APPLICATION NOTE

Gas Chromatography/
Mass Spectrometry

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Improved Analysis of Petroleum Isomer Distribution in Jet Fuel Using Cold EI GC/MS

Introduction

The hydrocarbon isomer distribution in petrochemicals contributes to many commercially important petrochemical characteristics such as boiling and melting points, octane number, combustion efficiency, flash point, viscosity, lubricity, solubility, and solvation power. These characteristics are strongly influenced by hydrocarbon chain branching[1].

This is especially important for jet engine fuels. If these are not to specification, jet fuel lines can freeze up or engines malfunction[2].

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 petrochemical mixture. One of its most valuable functions is to provide the molecular weight of a compound. However, for high molecular weight or highly branched compounds, this important ion may be small or absent because of energetic instability relative to its fragment ions. In that case analyte confirmation is more dependent upon measured retention time and comparison with established standards.

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In contrast, Cold Electron Ionization GC/MS (Cold EI GC/MS) can improve petroleum isomer distribution analysis by substantially increasing the molecular ion peak intensity of a compound while retaining the EI fragmentation pattern for spectral library searching without modification to established GC methodologies.

Cold EI enhances the molecular ion intensity by reducing fragmentation via vibrational cooling of the molecules. Figure 1 is a schematic representation of the Cold EI ionization source. The molecules exit the GC column, are mixed with make-up helium gas, and then pass through a supersonic nozzle.

Adiabatic expansion 'cools' the analyte molecules in a supersonic molecular beam, reducing internal vibrational energy. The analyte molecules concentrate into the center of the beam by the jet separator effect. Excess carrier gas is skimmed off, and the cold analyte molecules (now ~15 K or -258 °C) enter the ion source for ionization. The reduced analyte vibrational energy (temperature) allows excess energy from the ionizing electron to be better delocalized over the molecule without breaking chemical bonds, reducing fragmentation compared to a molecule at typical GC/MS temperatures (~200 °C). In conventional EI the absolute molecular ion intensity generally decreases with carbon number by about 20% for each additional carbon. In Cold EI it is approximately constant. Consequently, the relative abundance of the molecular ion in Cold EI increases exponentially[3] with carbon number up to a factor of 2500 for *n*-$C_{40}H_{82}$.

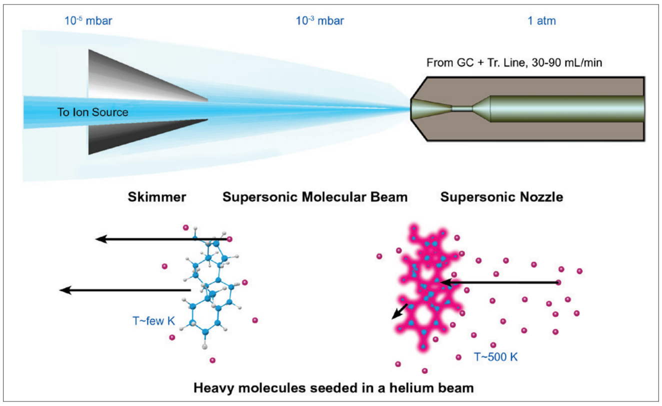


Figure 1. Cold EI GC/MS Ion Source.

When used in the novel PerkinElmer AxION® iQT™ GC/MS/MS, the enhanced molecular ion in Cold EI provides enhanced selectivity and valuable information on the isomeric content and distribution of petrochemical fluids.

Experimental

Experimental conditions are shown in Table 1. Spectra were acquired both in Cold EI and classical EI mode. The switch from Cold EI to classical EI was done by simply changing the MS method to one with a lower makeup gas flow and different ion source lens settings. Both sets of ion source conditions were previously established by the Autotune procedure.

Results and Discussion

A sample of Jet A fuel was injected neat, with a high split flow. Figures 2 through 5 compare classical EI and Cold EI chromatograms. The top chromatogram in each Figure is the Total Ion Current (TIC). The lower chromatograms are the Extracted Ion Chromatograms (EICs) for the selected alkanes, with boxes highlighting the time window expected for the isomers.

Table 1. Experimental Conditions.

