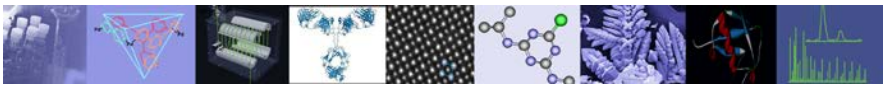

Applications Note

AccuTOF-GCx Series

GCxGC TOFMS Analysis of Base Oils with CI, PI, FI

Introduction

Structural elucidation of hydrocarbon classes in petroleum products are always in high demand. Comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (GCxGC-TOFMS) with electron ionization (EI) is a powerful method for characterizing complex mixtures such as base oils. However, EI data can often lack a strong molecular ion signal. Therefore, it is necessary to measure samples with soft-ionization methods such as positive chemical ionization (PCI), field ionization (FI), or photo-ionization (PI) for the detection of molecular ions. Each technique is a little different so it is important to understand the characteristics of each soft ionization method.

In this application note, we compare the mass spectra of a base oil analyzed by GCxGC-TOFMS with EI, PCI, FI, and PI.

Experiment

The details for sample dilution in hexane as well as the instrumental conditions are listed in Table 1.

Results

Identification of each peak was carried out by a library search of the EI mass spectra and elemental composition estimation for the molecular ions ($M^{+\cdot}$) from the soft ionization results (Fig. 1, Fig.2 and Table 2). A *n*-paraffin (Peak A) and a branched-paraffin (Peak B) were identified in the base oil and showed a different peak pattern for each mass spectrum, especially in the FI results. The EI results consisted mainly of fragment ions with the paraffins showing very low intensity molecular ions. The PCI results showed many fragment ions along with the molecular ion, most commonly as $[M-H]^+$, thus making it less easy to identify the molecular ion from these results than for the FI and PI results. Steroids (peak C) and aromatics (peak D) showed mostly molecular ion for the FI and PI results, respectively.

Table 1. Sample and measurement conditions

Sample	Base oil dilution with Hexane (1:25(PCI, FI, PI), 1:100(EI))
Instruments	*AccuTOF GCv 4G* (JEOL Ltd.) ZX-2 (GCxGC module : ZOEX Corporation)
GCxGC conditions	
Inlet	Cool on column
Inlet mode	Track Oven
1st column	ZB-1HT Inferno (15 m x 0.25 mm, firm thickness 0.1 µm)
Modulator loop	Guard column IP Deact (0.8 m x 0.18 mm)
2nd column	ZB-35HT Inferno (1 m x 0.1 mm, firm thickness 0.05 µm)
Transfer line	Guard column IP Deact (0.3 m x 0.1 mm)
Oven temp. program	50˚C (1min) => 3˚C/min => 370˚C (23min)
Carrier gas flow	1.2 mL/min (He, Constant flow)
Modulation period	5 sec
Injection Volume	0.5 µL
MS conditions	
Ion source	EI/PI, EI/CI, EI/FI/FD
Ionization method	EI(+) : 70 eV, 300 µA CI(+) : 200 eV, 300 µA, CH_4 (95%) + NH_3 (5%), 1.0mL/min PI(+) : D_2 lamp FI(+) : -10 kV, Carbon emitter
Interface temp.	300˚C
Ion source temp.	EI : 200 ˚C CI : 200 ˚C PI : 200 ˚C FI : OFF
Spectrum recording interval	25 Hz (0.04 sec/spectrum)
m/z range	EI, PI, FI : 40 ～ 900 CI : 100 ～900

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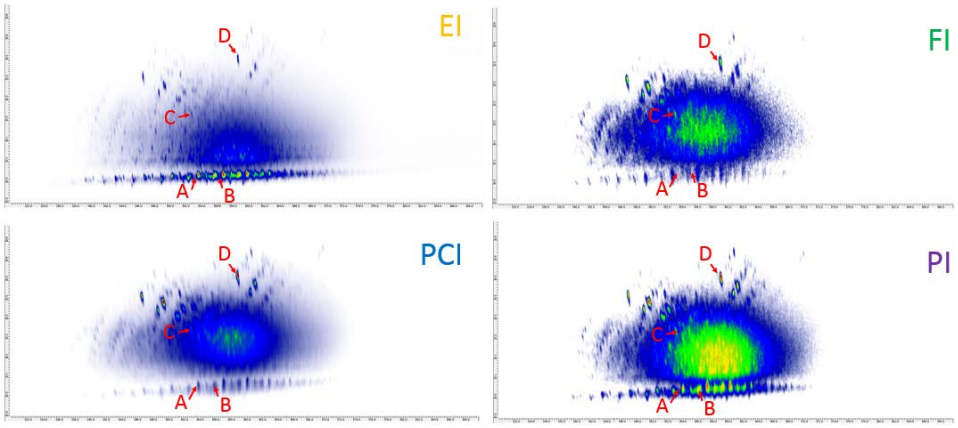


Fig. 1. Base oil 2D map for each ionization method.

