

# AccuTOF-GCv Series

## GC x GC/EI and GC x GC/FI Measurements Using the EI/FI Combination Ion Source

### Introduction

Comprehensive 2-dimensional GC (GC x GC) provides higher-separation capabilities for complex mixtures than the typical 1-dimensional GC measurements. However, this technique requires high speed data acquisition, e. g. > 20 Hz, for the GC detectors due to the shorter 2<sup>nd</sup> GC column (comparable to those used for the ultra-fast GC measurements) which elutes samples within just a few seconds.

Recently, JEOL has developed a new generation GC-HRTOFMS system called the “AccuTOF GCv 4G”. The AccuTOF GCv 4G has high sensitivity, high resolution, high mass accuracy and high speed data acquisition, all simultaneously. Also JEOL has developed a unique EI/FI combination ion source for this system which provides the capabilities of GC/EI and GC/FI measurements without having to break vacuum in order to switch between each ionization mode. Additionally, this combination is particularly powerful in that it provides library searchable fragmentation information by using EI and high mass accuracy molecular ion information by using FI.

In this work, we measured diesel fuel using both the GC x GC/EI and GC x GC/FI techniques on the AccuTOF GCv 4G.

### Experimental

Sample information and measurement conditions are shown in Table 1.

### Results

The GC x GC/EI and GC x GC/FI total ion chromatograms (TICs) for the diesel fuel sample are shown in Figures 1 and 2, respectively. Both chromatograms showed the presence of a wide variety of components in the sample.

Several EI and FI mass spectra for this sample are shown in Figure 3. The FI mass spectra (Right side) showed that the molecular ions were the dominant peaks observed in the mass spectra. Additionally, the mass accuracy was less than 2 mDa for the molecular ions measured by both EI and FI using the external one-point calibration method.

Condition	GC x GC/EI	GC x GC/FI
Sample	Diesel Fuel	
Concentration	1/100 (Hexane)	
GCxGC system	ZX2 thermal modulator (ZOEX)	
1st column	Rxi-5SiIMS, 30 m x 0.25 mm, 0.25 $\mu$ m	
2nd column	Rxi-17SiIMS, 2 m x 0.15 mm, 0.15 $\mu$ m	
Modulator	Deactivated fused silica, 1.5 m x 0.15 mm	
Modulator period	8 sec	
Modulator duration	400 msec	
Hot jet temp.	270 C	
Hot jet gas pressure	40 psi	
Cold jet flow	18 L/min	
Inlet pressure	200 kPa (Out flow: 2mL/min)	
Inlet mode	Split 10:1	Splitless
Oven temp.	5 0C(1 min) $\rightarrow$ 3 C/min $\rightarrow$ 300 C(6 min)	
GC-TOFMS system	AccuTOF GCv 4G (JEOL)	
Ion source	EI/FI combination	
Ionization mode	EI+	FI+
<i>m/z</i> range	<i>m/z</i> 35-500	
Acquisition speed	50Hz	33Hz
External calibrant	<i>m/z</i> 207.0329 (C <sub>5</sub> H <sub>15</sub> O <sub>3</sub> Si <sub>3</sub> <sup>+</sup> )	<i>m/z</i> 226.2661 (C <sub>16</sub> H <sub>34</sub> <sup>+</sup> )