Gas Chromatograph:	PerkinElmer Clarus® 680
Injector Type:	Programmable Split/Splitless
Injector temperature	250 °C
Injection:	0.4 µL, split 200:1
Oven Program:	50 °C, ramp to 240 °C at 20 °C/min
Analytical Column:	PerkinElmer Elite™ - 5MS 30 m x 0.25 mm ID x 0.25 µm
Carrier Gas:	1 mL/min Helium 99.999+% purity
Sample:	"Jet A" jet fuel

Mass spectrometer:	PerkinElmer AxION iQT MS/MS
GC Transfer Line Temperature:	250 °C
Ion Source Temperature:	200 °C
Acqusition Range:	*m/z* 40-400
Acquisition Time:	0.20 sec
Solvent Delay:	none
Ion Source Type:	Cold EI
Ion Source Mode:	Cold EI
Background Noise Removal:	On
Cold EI makeup gas:	50 mL/min
Ion Source Mode:	Classical EI
Cold EI makeup gas:	2 mL/min
Filament:	5 µA

Figure 2 shows the Classical EI TIC and EICs of the molecular ions of C_8 to C_{14} alkanes.

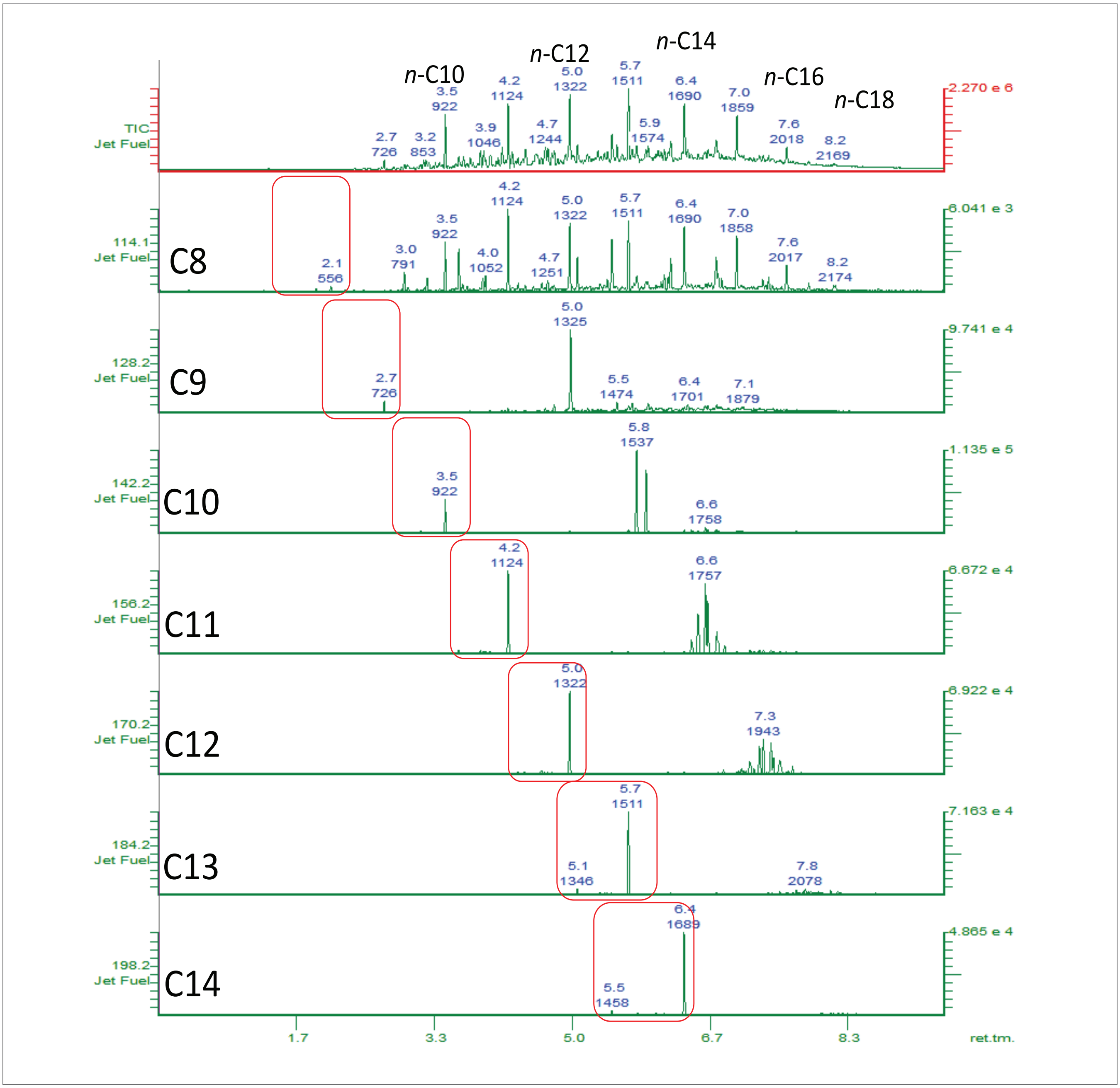


Figure 2. "Jet A" Jet Fuel, C_8 - C_{14} by EI GC/MS.

