



# AccuTOF-GCx Series

## Comparison of performance between PI and FI by using GC-HRTOFMS

### Introduction

Electron ionization (EI) is a common ionization technique for gas chromatography/mass spectrometry (GC/MS).

However, EI often does not produce strong molecular ions ( $M^{+}$ ) because the excess energy generates fragment ions during the ionization process.

The detection of the molecular ion is very important for confirming the molecular weight of the target compounds. Therefore, a soft ionization technique is often necessary to determine the molecular weight information.

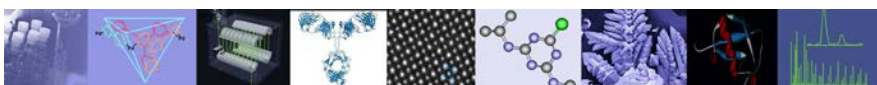
Field ionization (FI) is well known as one of the softest ionization techniques commercially available. Similarly, photoionization (PI) can produce molecular ions. In this application note, the characteristics of PI and FI were investigated by using various compounds. Furthermore, the performance between EI, FI and PI for these compounds in diesel fuel were investigated.

### Experiment

All samples were analyzed by using JMS-T100GCV (JEOL Ltd.) with the optionally available EI/FI combination ion source and PI ion source. EI data was acquired by using the standard 70eV ionization energy with the EI/FI combination source. FI data was acquired by using a 5 $\mu$ m carbon emitter (Carbotec Analytik) with the combination EI/FI source. A deuterium lamp with a magnesium fluoride window (Hamamatsu Photonics K.K.) was used as the PI source. This lamp has an irradiation wavelength range from 115 to 400 nm (equivalent to the energy range from 3.1 to 10.7 eV) in which the maximum radiation intensity is at 160 nm (7.7 eV). And finally, the EI, FI and PI measurements were done with the same detector voltage so that the peak intensities could be directly compared for each ionization method.

Table 1. Measurement Conditions

Instrument	JMS-T100GCV "AccuTOF GCv 4G" (JEOL Ltd.)
Inlet temp.	280°C
Injection mode	Standard reagents : Split 30:1 Diesel fuel : Split 100:1
Column	ZB-5MSi, 30 m x 0.25 mm, film thickness 0.25 $\mu$ m
Oven temp. program	50°C (1 min) => 10°C /min => 320°C (10min)
Carrier gas	He (Constant flow : 1.0 mL/min)
Sample volume	Standard reagents : 1 $\mu$ L Diesel fuel : 0.1 $\mu$ L
Ionization mode	EI(+) : 70 eV, 300 $\mu$ A PI(+) : D <sub>2</sub> lamp (Hamamatsu Photonics K.K.) FI(+) : -10 kV, 0 mA ; Baked at 8 mA (20 msec) after recording interval
Transfer line temp.	270°C
Chamber temp.	EI : 300°C, FI and PI : 100°C
m/z range	35-800
Data acquisition interval	0.5 sec



## Results

- All compounds produced molecular ions by FI.
- Several compounds produced very low intensity molecular ions by PI.
- Aromatic compounds such as 2,6- dimethyl phenol produced high intensity molecular ions by PI.
- *n*-Octanol produced fragment ions by both PI and FI. These fragment ions were different from the EI fragment ions.
- EI did not show a molecular ion for *n*-octanol.

Various *n*-alkanes and aromatic compounds were detected in the diesel fuel (Fig.2 and Fig.3). The TICC in Figure 2 for EI, FI and PI show the *n*-alkanes as the highest intensity peaks (blue circles) observed in the diesel fuel. Additionally, the average FI mass spectrum in Figure 3 shows high intensity molecular ions for the *n*-alkanes.

However, the average PI mass spectrum showed higher relative intensity molecular ions for the aromatic compounds than for the *n*-alkanes. Even so, more fragmentation was observed in the average PI mass spectrum relative to the average FI mass spectrum. The average EI mass spectrum for the diesel fuel was dominated by hydrocarbon fragments in the low mass region.