Table 1. Measurement Conditions

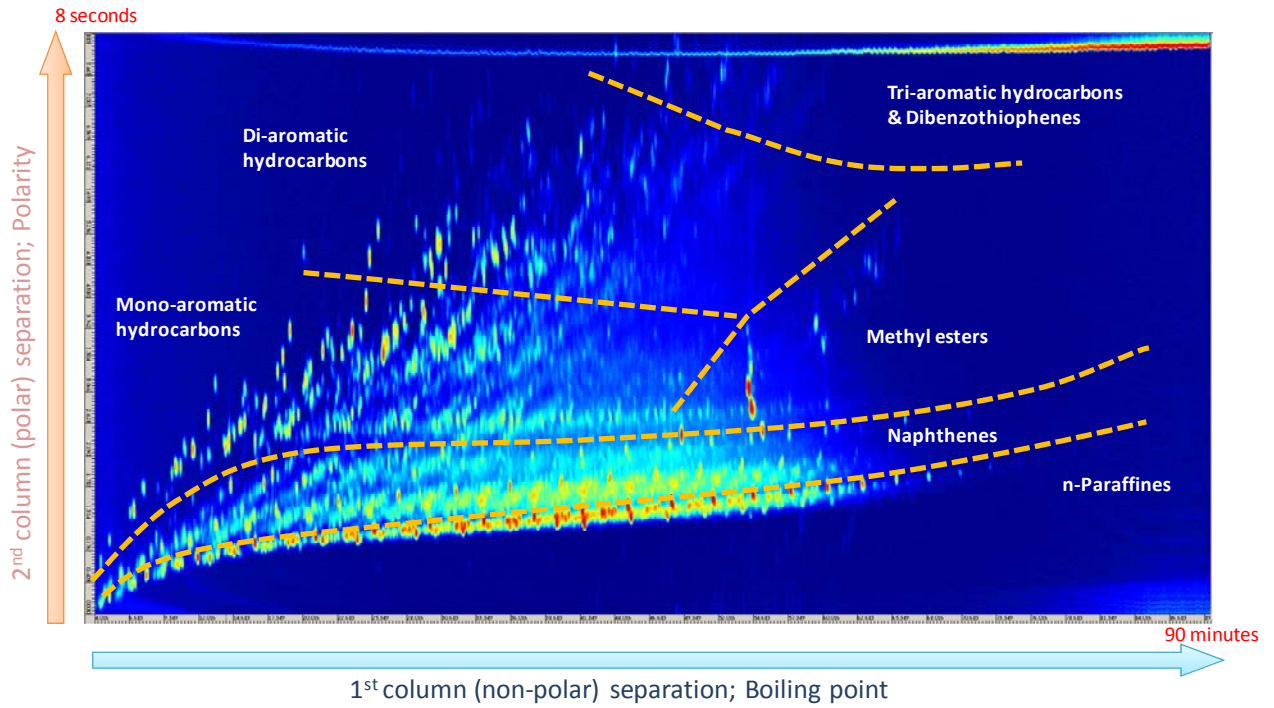
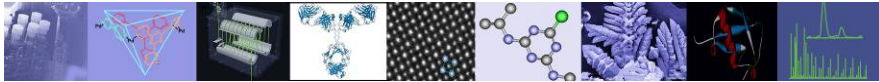


Figure 1. GCxGC/EI TIC for diesel fuel

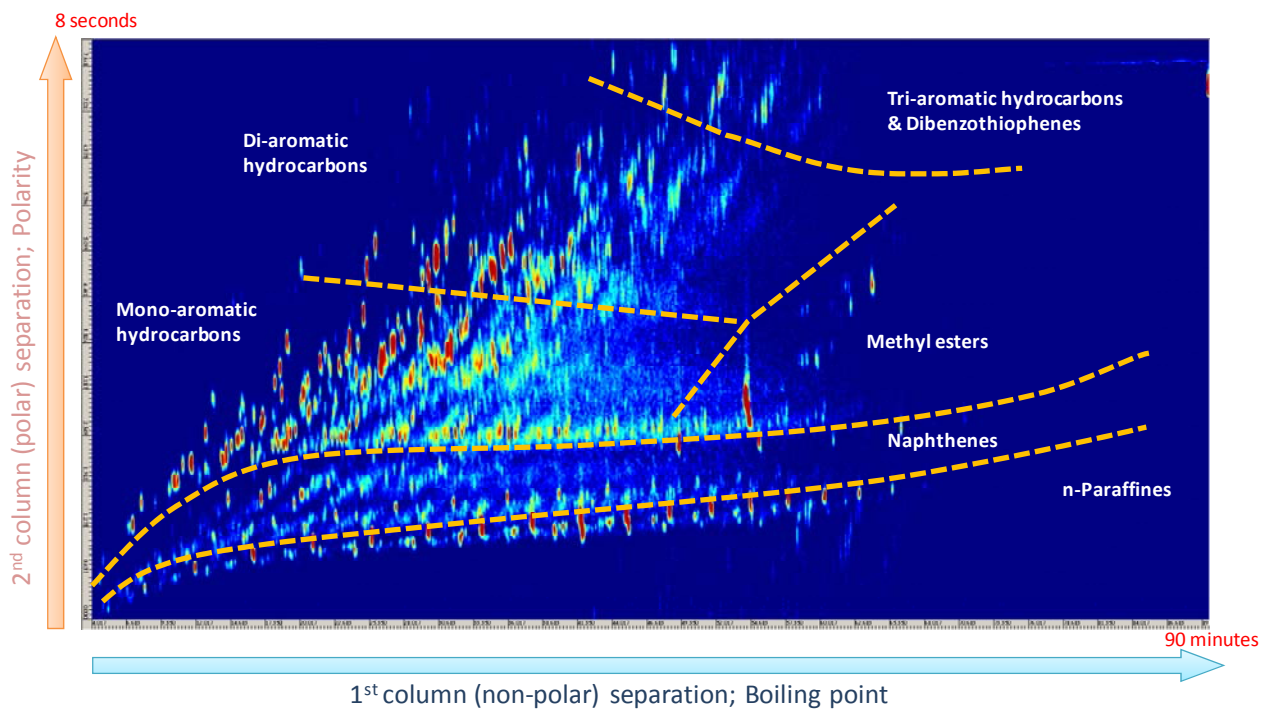
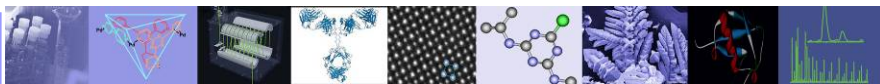
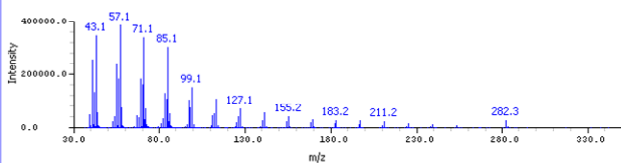