Other than the *n*-alkane (which is always the last isomer to elute), no other isomers are observed at any significant intensity. Similar results were obtained using a conventional EI ion source. Figure 3 shows the same chromatography, but using Cold EI.

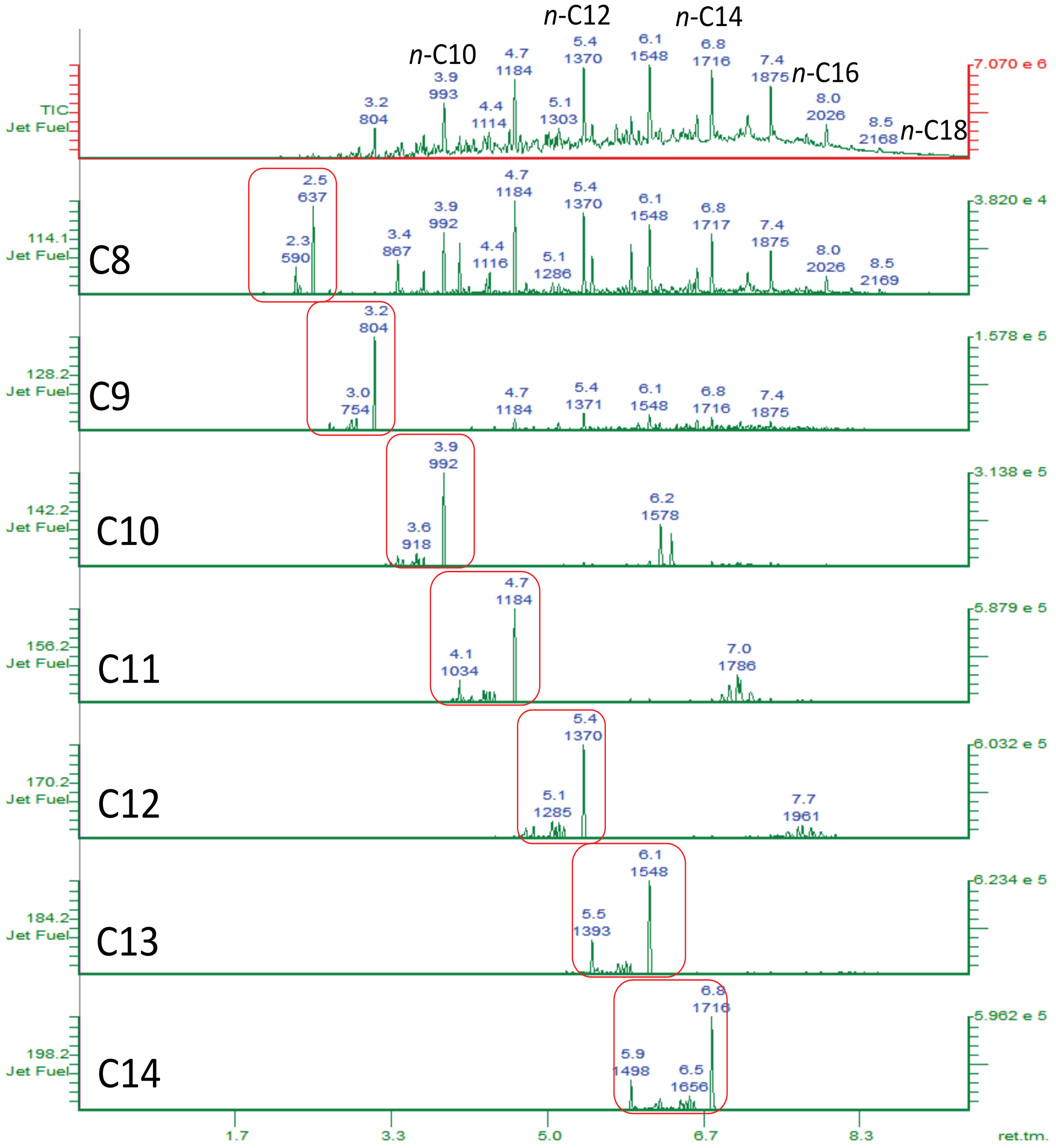


Figure 3. "Jet A" Jet Fuel, C_8 - C_{14} by Cold EI GC/MS.

Branched isomers of the alkanes are now clearly observed. Figure 4 shows the C_{15} to C_{20} range using EI. C_{15} and C_{16} show one small isomer peak other than the *n*-alkane. The molecular ions for C_{17} through C_{20} are lost in the noise because of the poor molecular ion intensity.