## Conclusion

FI showed strong molecular ions for all compounds measured in this application. PI also showed molecular ions but also produced more fragment ions relative to FI. Also, PI is sensitive for the measurement of aromatic compounds, making it particularly useful for looking at polycyclic aromatics. This application note confirms that PI and FI are soft ionization techniques that can be used to complement the EI results.

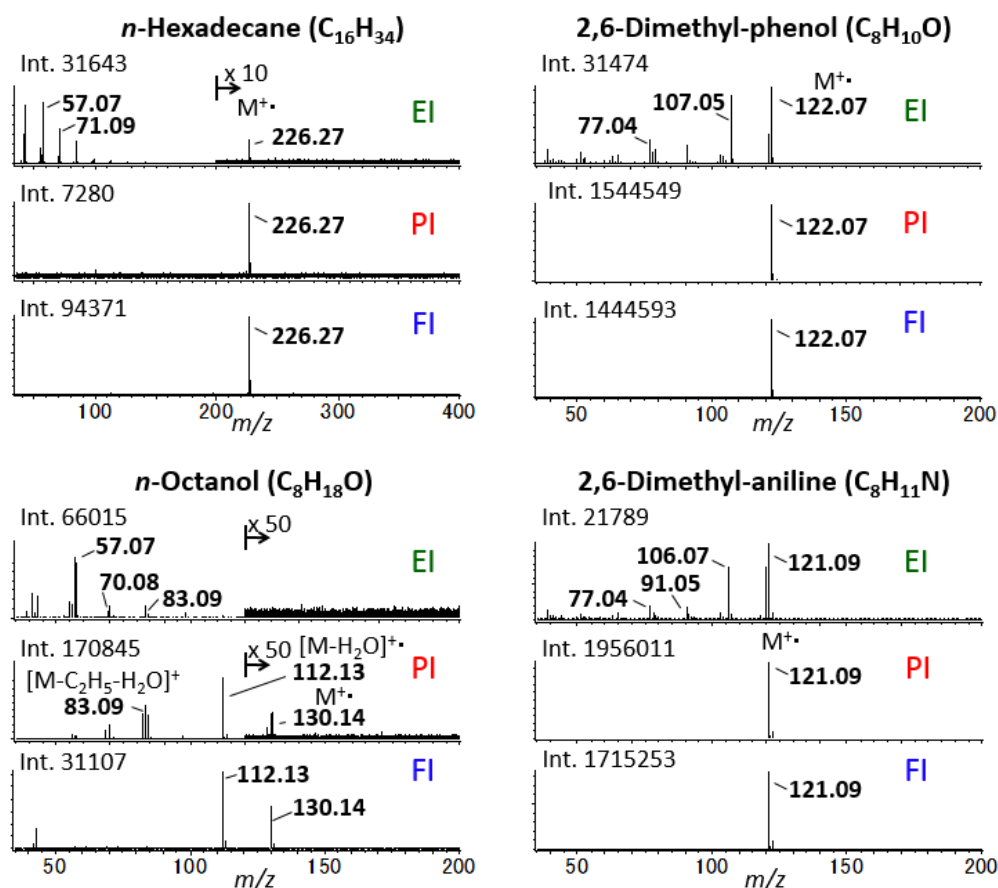


Fig. 1. Compared mass spectra by EI (top), PI (middle) and FI (bottom)

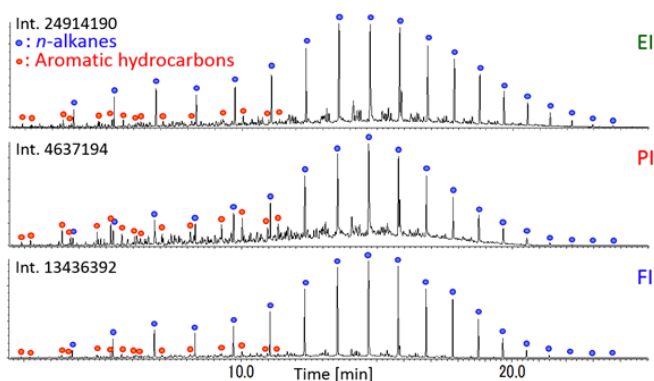
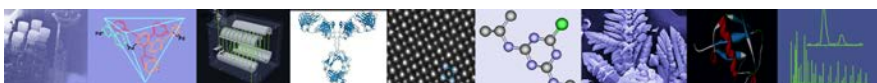


