# *“AccuTOF GCv 4G“ :*
# Petroleum Sample Analysis with EI/FI/FD combination ion source and Applications.

*JEOL USA, Inc.*

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# Topics

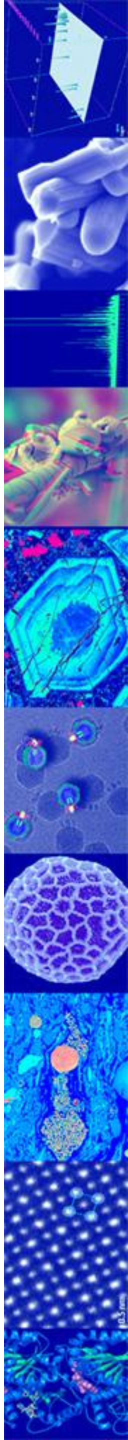
1. Instrument
2. Samples and Measurement conditions
3. TIC chromatogram
4. Mass spectra of EI and FI
5. Conclusion
6. Examples of other hydrocarbon applications

# 1. Instrument

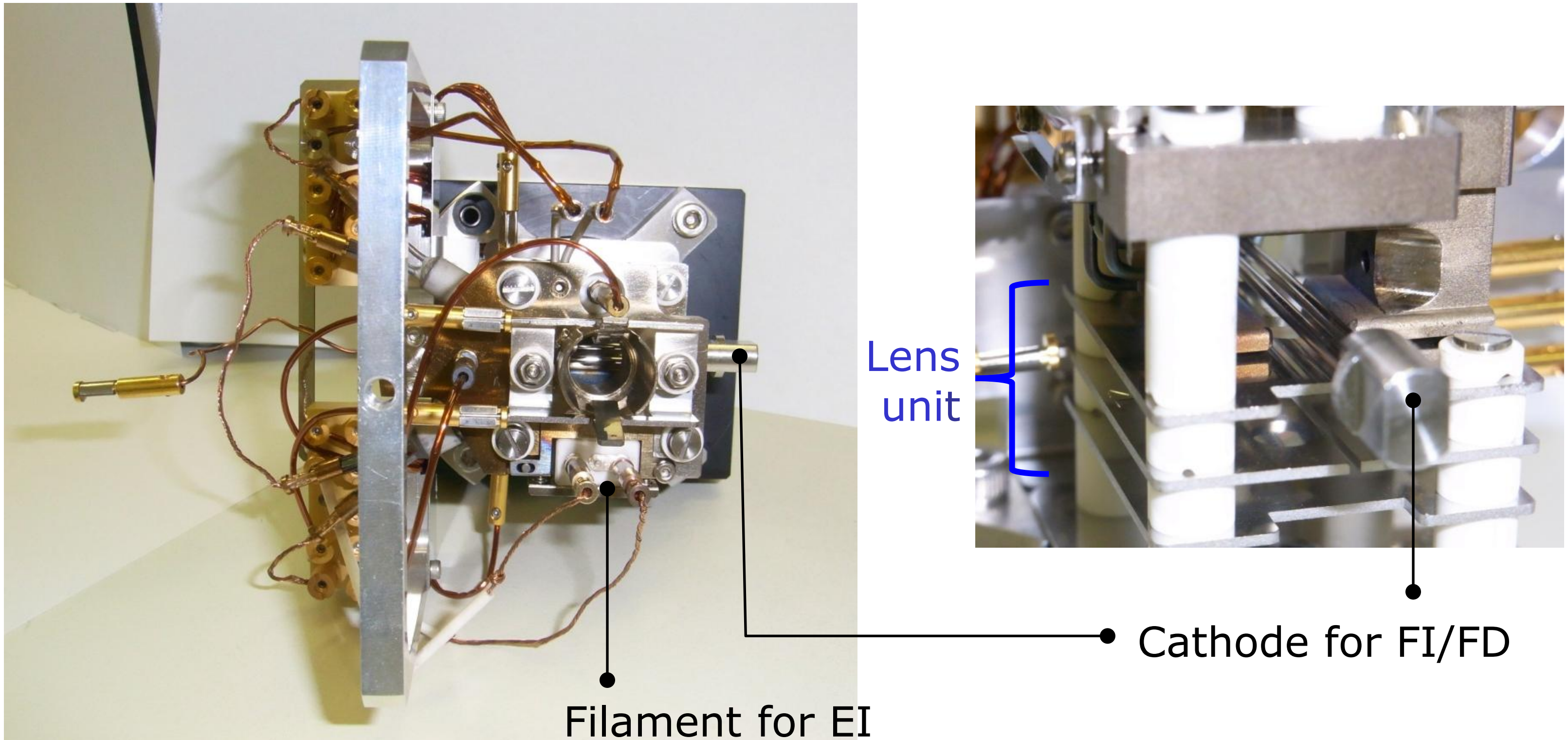
- JMS-T100GCV *“AccuTOF GCv 4G”* basic unit
  - Resolving power: R≥8,000 (FWHM) @ *m/z* 617
  - Mass range: *m/z* 4-5000
  - Mass accuracy: 1.5 mDa or 4 ppm (RMS)
  - Sensitivity: S/N ≥ 100 for 1pg OFN (using with EI standard ion source)
  - Acquisition rate: 50 spectra/s
  - Auto Tuning for all ionization modes
- “EI/FI/FD Combination Ion Source” option
  - EI, FI and FD modes can be switched without breaking vacuum
  - Suitable for petroleum analysis
- Additional options
  - CI mode (Positive and Negative)
  - Direct insertion: DEP, DIP, FD, LIFDI*

    Liquid Injection Field Desorption Ionization:

    Allows continuous sample introduction onto the FD emitter without removing the probe.



# 1. EI/FI/FD Combination Ion Source




EI, FI and FD modes can be switched without breaking vacuum

# 2. Samples and Measurement Conditions

- Sample:
  - Diesel oil
- Measurement conditions:
  - Column: DB-5ms, 30 m x 0.25 mm, 0.25 um
  - Oven: 50 C(1min) $\rightarrow$ 20 C/min $\rightarrow$ 300 C(6.5 min)
  - Inlet:  300 C, Split 200:1, 0.2 uL inj.
  - EI: 70 eV, 300 uA
  - FI: -10 kV (Cathode), 45 mA (30 msec: Refreshed every spectra recording
  - Mass range: *m/z* 35-800



