

Jet Fuel Analysis by High Resolution TOFMS: The Combined Power of EI, CI, and Accurate Mass



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1. Introduction

Jet fuel is a complex mixture of organic compounds whose composition depends on its specific refinement process.¹ It is primarily composed of linear and branched alkanes, and aromatic hydrocarbons. Alkanes provide higher hydrogen content which improves combustion efficiency and increases overall energy output. Jet fuel is not only a propellant, but also functions as a primary coolant in modern aircraft.² However, increased quantities of aromatic compounds promote sooting during combustion and can lead to formation of carbonaceous solids which may reduce engine performance or cause failures.^{3,4,5}

Chemical ionization has traditionally been used to provide evidence of pseudo-molecular ions for unknown identification. In this note we use an HR-CI analysis to strengthen and expand the standard EI identification approach. In this application note we use accurate mass chemical ionization (HR-CI) and electron impact ionization (EI) to characterize a sample of jet fuel.

2. Results and Discussions

Fuel quality is most effectively assessed by determining its chemical composition, since combustion and cooling properties are related to functional group distribution in the mixture. Sooting properties of fuels have been directly correlated to molecular structure.⁶ For example, unsaturated compounds such as naphthalenes produce more soot than alkanes or cycloalkanes. The relative order of increasing sooting tendency in fuel is: *n*-alkanes < branched alkanes < cycloalkanes < alkynes < alkyl benzenes < naphthalenes.

High resolution time-of-flight mass spectrometry is a practical choice for the analysis of fuels since it can provide comprehensive profiles of samples in single injections. Resolving powers greater than 25,000 minimize background interferences and can separate isobaric ions. Mass accuracies less than one part per million allow for more confident formula determinations which together with high quality spectral data can be used to confidently characterize the individual components of the sample.

EI Data

In this analysis, EI and HR-CI were used to fully characterize compounds in jet fuel. Over 1000 compounds were found in the sample (Figure 1). These included *n*-alkanes, branched alkanes, cycloalkanes, aromatics (e.g., substituted benzenes, naphthalenes and higher aromatics), and heteroatomic compounds (e.g., benzothiophenes).

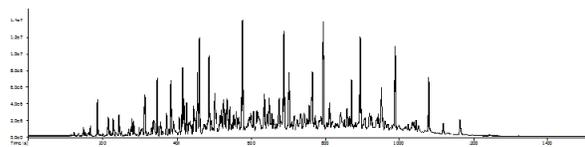


Figure 1. TIC of jet fuel.

Peak True (Deconvoluted) mass spectra for two linear alkanes, *n*-hexane and *n*-hexadecane, are displayed in Figure 2. The spectral data was searched against NIST 2011 and resulted in library match values (LM) of 997 and 885 out of a possible 1000.

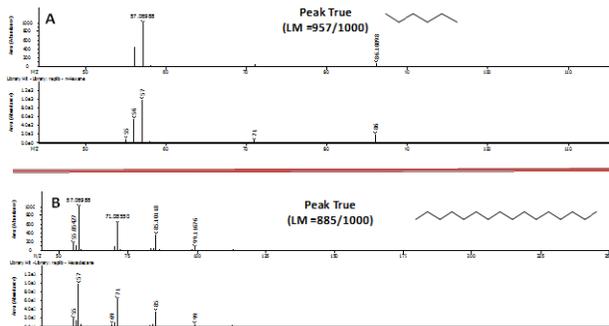


Figure 2. Peak True and Library Mass Spectra for Hexane (A) and Hexadecane (B).

Table 1 lists some representative branched alkanes, cycloalkanes, and aromatic compounds in this sample. Mass accuracy (MA) values for these compounds ranged from -0.91 to 0.95 ppm. In general, branched alkanes were more difficult to identify solely through library comparisons since many of them produce similar spectra. In addition, the likelihood of observing molecular ions in the EI mass spectra of substituted alkanes decreases as the extent of branching increases. This is clearly evident from the low intensity molecular ions in the mass spectra of 3-methyloctane and 3,4,5,6-tetramethyloctane (Figure 3). The LM values for these branched alkanes were 920 and 881 respectively.