Table 2. Comparison of the molecular-ion detection by FI and PI

F.I. : Fragment ion

Compounds name	FI		SPI	
	Sensitivity	F.I.	Sensitivity	F.I.
<i>n</i> -Hexadecane	++	+	+	+
Naphthalene	+	+	++	+
<i>n</i> -Octanol	++	-	+	-
2,6-Dimethyl phenol	+	+	++	+
2-Octanone	++	-	+	-
Benzophenone	++	+	+	+
2,6-Dimethyl aniline	+	+	++	+
Methyl stearate	++	+	+	+

Fig.2. TICC chromatograms of diesel fuel

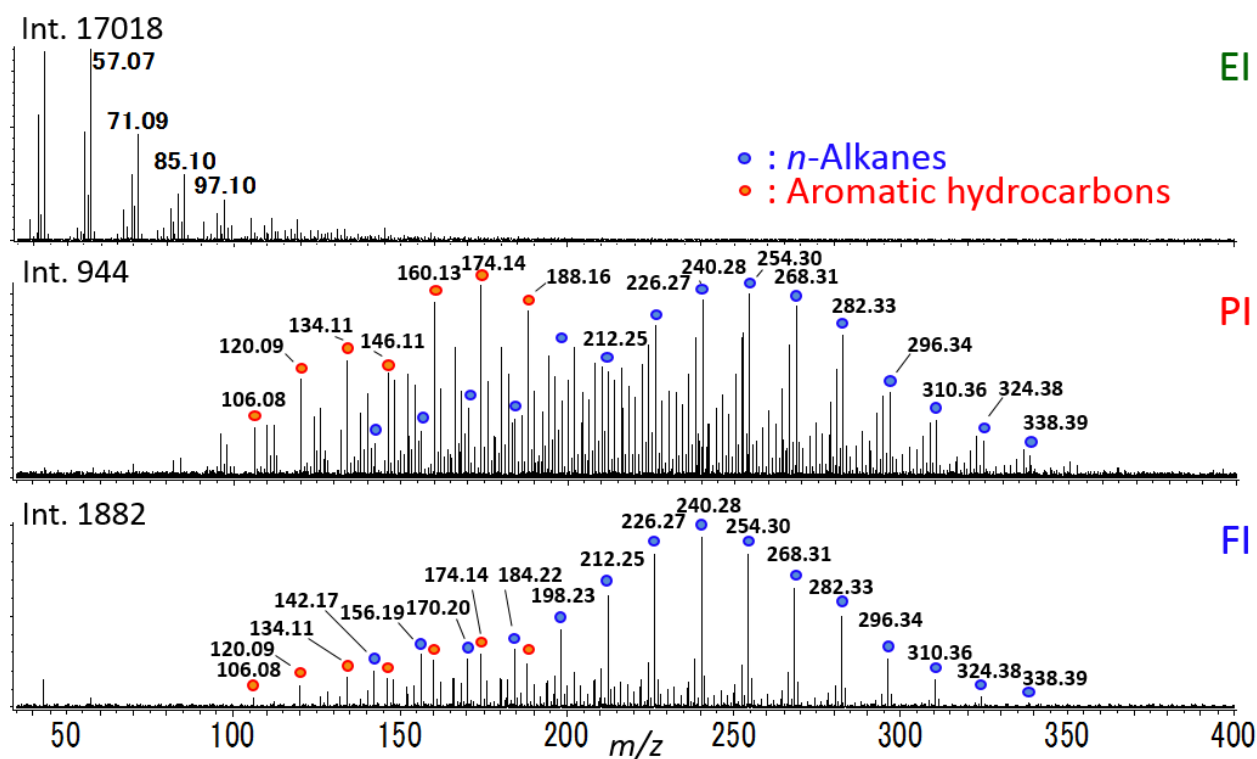


Fig.3. Average mass spectra of diesel fuel