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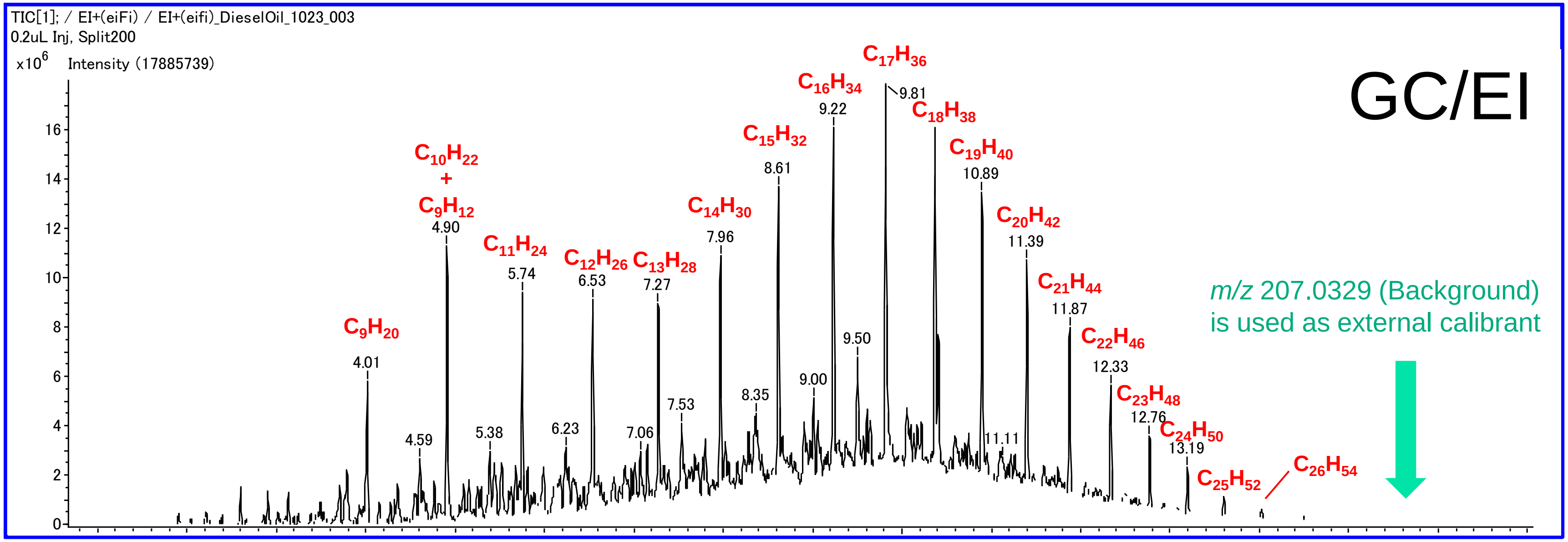
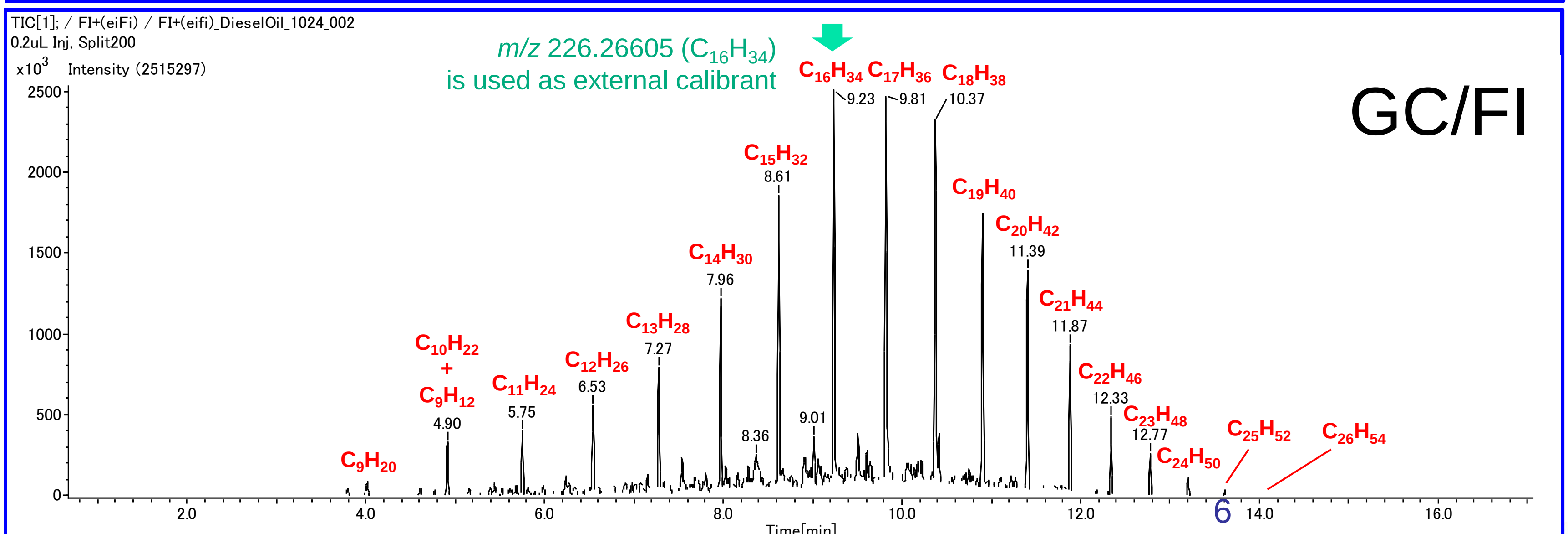
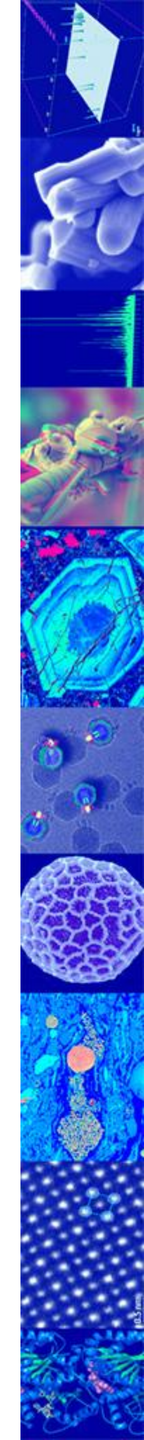
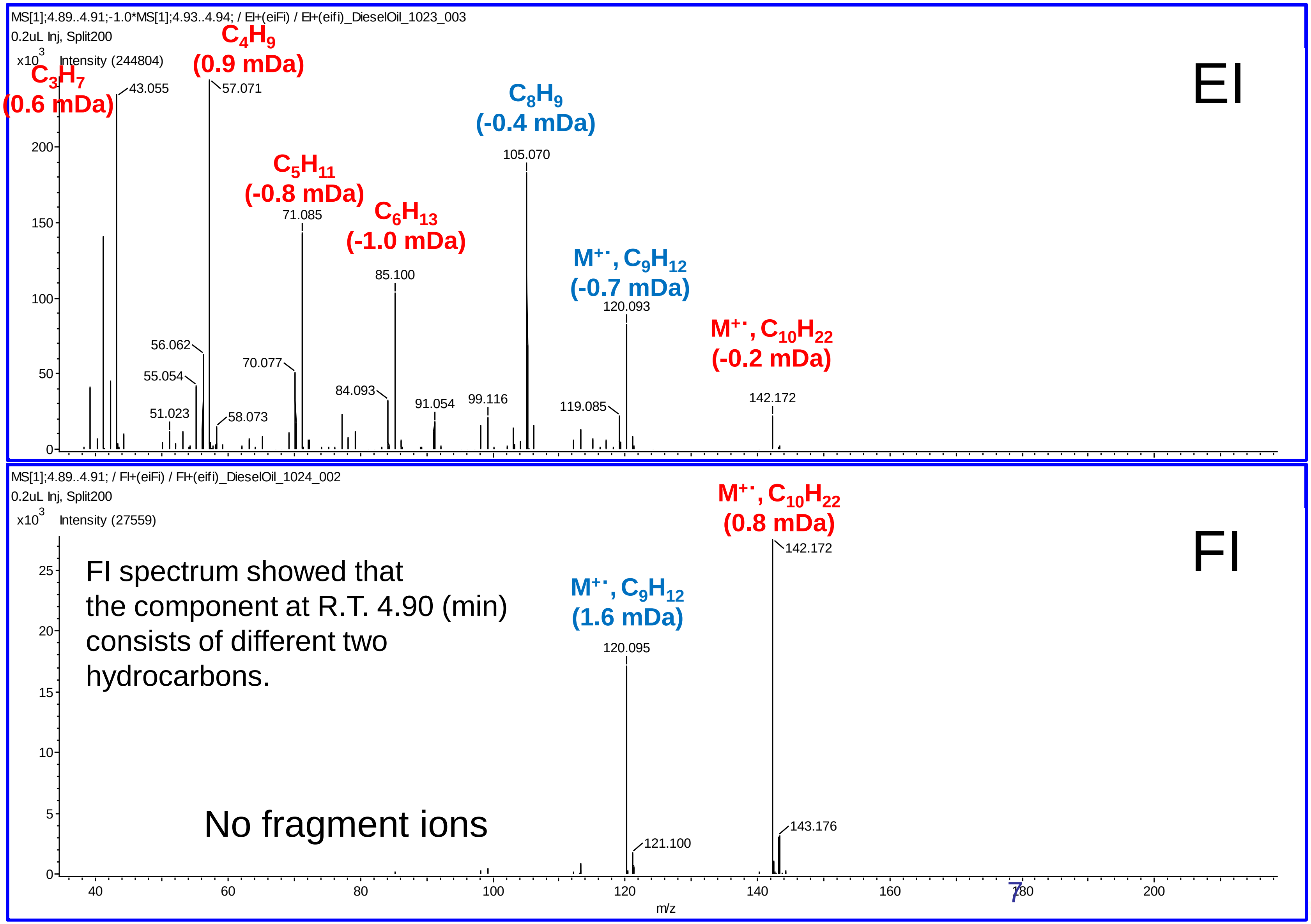
# 3. TIC Chromatograms