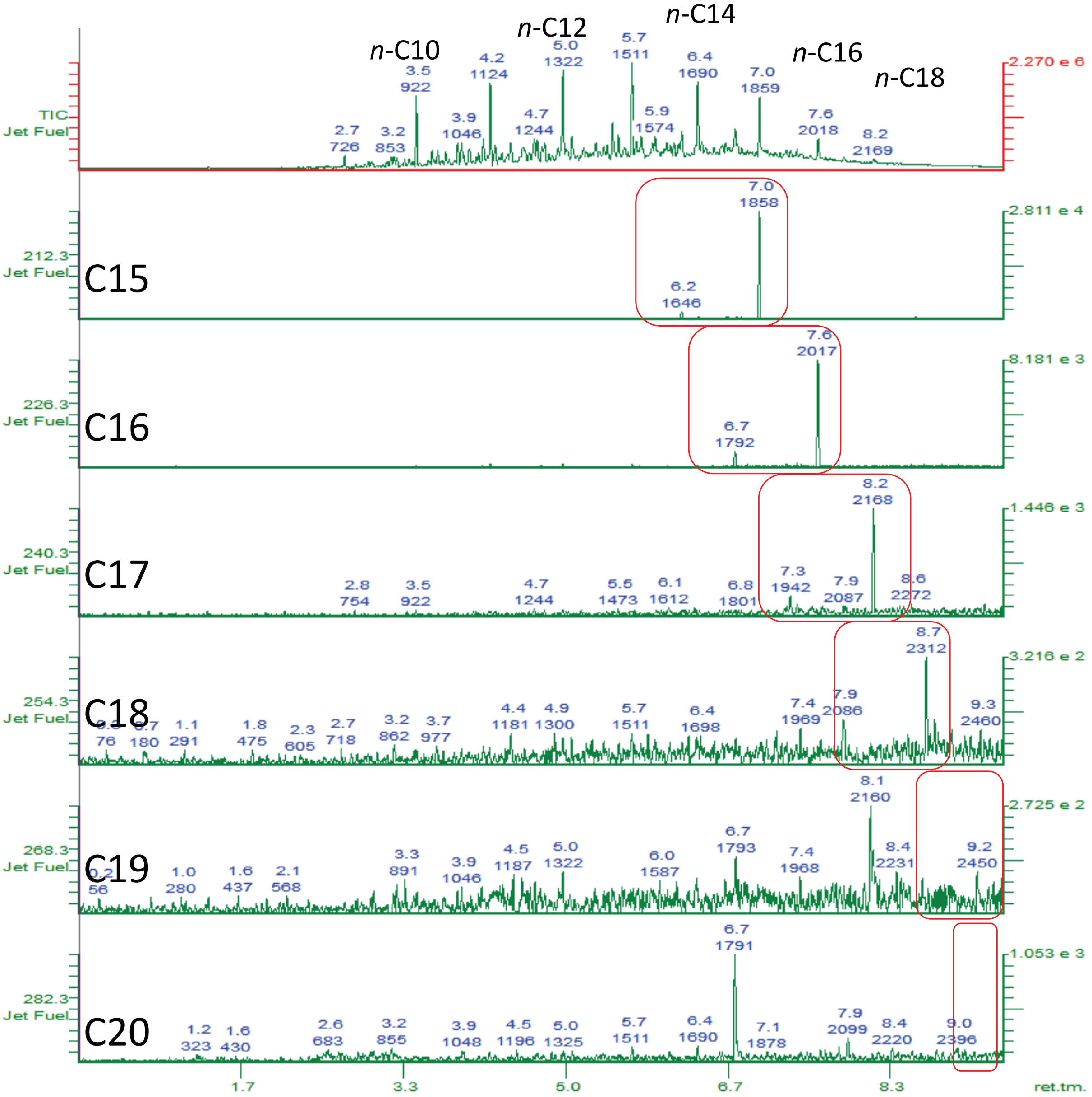


Figure 4. "Jet A" Jet Fuel, $C_{15} - C_{20}$ by EI GC/MS.

In contrast, the Cold EI in Figure 5 shows very strong chromatograms for the *n*-alkane and multiple isomers.