Table 1. Representative Branched Alkanes, Cycloalkanes and Aromatic Compounds in Jet Fuel.

Name	Formula	Species	Expected Ion m/z	Observed Ion m/z	Mass Delta (m/z)	Mass Accuracy (ppm)
Octane, 3-methyl-	C ₉ H ₂₀	M ⁺	128.15595	128.15607	0.0001221	0.95
Octane, 3,4,5,6-tetramethyl-	C ₁₂ H ₂₆	M ⁺	170.20290	170.20305	0.0001481	0.87
Cyclopentane, 1-ethyl-2-methyl-	C ₈ H ₁₆	M ⁺	112.12465	112.12455	-0.0001019	-0.91
trans-Decalin, 2-methyl-	C ₁₁ H ₂₀	M ⁺	152.15595	152.15596	0.0000083	0.05
Benzene, 1-ethyl-2,4-dimethyl-	C ₁₀ H ₁₄	M ⁺	134.10900	134.10903	0.0000256	0.19
Benzene, 1,2,3,5-tetramethyl-	C ₁₀ H ₁₄	M ⁺	134.10900	134.10906	0.0000603	0.45
Naphthalene, 2-methyl-	C ₁₁ H ₁₀	M ⁺	142.07770	142.07768	-0.0000201	-0.14
Naphthalene, 1,5-dimethyl-	C ₁₂ H ₁₂	M ⁺	156.09335	156.09338	0.0000255	0.16

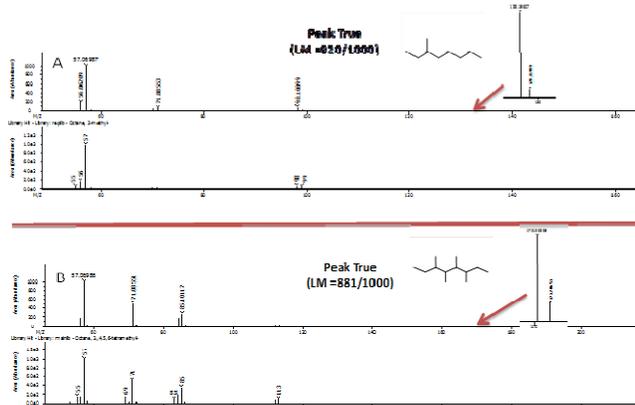


Figure 3. Peak True and Library Mass Spectra for 3-Methyloctane (A) and 3,4,5,6-Tetramethyloctane (B).

The substituted benzenes and naphthalenes listed in Table 1 are examples of fuel components that reduce the overall performance of jet fuel. These aromatic compounds produce relatively intense molecular ion peaks as seen in the Peak True spectra for structural isomers 1-ethyl-2,4-dimethylbenzene and 1,2,3,5-tetramethylbenzene (Figure 4). The mass accuracy of 1-ethyl-2,4-dimethylbenzene's molecular ion ($m/z = 134.10903$) is 0.20 ppm. Fragmentation at the benzylic position of the molecule produced a disubstituted tropylium ion at $m/z = 119.08556$ ($MA = 0.30$ ppm). The $[M]^{+*}$ and substituted phenyl cation $[M-CH_3]^+$ for 1,2,3,5-tetramethylbenzene produced ions at $m/z = 134.10906$ and 119.08555 ($MA = 0.45$ and 0.30 ppm). Base peaks for polyaromatic 1-methylnaphthalene and 1,5-dimethylnaphthalene were the molecular ions at $m/z = 142.07768$ and 156.09338 (Figure 5). Mass accuracy values for these ions were -0.14 ($C_{11}H_{10}$) and 0.16 ppm ($C_{12}H_{12}$).