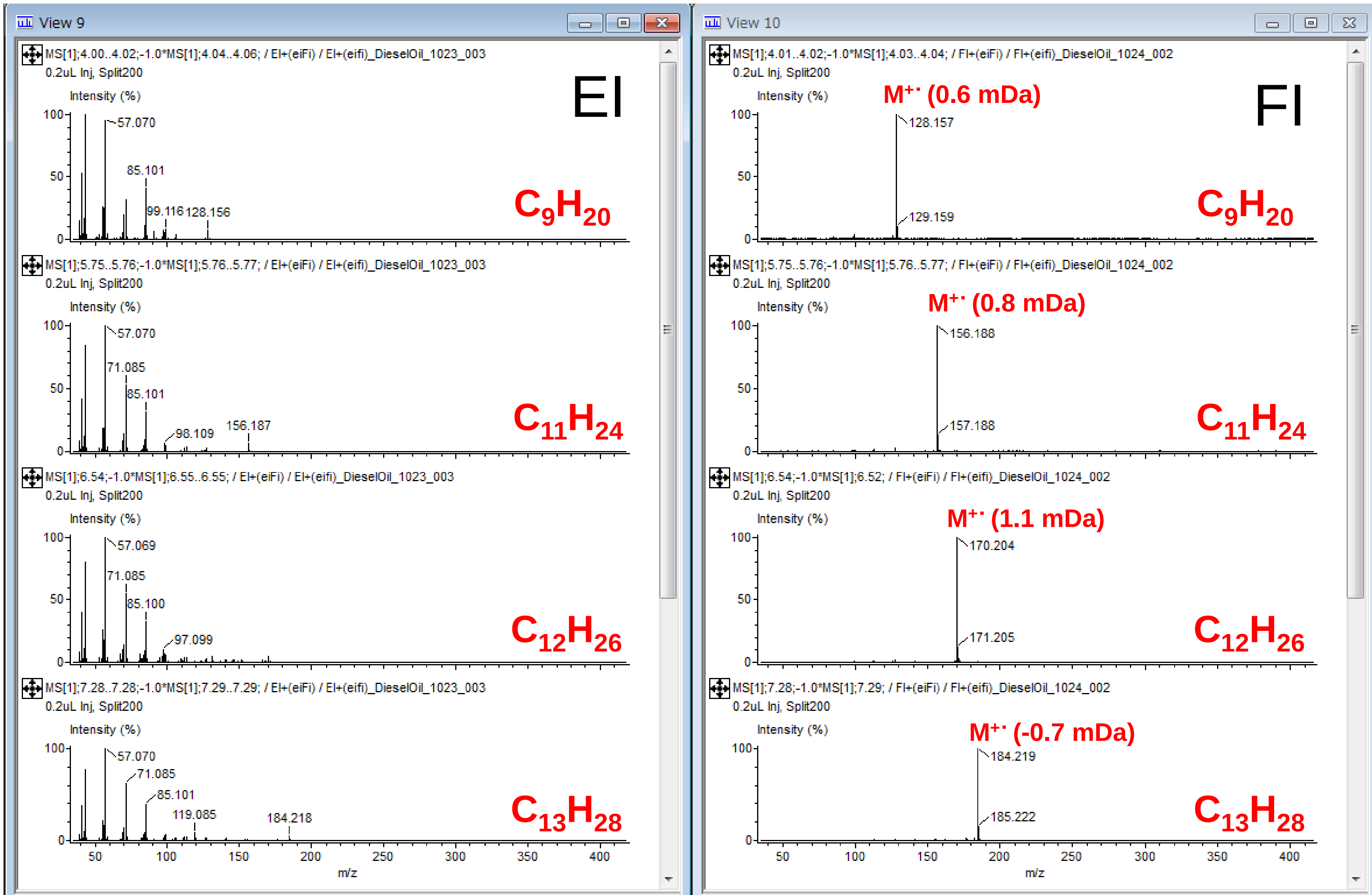



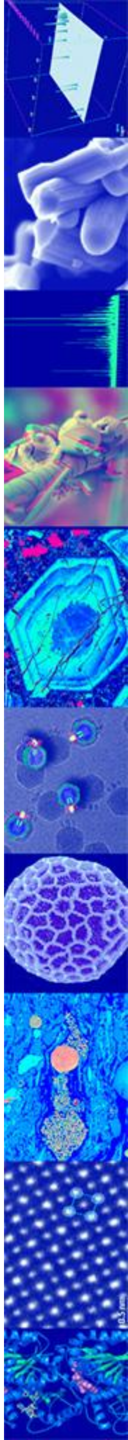



# 4. Mass spectra of the component at R.T. 4.90

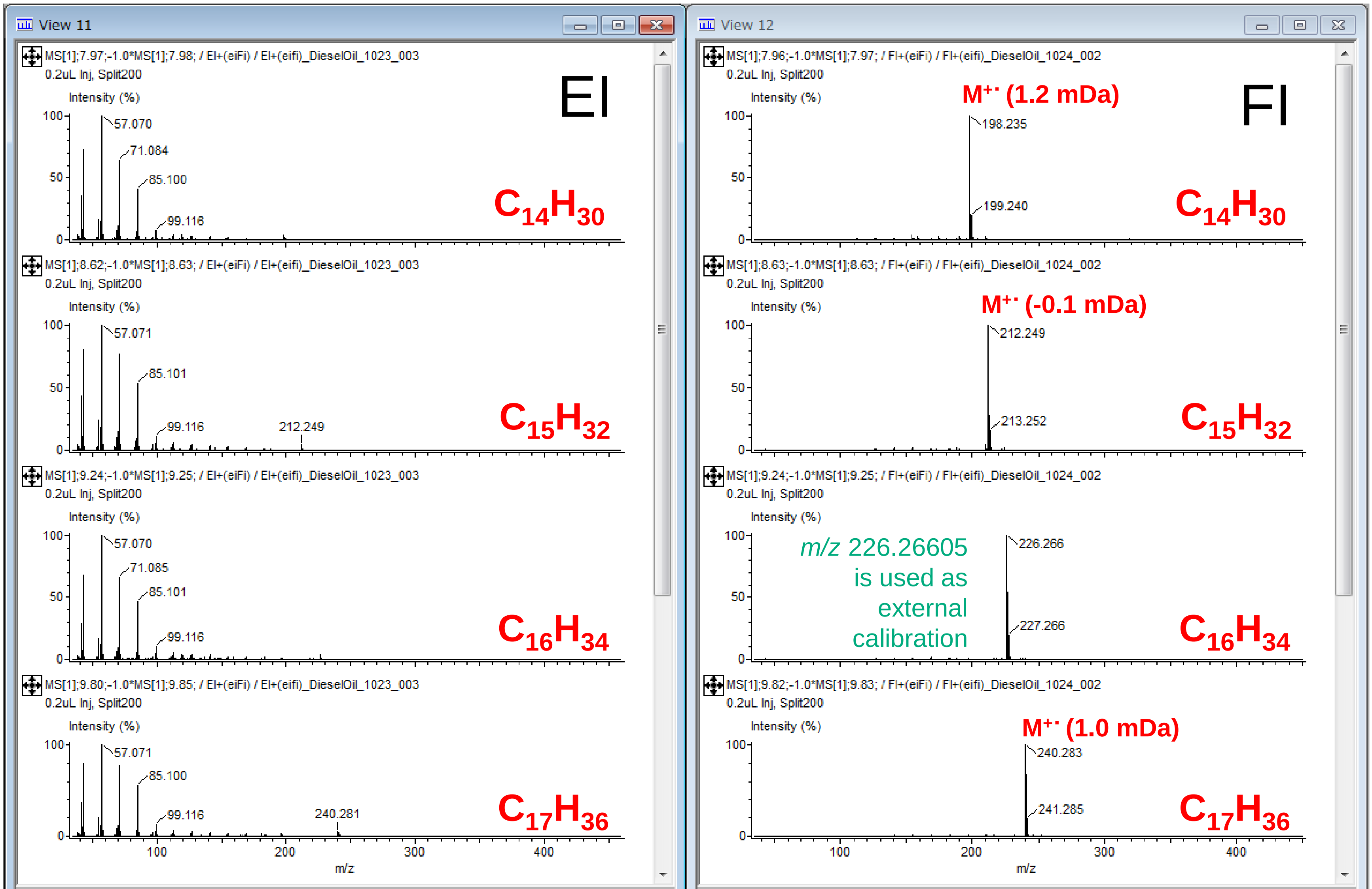


# Mass Spectra of *n* - Paraffins 1

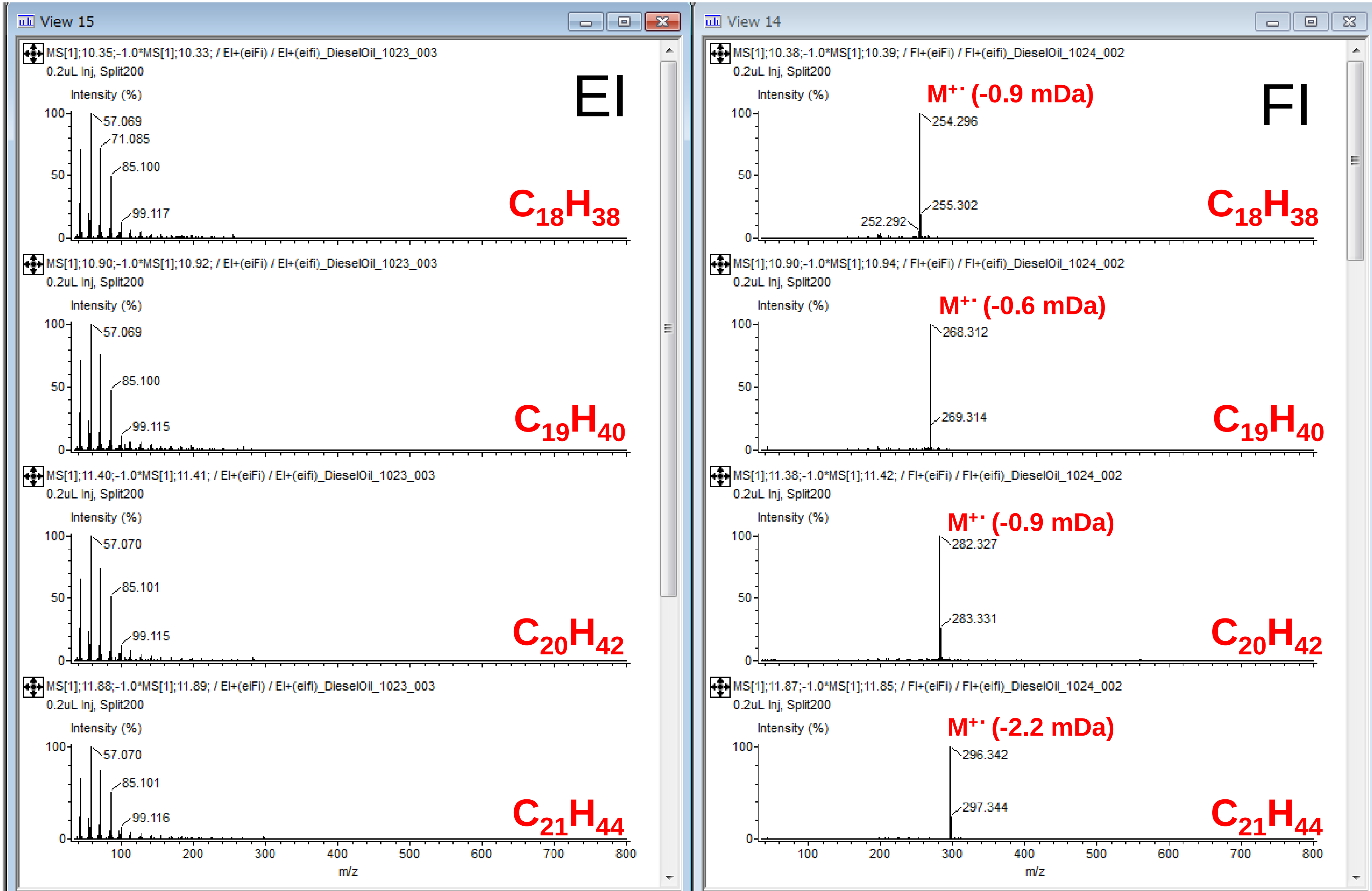


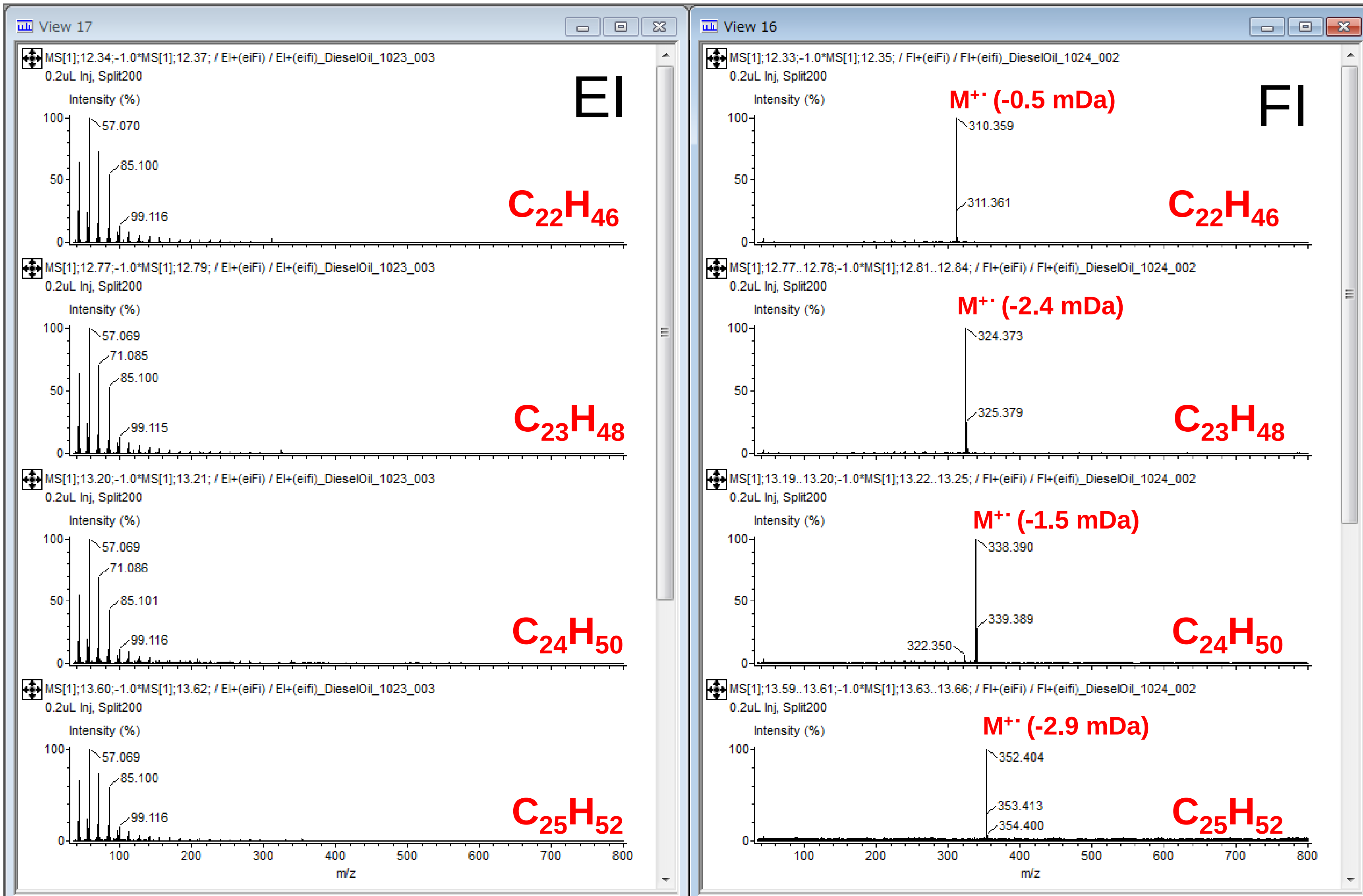
# Mass Spectra of *n* - Paraffins 2



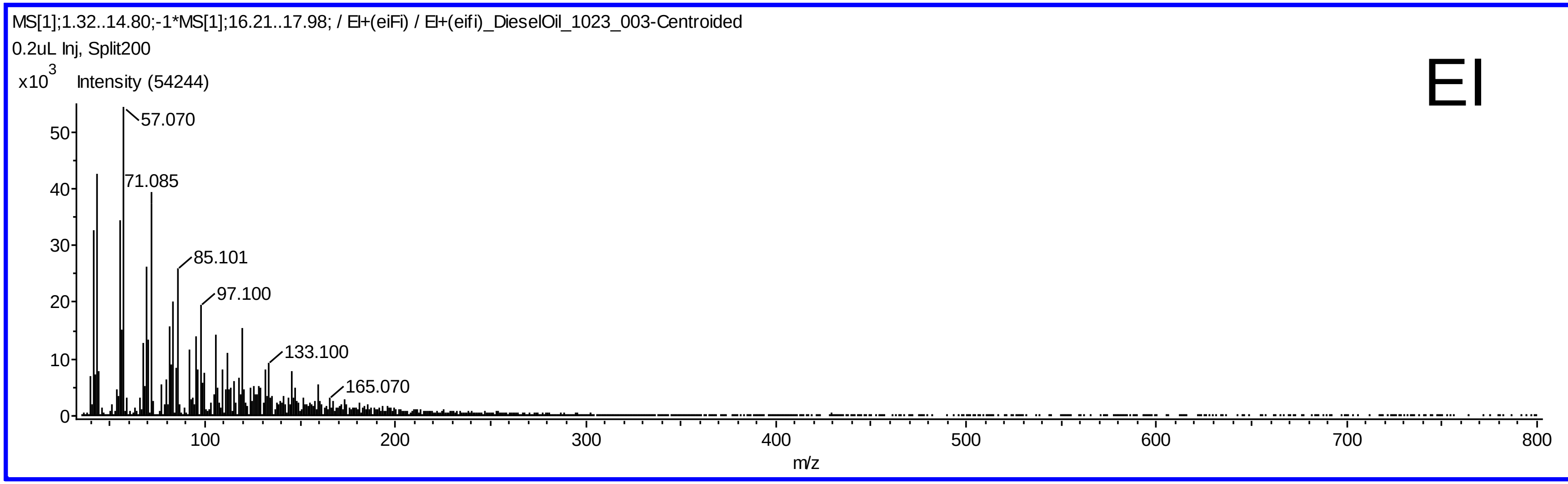
