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GCxGC-HRTOFMS Analysis of Base Oils with Chemical Ionization, Field Ionization and Photoionization

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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, we need 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. It is important to understand the characteristics of each soft-ionization method.

In this work, we compare the mass spectra of base oil analyzed by GCxGC-TOFMS with each soft-ionization method.

Methods

Table 1. Measurement Conditions

- Sample -	Base oil dilution with Hexane (1:25(PCI, FI, PI), 1:100(EI))
- Instruments -	*AccuTOF GCv 4G* (JEOL Ltd.) KT2006 (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℃
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

Results

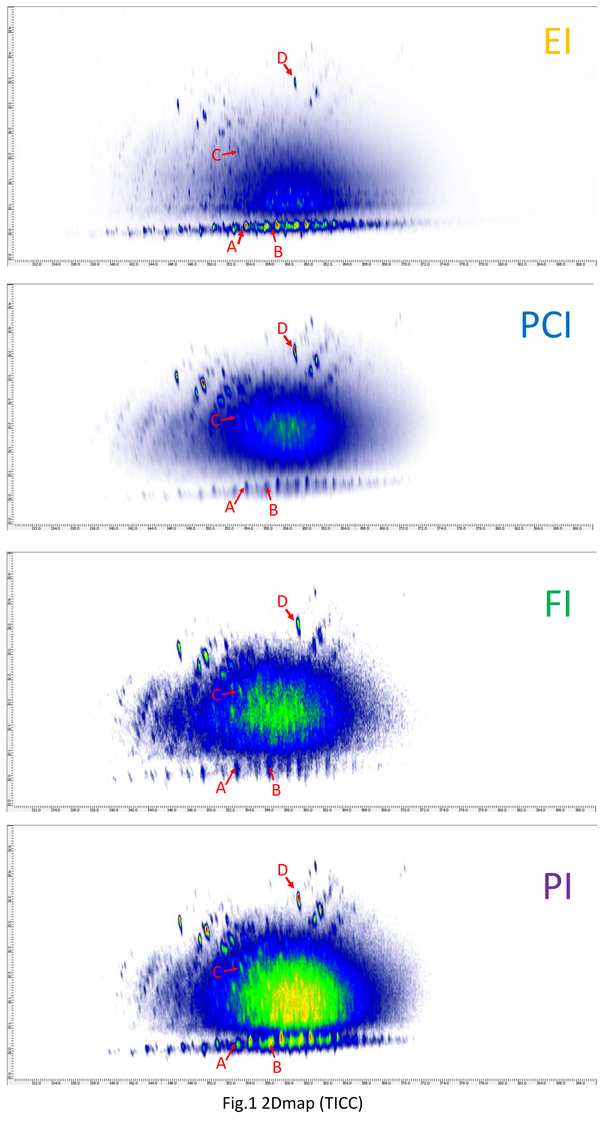

Fig.1 2Dmap (TICC)

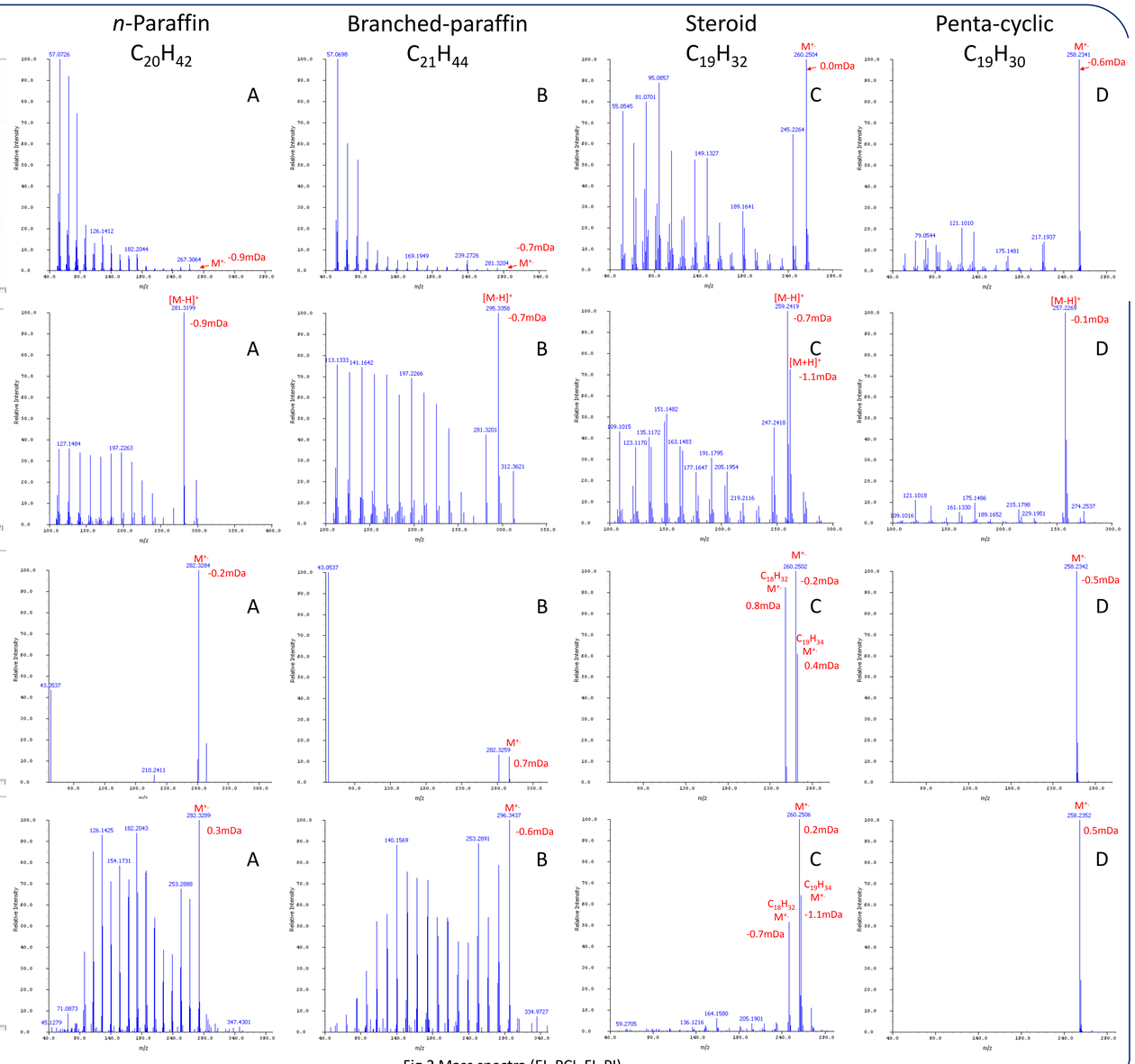

Fig.2 Mass spectra (EI, PCI, FI, PI)

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 the FI results. The EI results consisted mainly of fragment ions, molecular ion from small 2Dmap peaks of paraffin were not detected in EI results. 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. 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.

Table 2. Detected peaks

	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)	$M^{+\cdot}$	$M^{+\cdot}$

Conclusions

- For structural elucidation of compounds
  - Structural information = Fragment ions and their ion patterns
    = Verification from the library search of the EI mass spectra
  - Molecular ion = elemental composition estimations of molecular ions by using soft-ionization
- PI and FI are easiest techniques for identifying the molecular ions.
  - FI is the softest ionization method for intact compounds.
  - PI mass spectra showed strong molecular ions and fragment ions.
  - EI/FI ion source and EI/PI ion source offer the best combinations.