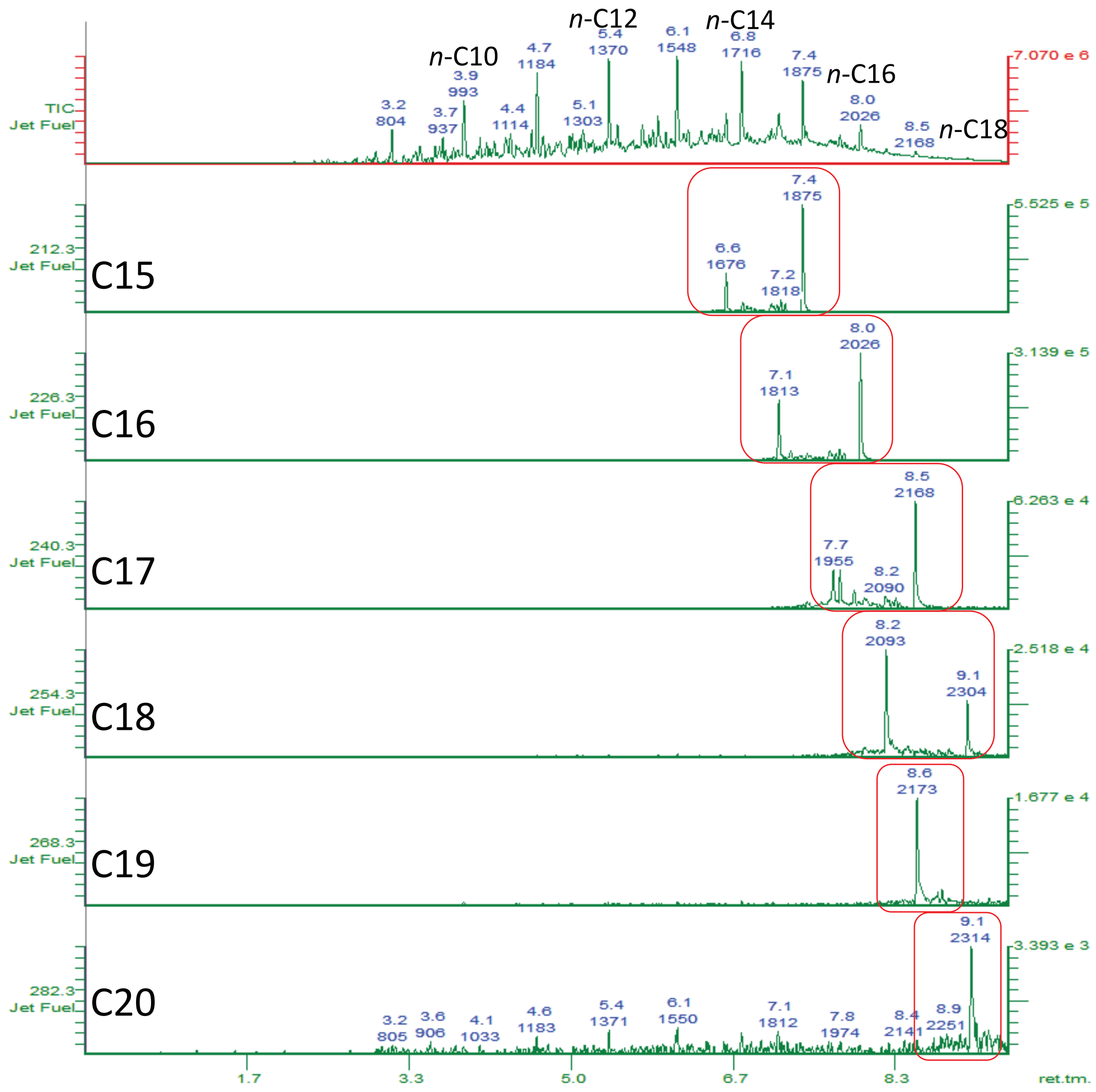
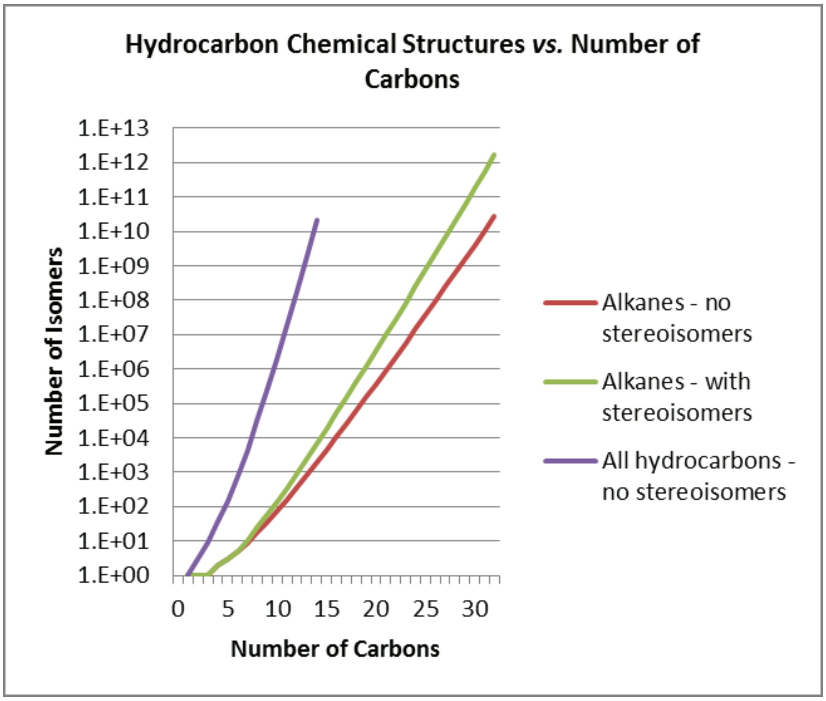