# Mass Spectra of *n* - Paraffins 3

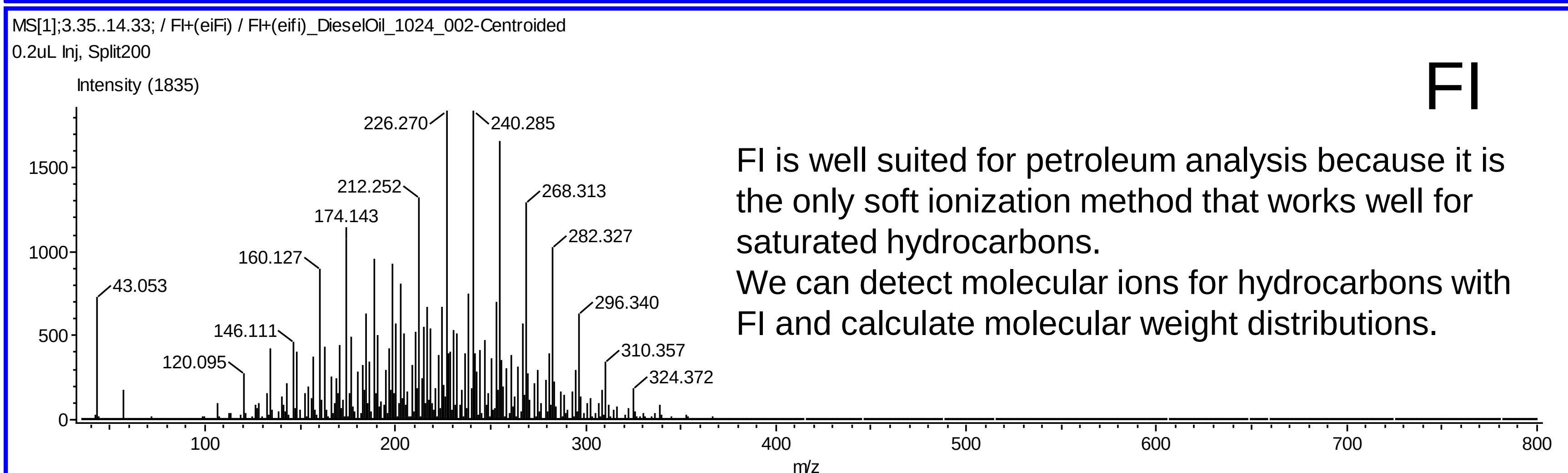


# Mass Spectra of *n* - Paraffins 4



# Sum Over the Entire R.T. Range

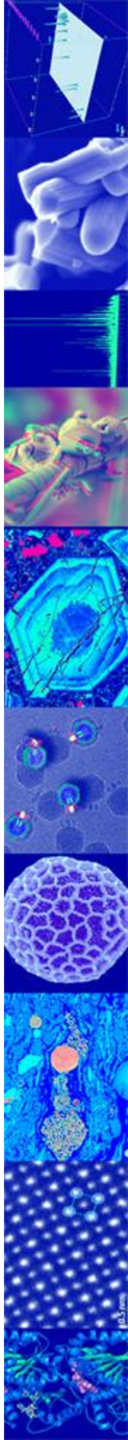



FI is well suited for petroleum analysis because it is the only soft ionization method that works well for saturated hydrocarbons.