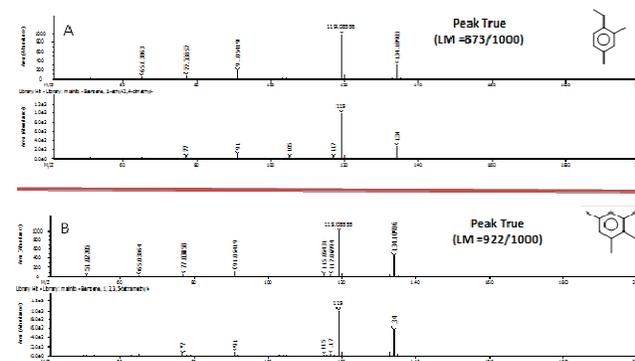


Figure 4. Peak True and Library Mass Spectra for 1-Ethyl-2,4-dimethylbenzene (A) and 1,2,3,5-Tetramethylbenzene (B).

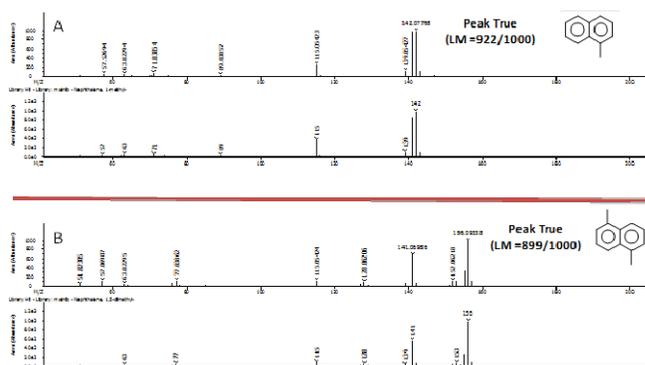


Figure 5. Peak True and Library Mass Spectra for 1-Methylnaphthalene (A) and 1,5-Dimethylnaphthalene (B).

CI Data

Confident formula or structural assignments using strictly EI can be challenging for labile compounds, despite having library similarity and accurate mass information. The soft ionization capability of HR-CI provides formula confirmation for labile compounds in combination with high resolving power and significantly reduces matrix interferences in complex samples. The TIC resulting from the HR-CI analysis of jet fuel is shown in Figure 6. Formula searches for n -alkane $[M-H]^+$ ions resulted in mass accuracy values ranging from -0.33 to 0.20 ppm (Table 2).

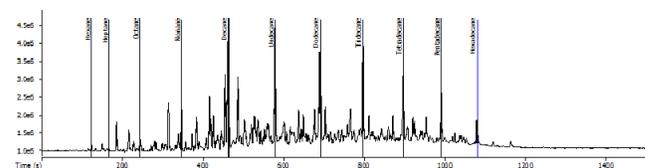


Figure 6. HR-CI: TIC for jet fuel sample.

Table 2. Summary HR-CI Data for n-Alkanes in Jet Fuel.