Figure 5. "Jet A" Jet Fuel, C_{15} – C_{20} by Cold EI GC/MS.

Figure 6 shows that the number of isomers increases exponentially with the number of carbons in the chain. Even for C_{14} and ignoring stereoisomers there are over 6500 possible alkane 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.

Figure 6. Exponential increase in possible isomers with carbon number.

Figures 7 through 9 compare Classical EI and Cold EI spectra, with arrows indicating the height of the molecular ion.

Figure 7 shows the Cold EI spectra of four C_{17} isomers. In all cases the molecular ion is clearly observed.

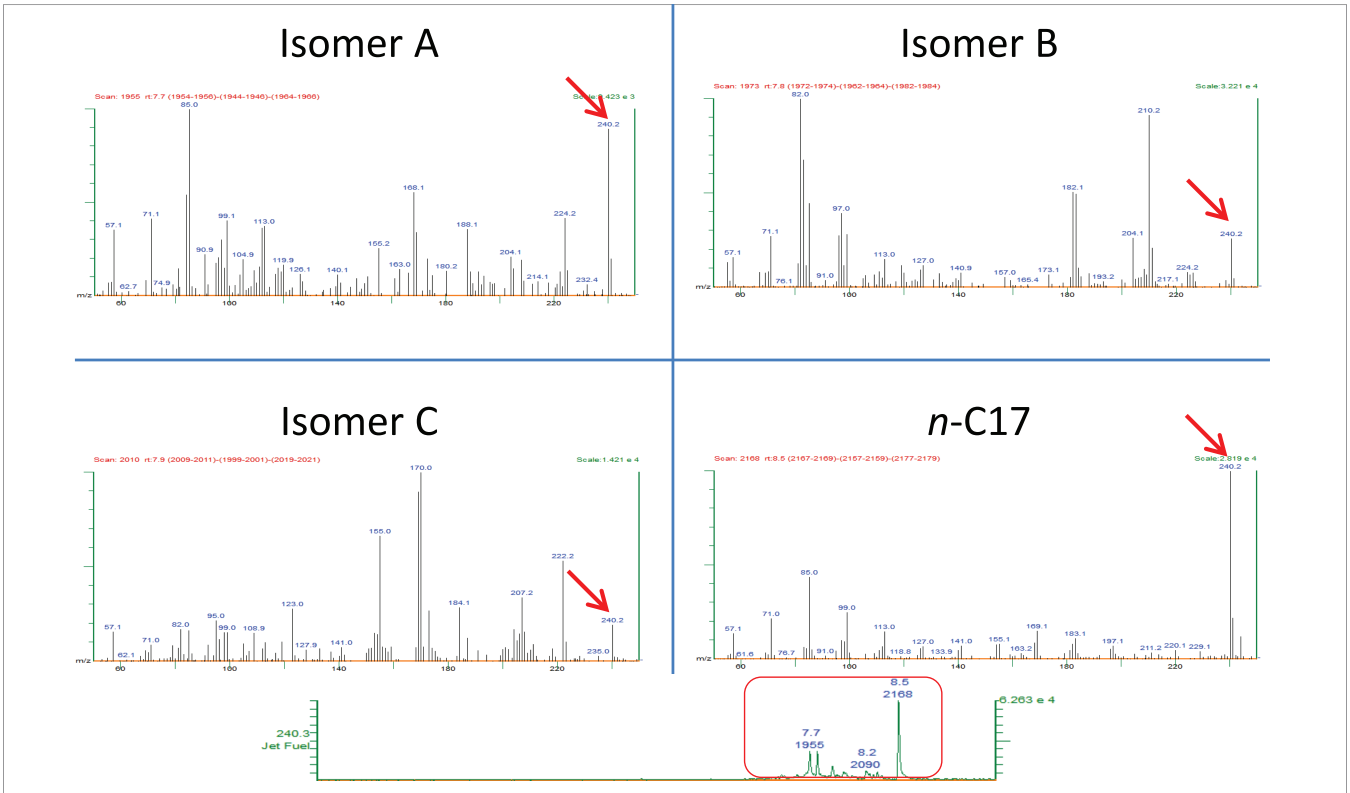


Figure 7. "Jet A" Jet Fuel, C_{17} isomers all show Molecular Ion in Cold EI.