We can detect molecular ions for hydrocarbons with FI and calculate molecular weight distributions.

# 5. Conclusion

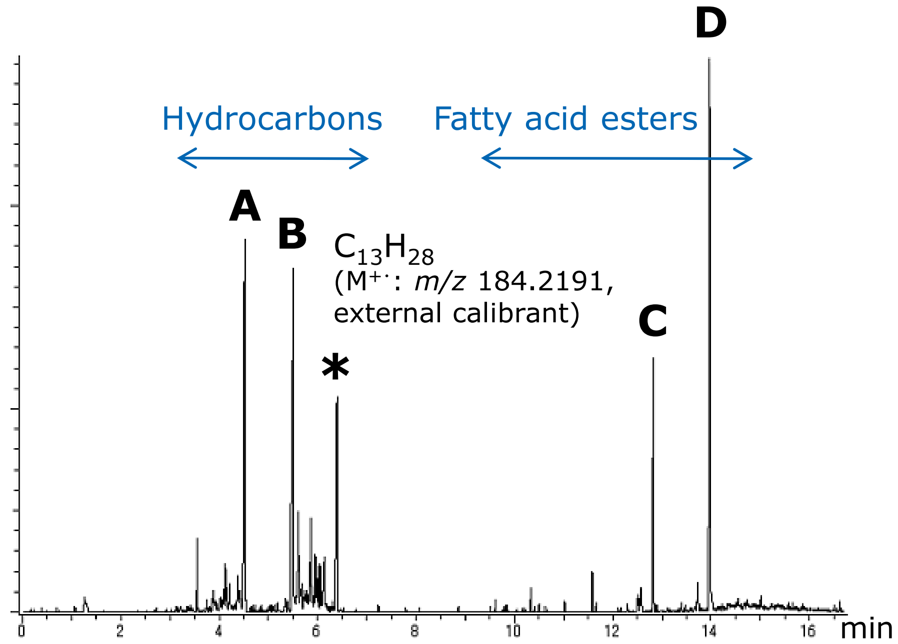
- The AccuTOF GCv has a unique EI/FI/FD combination ion source. There is no need to break vacuum when you switch ion modes. It is only necessary to replace the EI repeller probe with the FI/FD emitter probe without breaking vacuum.
- FI method is well suited for petroleum analysis, because it can generates molecular ions for saturated hydrocarbons with minimal fragmentation.
- EI and FI mass spectra both showed excellent mass accuracy.
- The AccuTOF GCv can be used for GCxGC measurement. We have also demonstrated applications for GCxGC/FI with high-resolution mass spectra.