Name	Formula	R.T. (s)	Peak S/N	Area	Species	Expected Ion m/z	Observed Ion m/z	Mass Delta (m/z)	Mass Accuracy (ppm)
Hexane	C ₆ H ₁₄	121.773	14399	1920778	[M-H] ⁺	85.10118	85.10118	-0.0000047	-0.01
Heptane	C ₇ H ₁₆	165.825	3165	445390	[M-H] ⁺	99.11683	99.11681	-0.00001629	-0.16
Octane	C ₈ H ₁₇	241.87	22125	3491648	[M-H] ⁺	70.07770	70.07768	-0.00002312	-0.33
Nonane	C ₉ H ₂₀	345.218	52738	8900162	[M-H] ⁺	85.10118	85.10119	0.00001719	0.20
Decane	C ₁₀ H ₂₂	461.63	84047	18258157	[M-H] ⁺	141.16378	141.16378	0.00000276	0.02
Undecane	C ₁₁ H ₂₄	578.043	64041	14912390	[M-H] ⁺	155.17943	155.17945	0.00002526	0.16
Dodecane	C ₁₂ H ₂₆	689.598	45252	10603272	[M-H] ⁺	169.19508	169.19504	-0.00003661	-0.21
Tridecane	C ₁₃ H ₂₈	795.625	33273	7622736	[M-H] ⁺	183.21073	183.21065	-0.00008003	-0.44
Tetradecane	C ₁₄ H ₃₀	895.79	24911	5514127	[M-H] ⁺	197.22638	197.22632	-0.00005264	-0.27
Pentadecane	C ₁₅ H ₃₂	990.093	20877	4267226	[M-H] ⁺	211.24203	211.24196	-0.00006367	-0.30
Hexadecane	C ₁₆ H ₃₄	1078.87	11575	2235957	[M-H] ⁺	225.25768	225.25767	-0.00001082	-0.05

As mentioned above, branched alkanes can be problematic due to their tendency to fragment under high energy electron impact ionization. They form relatively stable fragments and their molecular ions are often small or not observable in EI mass spectral data. In addition, branched compounds can produce similar spectra that are difficult to accurately match against commercial library databases. For example, the top hit for a branched hydrocarbon with a retention time of 15.9 minutes was 2,6,10,14-tetramethylheptadecane ($C_{21}H_{44}$) with an LM value of 898 (Figure 7). However, quick inspection of the HR-CI data revealed a formula of $C_{16}H_{34}$ for this compound ($MA = -0.59$ ppm)!

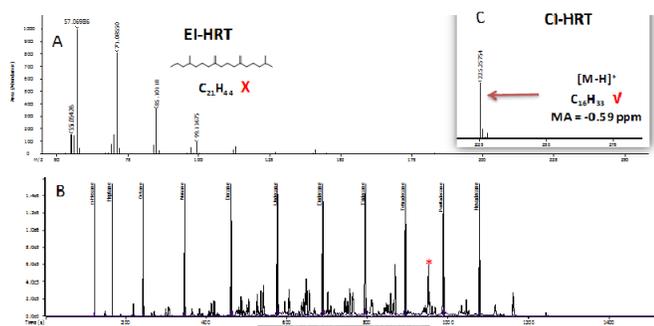


Figure 7. EI XIC of Alkanes in jet fuel (B). EI (A) and HR-Cl (C) Peak True Mass Spectra for a Branched Alkane ($C_{21}H_{44}$) in jet fuel.

3. Conclusions

The combination of HR-Cl and EI on the Pegasus GC-HRT provides an unparalleled analysis tool for jet fuel characterization. In particular, for labile branched chain alkanes, the confirmation of intact molecular ions is facilitated by HR-Cl. Characterization of these branched species are vital to jet fuel producers.

4. References

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5. Sample Preparations

The jet fuel sample was not modified and injected neat into the GC-HRT instrument.

6. Experimental Conditions

Chromatographic Parameters

Gas Chromatograph: Agilent 7890/7693

Auto Sampler

Column:

Restek Rxi-5Sil MS

(30 m x 0.25 mm x 0.25 μ m)

Carrier Gas/Flow:

He; 1.0 mL/min

Injection:

Split 200:1 (CI, 100:1), 0.5 μ L

Temp. Program:

40°C (0.50 min hold) to

240°C at 8°C/min

Mass Spectrometry Parameters

Mass Spectrometer: LECO Pegasus® GC-HRT

Transfer Line Temp: 300°C

Ion Source Temp: 280°C (CI-MS 180°C)

Ionization: EI (70 eV); CI (140 eV);

positive ions

Mass Range (m/z): 45 to 510

Acquisition Rate: 6 spec/s

Flight Path: High Resolution

Mass Calibration: PFTBA

CI Reagent Gas: Methane