By contrast, Figure 8 shows these same compounds using EI. Except for the *n*-alkane, the other isomers have little to no molecular ion which would make their identification as a C_{17} isomer difficult to impossible. One of the isomers could not be detected at all because of coeluting compounds and the lack of any unique ions in EI.

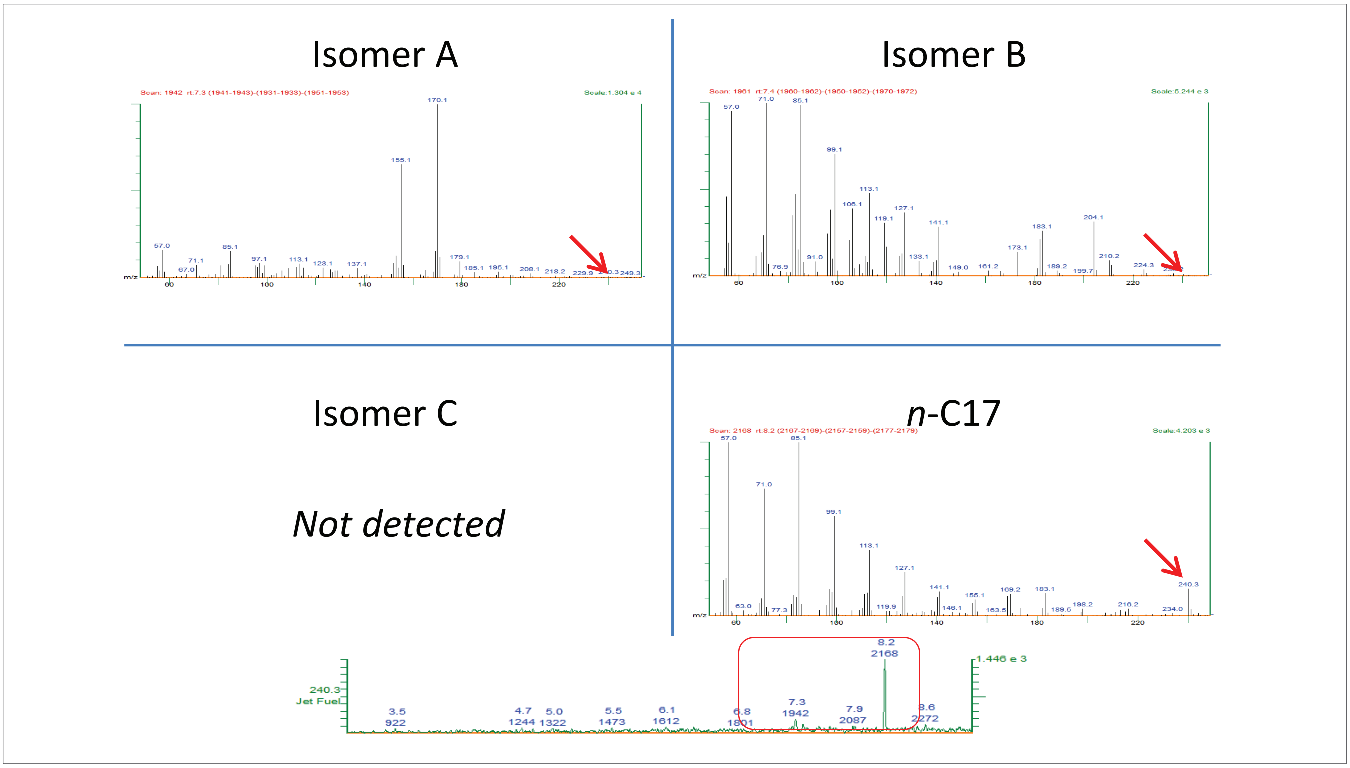


Figure 8. "Jet A" Jet Fuel, C_{17} isomers show small or no Molecular Ion with EI.