# 6. Other Hydrocarbon Applications

- Commercial Lubricants Analysis with GC/FI
- Crude Oil Measurement with GC/FI
- Type Analysis of Crude Oil using a FI Mass Spectrum
- Microcrystalline Wax measurement with FD
- Rapid analysis using inactivated fused silica tube as a sample inlet
- GC x GC/EI - Dibenzothiophenes analysis in Kerosene
- GC x GC/FI technique with normal and reverse column set

# Commercial Lubricants Analysis with GC/FI




| | Formula | Calc. *m/z* | Meas. *m/z* | Mass error (mDa) |
|---|---|---|---|---|
| A | $C_{11}H_{24}$ | 156.1878 | 156.1868 | -1.0 |
| B | $C_{12}H_{26}$ | 170.2034 | 170.2030 | -0.4 |
| C | $C_{20}H_{40}O_2$ | 312.3028 | 312.3046 | 1.8 |
| D | $C_{22}H_{44}O_2$ | 340.3341 | 340.3356 | 1.5 |



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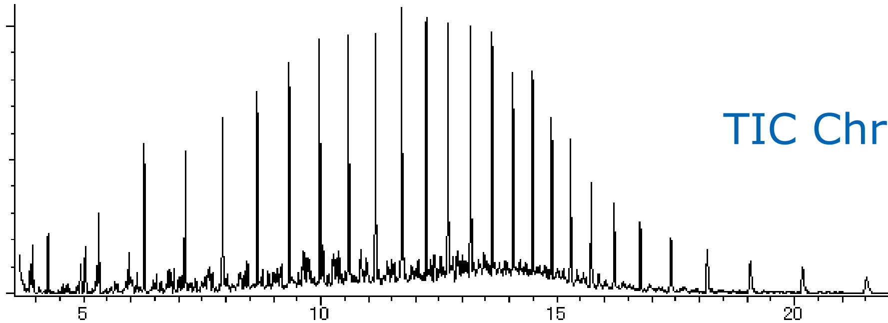
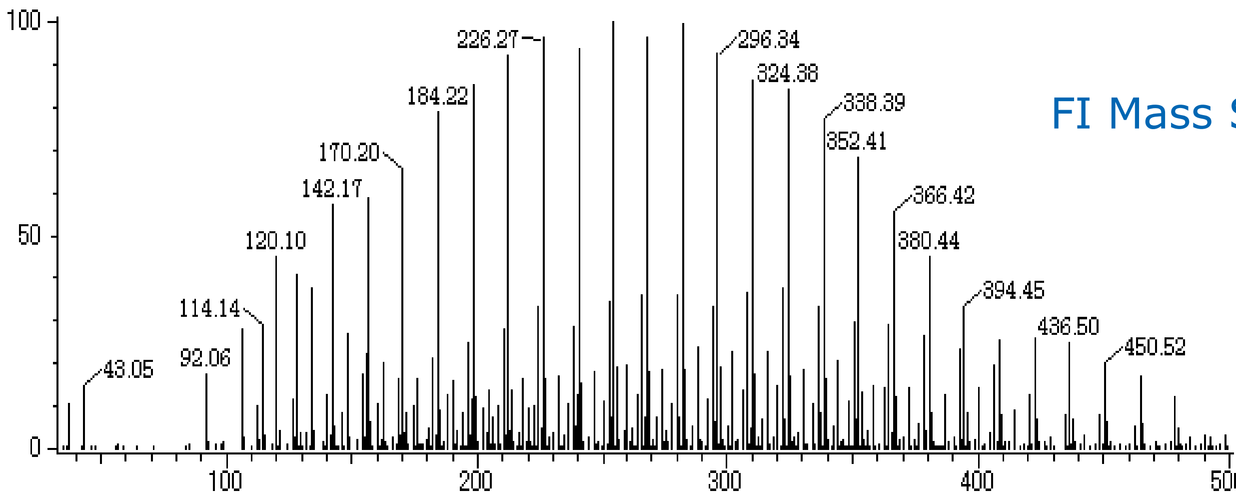
# Crude Oil Measurement with GC/FI