Figure 2. GCxGC/FI TIC for diesel fuel

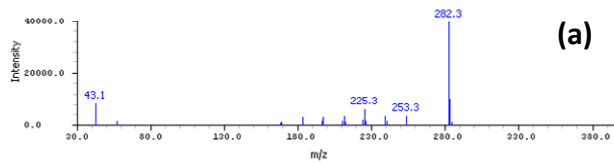


## Electron Ionization

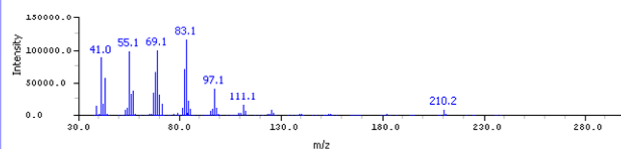
## Field Ionization



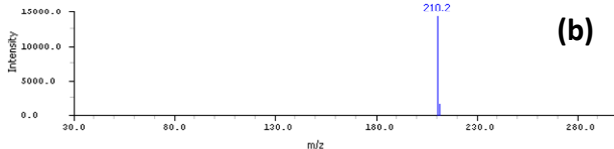
Formula ▲	Mass	Difference (mmu)
C <sub>20</sub> H <sub>42</sub> <sup>+</sup>	282.328103	0.599596



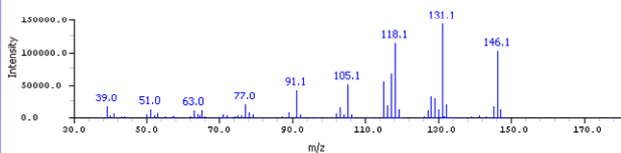
Formula ▼	Mass	Difference (mmu)
C <sub>20</sub> H <sub>42</sub> <sup>+</sup>	282.328103	1.674657



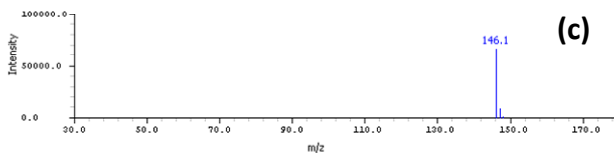
Formula ▲	Mass	Difference (mmu)
C <sub>15</sub> H <sub>30</sub> <sup>+</sup>	210.234202	-1.675281



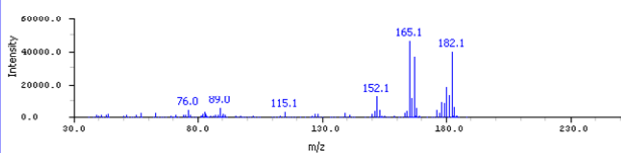
Formula ▼	Mass	Difference (mmu)
C <sub>15</sub> H <sub>30</sub> <sup>+</sup>	210.234202	0.436990



