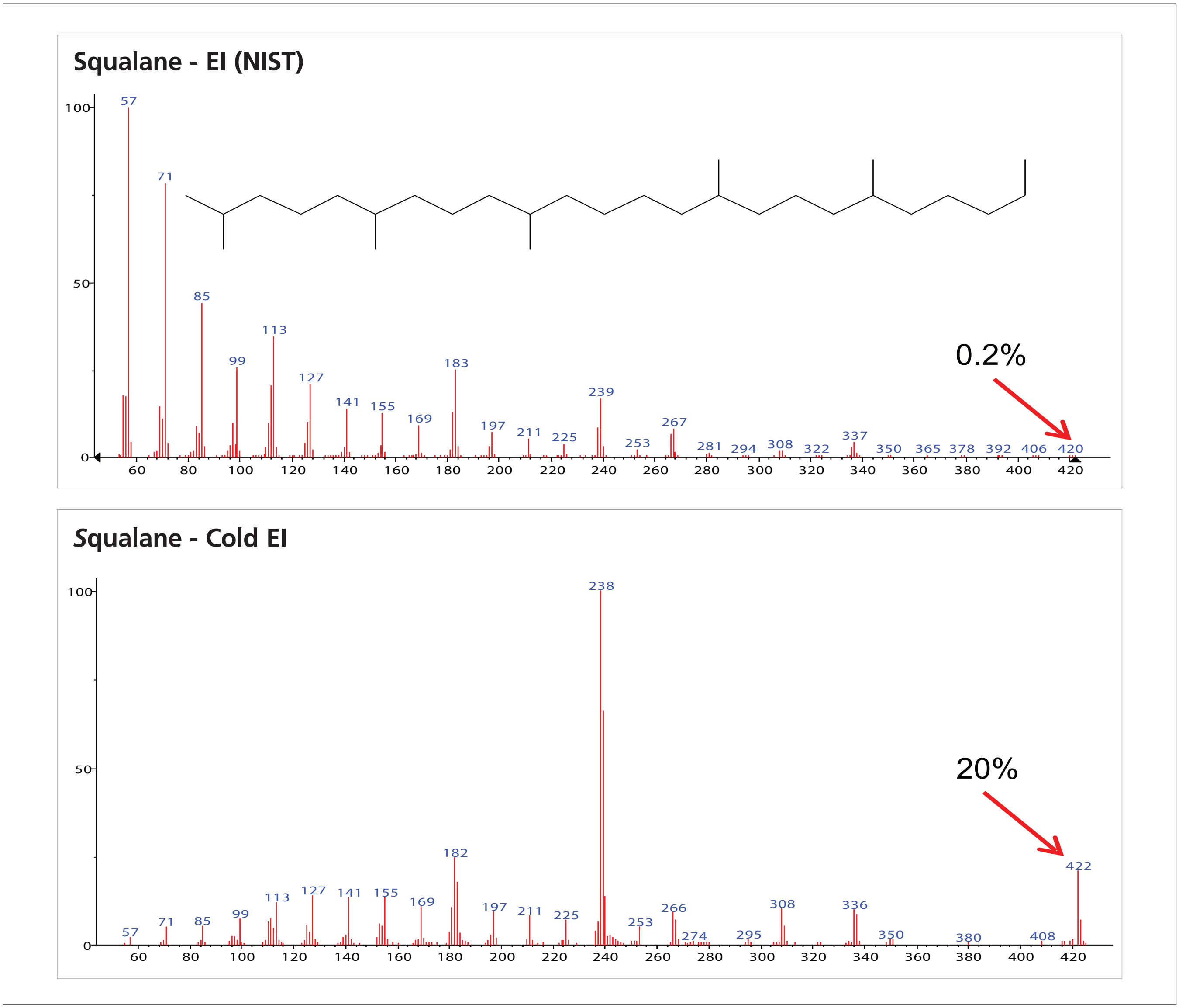


Figure 5 a, b. Squalane ($C_{30}H_{62}$) EI and Cold EI Spectra.