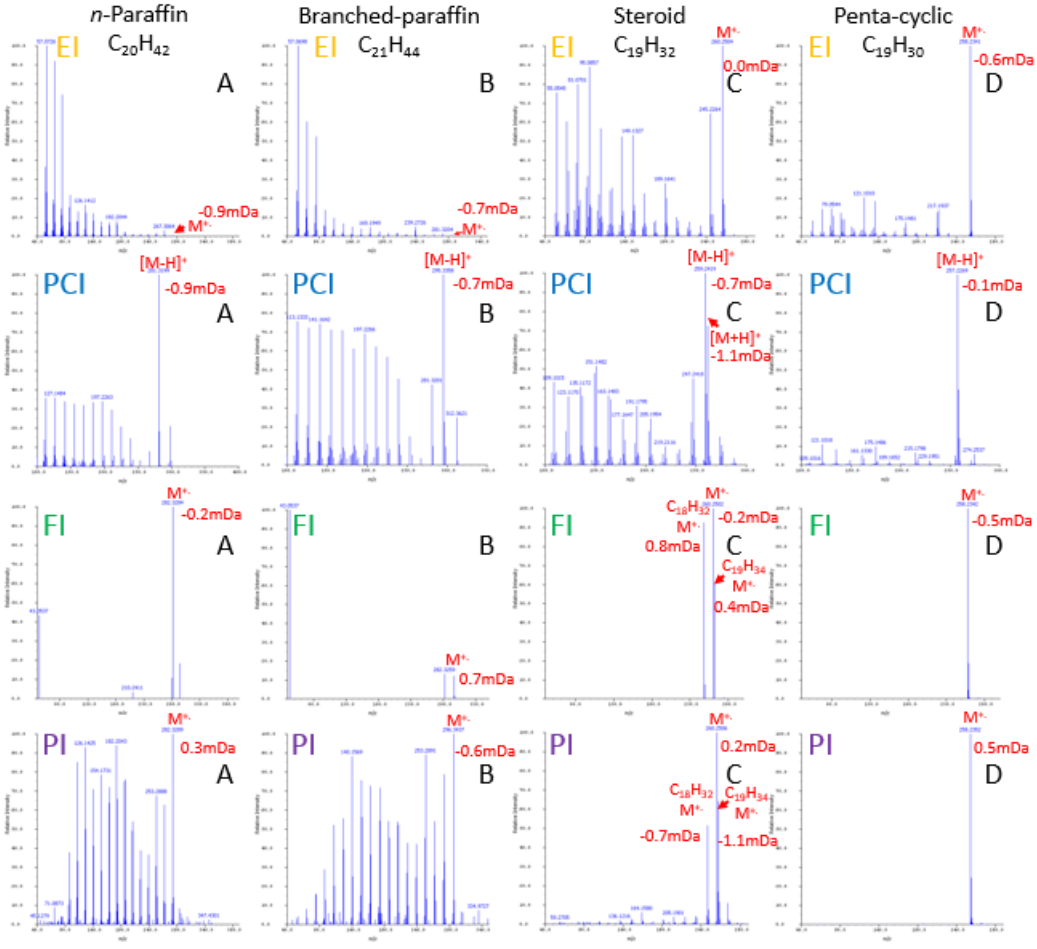
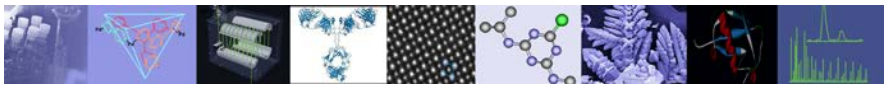


Fig. 2. Mass spectra for EI, PCI, FI, and PI.



Overall, the FI results showed the lowest number of fragment ions for all compounds, thus making it possible to perform type analyses. The PI results showed both molecular ion and fragment ion information, for simplified structural analyses.

Conclusion

The NIST library search of the EI mass spectra is a powerful verification tool for structural elucidation of compounds. However, the EI molecular ion peak intensities can be low for compounds like n-paraffins and branched paraffins. In fact, these molecular ions are often not detected when the compound concentration is too low. As a result, the identification of these compounds using the NIST library search becomes less reliable with the absence of the molecular ions in the EI spectrum.

On the other hand, using soft ionization with accurate mass measurements allows for the elemental composition estimations of the molecular ions. FI is the softest ionization method for showing the intact compounds. PI mass spectra showed strong molecular ions along with fragment ions. As the results here showed, PI and FI are clearly the easiest techniques for identifying the molecular ions, when compared to PCI.

Therefore, using a combination of EI for library searchable spectra and a soft ionization for molecular ion elemental composition estimations allows the analyst to more reliably identify the compounds of interest. The JEOL AccuTOF GC series offers an optionally available EI/FI combination ion source as well as an optionally available EI/PI combination ion source to allow soft and hard ionization to occur without breaking vacuum.

Table 2. Detected peaks by each ionization technique

	EI	PCI	FI	PI
n-paraffin	Fragments (mainly) $M^{+\cdot}$ (Very weak)	$[M-H]^+$ (mainly) + Fragments	$M^{+\cdot}$	$M^{+\cdot}$ (mainly) + Fragments
Branched-paraffin	Fragments (mainly) $M^{+\cdot}$ (Very weak)	$[M-H]^+$ (mainly) $[M+H]^+$ + Fragments	Fragments (mainly) $M^{+\cdot}$	$M^{+\cdot}$ (mainly) + Fragments
Steroids	$M^{+\cdot}$ (mainly) + Fragments	$[M-H]^+$ (mainly) + Fragments	$M^{+\cdot}$ (mainly) + Fragments	$M^{+\cdot}$ (mainly) + Fragments
Aromatics	$M^{+\cdot}$ (mainly) + Fragments	$[M-H]^+$ (mainly) + Fragments (weak)	$M^{+\cdot}$	$M^{+\cdot}$