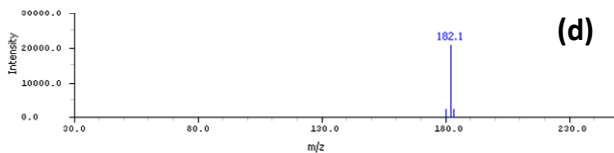
Formula ▲	Mass	Difference (mmu)
C <sub>11</sub> H <sub>14</sub> <sup>+</sup>	146.109002	-0.538154



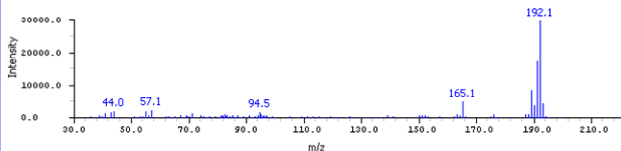
Formula ▼	Mass	Difference (mmu)
C <sub>11</sub> H <sub>14</sub> <sup>+</sup>	146.109002	-1.267696



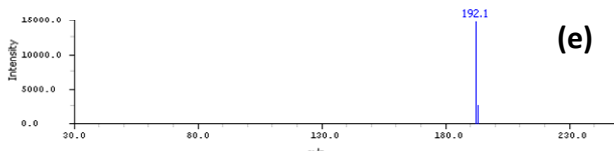
Formula ▲	Mass	Difference (mmu)
C <sub>14</sub> H <sub>14</sub> <sup>+</sup>	182.109002	-1.570539



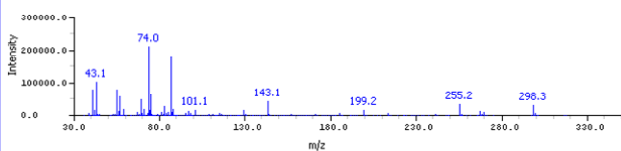
Formula ▼	Mass	Difference (mmu)
C <sub>14</sub> H <sub>14</sub> <sup>+</sup>	182.109002	0.111317



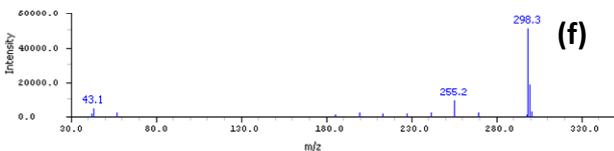
Formula ▲	Mass	Difference (mmu)
C <sub>15</sub> H <sub>12</sub> <sup>+</sup>	192.093352	-0.541810



Formula ▼	Mass	Difference (mmu)
C <sub>15</sub> H <sub>12</sub> <sup>+</sup>	192.093352	0.288982

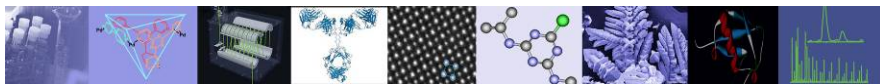


Formula ▲	Mass	Difference (mmu)
C <sub>19</sub> H <sub>38</sub> O <sub>2</sub> <sup>+</sup>	298.286632	-1.465507



Formula ▼	Mass	Difference (mmu)
C <sub>19</sub> H <sub>38</sub> O <sub>2</sub> <sup>+</sup>	298.286632	1.709336

Figure 3. EI and FI mass spectra for (a) n-parafin (C<sub>20</sub>H<sub>42</sub>), (b) naphthenes (C<sub>15</sub>H<sub>30</sub>), (c) monoaromatic hydrocarbon (C<sub>11</sub>H<sub>14</sub>), (d) diaromatic hydrocarbon (C<sub>14</sub>H<sub>14</sub>), (e) triaromatic hydrocarbon (C<sub>15</sub>H<sub>12</sub>), (f) ethyl esters (C<sub>19</sub>H<sub>38</sub>O<sub>2</sub>).



### Conclusion

The AccuTOF GCv 4G has a unique EI/FI combination ion source which does not require breaking vacuum in order to switch between each ionization mode. Consequently, this system was able to easily measure the GC x GC/EI and GC x GC/FI data for diesel fuel. The resulting data provided structural information for the

chemical components using EI (hard ionization) and accurate mass molecular weight information using FI (soft ionization). The AccuTOF GCv 4G is a powerful tool for measuring both GC x GC/EI and GC x GC/FI mass spectra for very complex samples.