Discussion

Cold EI operates by expanding the GC effluent with a makeup gas through a small nozzle. The associated supersonic expansion and molecular beam formation lowers the vibrational and rotational energies of the molecules in the GC stream, "cooling" them from GC transferline temperature (up to 350 °C or 623 K) to about 20 K (-253 °C). Excess carrier gas is skimmed off. The cooled analyte molecules enter the ionization source in a supersonic molecular beam where they are ionized by electrons, similar to a traditional electron ionization source. However, because of the molecule's very low internal energy, the internal energies of the resulting Cold EI ions are far lower than with conventional EI. Because of the "cold" nature of these ions, fragmentation is substantially reduced and molecular intensity enhanced for many analytes. Generally, the larger the molecule, the greater the relative Cold EI molecular ion enhancement.

The PerkinElmer Cold EI source also utilizes a "fly through" design, to eliminate collisions between gas-phase molecules and ions with the ion source walls, which might lead to additional fragmentation or chromatographic peak tailing.

Figure 6[4] shows that, when analyzed by conventional EI, both the relative and absolute molecular ion abundance of *n*-alkanes is reduced by about 20% for each additional carbon in the chain. However, in Cold EI the absolute molecular ion abundance is roughly unchanged.

The absolute ion abundance enhancement thus exponentially increases with carbon number as shown in Figure 7[4], up to a factor of 2500 for $C_{40}H_{82}$.

To summarize, Cold EI substantially increases the molecular ion intensity for both linear and branched hydrocarbons. As the carbon number increases, the Cold EI enhancement effect is exponentially larger. These features of Cold EI show that it is well-suited to applications requiring reliable and routine characterization of hydrocarbons and their isomers in complex mixtures.

References

1. NIST/EPA/NIH Mass Spectral Library, NIST Standard Reference Database 1A, 2014.
2. Wiley Registry of Mass Spectral Data, 10th Edition, 2013.
3. http://www.chemspider.com.
4. Aviv Amirav, Uri Keshet, Tal Alon, Alexander B. Fialkov; *http://blog.avivanalytical.com/2012/09/how-much-is-molecular-ion-enhanced-in.html.*

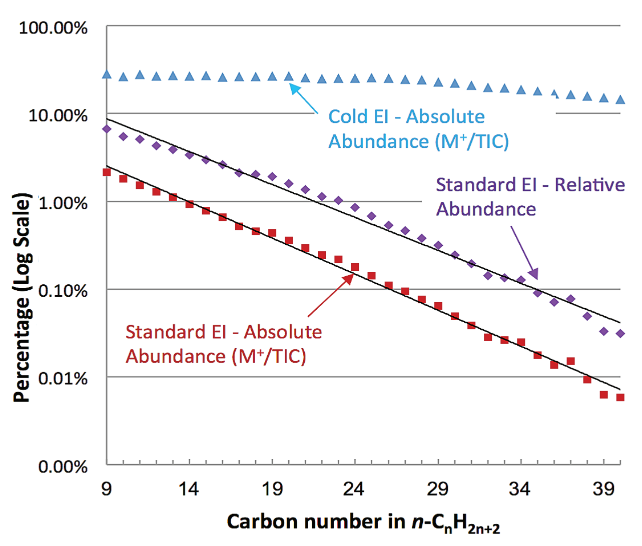


Figure 6. Molecular Ion Abundance in EI.

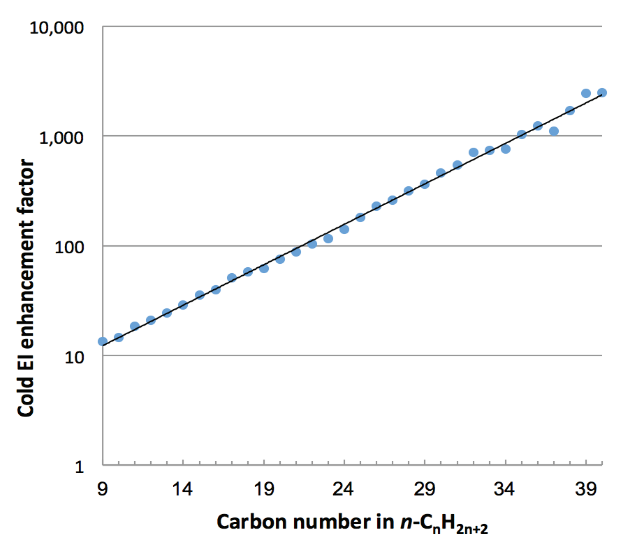


Figure 7. Cold EI Absolute Abundance Enhancement.

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