Figure 9 shows a direct comparison of one isomer, denoted "Isomer A" using both EI and Cold EI.Even with background spectral subtraction, coeluting compounds dominate the EI spectrum and make it impossible to identify this compound as a C_{17} alkane. While there are still coeluting issues, the strong molecular ion unambiguously identifies this compound as a C_{17} alkane isomer. The EI and Cold EI spectra of the *n*-alkane are also shown.

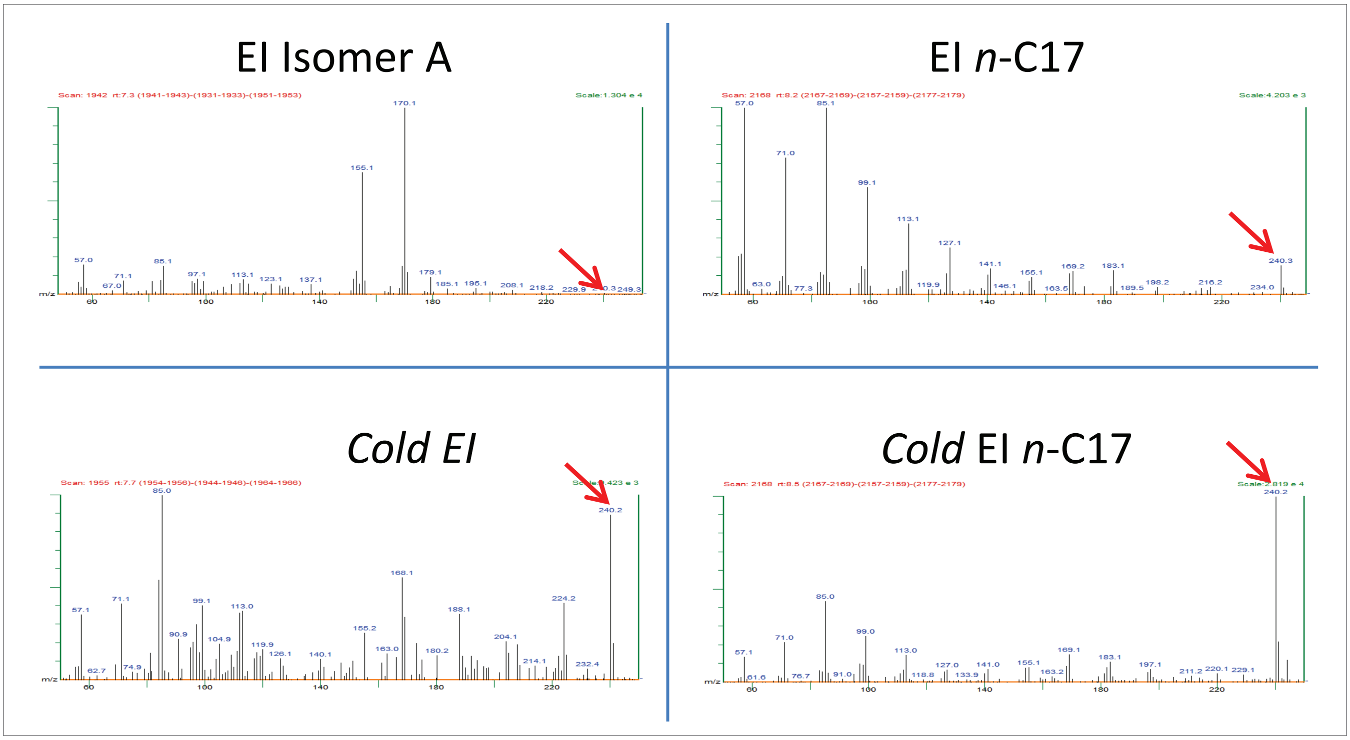


Figure 9. "Jet A" Jet Fuel, EI vs. Cold EI.

The Cold EI spectrum demonstrates the strong enhancement of the molecular ion, while still retaining the characteristic alkane fragmentation pattern.

Conclusions

Cold EI has been shown to strongly enhance the molecular ion of alkane isomers in jet fuel. This makes it possible to identify compound isomers, which are important for determining performance characteristics. Knowledge of the hydrocarbon isomer distribution can aid in the development of refining processes, monitor catalyst performance and refining process yield, and help maximize product value.

References

1. James G. Speight, Handbook of Petroleum Product Analysis, 2nd Ed., p. 22, John Wiley & Sons, Hoboken, NJ, 2015.
2. Solash, J., Hazlett, R.N., Hall, J.M. and Nowack, C.J., *Fuel*, 57, 521 (1978).
3. Aviv Amirav, http://blog.avivanalytical.com/2012/09/how-much-is-molecular-ion-enhanced-in.html

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