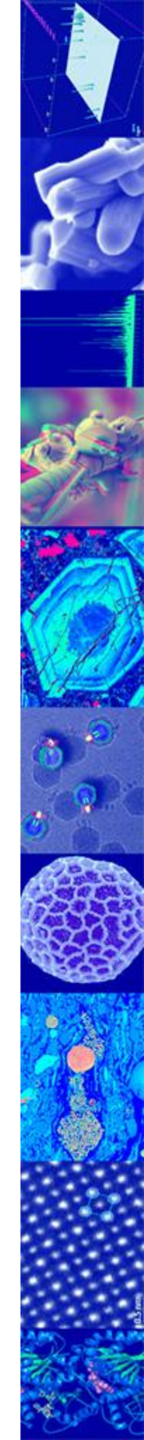

TIC Chromatogram

Accumulation over entire time range

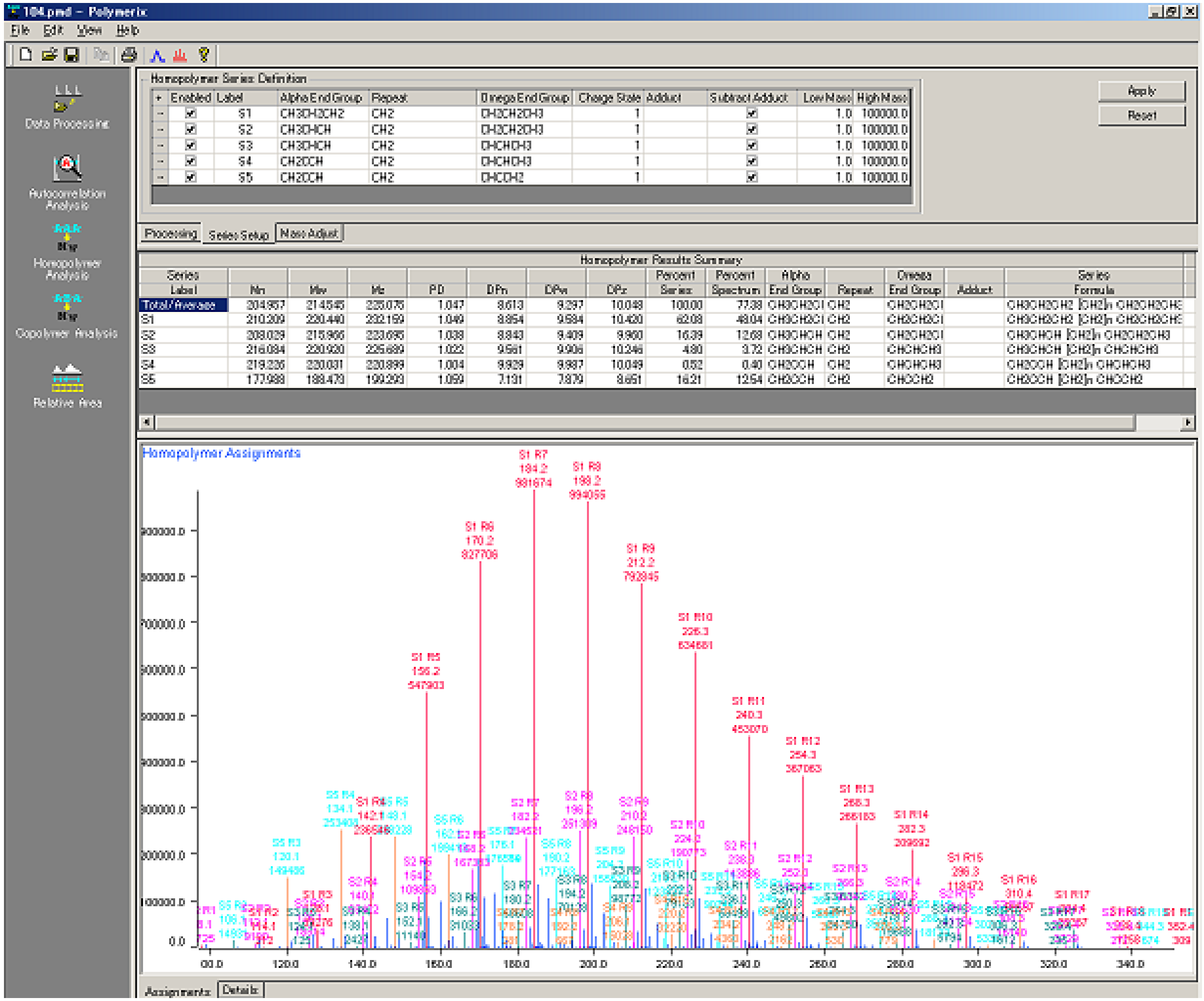



FI Mass Spectrum

Hydrocarbons could be detected as molecular ions



# Type Analysis of Crude Oil by using an FI Mass Spectrum




* Polymerix software (Sierra Analytics, Inc.)



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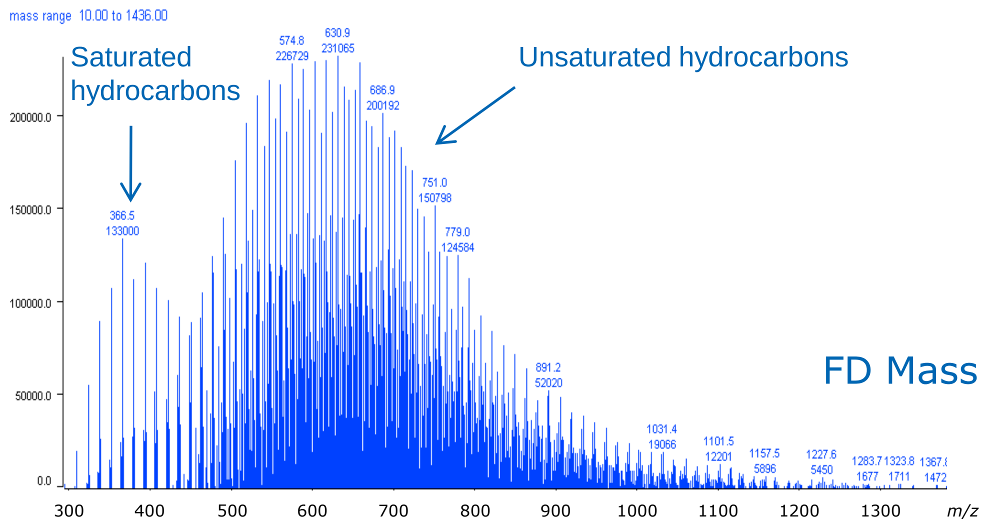
# Microcrystalline Wax measurement with FD




FD Mass Spectrum

Type Analysis of Microcrystalline Wax

| Series Label | | Mn | Mw | Mz | PD | DPn | DPw | DPz | Percet Series | Percent Spectrum |
|---|---|---|---|---|---|---|---|---|---|---|
| Total/Average | | 657.0 | 686.9 | 718.9 | 1.0 | 40.1 | 42.2 | 44.5 | 100.0 | 64.1 |
| S1 | $C_nH_{2n+2}$ | 571.1 | 617.3 | 665.3 | 1.1 | 33.6 | 36.9 | 40.3 | 17.3 | 11.1 |
| S2 | $C_nH_{2n}$ | 529.7 | 655.0 | 680.8 | 1.0 | 37.9 | 39.7 | 41.6 | 24.2 | 15.5 |
| S3 | $C_nH_{2n-2}$ | 670.5 | 692.3 | 715.6 | 1.0 | 41.0 | 42.5 | 44.2 | 13.1 | 8.4 |
| S4 | $C_nH_{2n-4}$ | 715.6 | 739.0 | 764.7 | 1.0 | 44.3 | 46.0 | 47.8 | 8.4 | 5.4 |
| S5 | $C_nH_{2n-6}$ | 688.3 | 717.9 | 751.1 | 1.0 | 42.5 | 44.7 | 47.0 | 22.5 | 14.5 |
| S6 | $C_nH_{2n-8}$ | 710.0 | 739.6 | 772.8 | 1.0 | 44.2 | 46.3 | 48.7 | 14.5 | 9.3 |

Mn:Number-average M.W.
Mw:Weight-average M.W.
Mz:Z-average M.W.
PD:Mw/Mn
DPn: Mn/R
DPw: Mw/R
DPz: Mz/R
(R: Repeating unit)

FD type analysis can provide information such as component ratios and average molecular weight.



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# Rapid analysis using inactivated fused silica tube (a.k.a. “guard column”) as a sample inlet

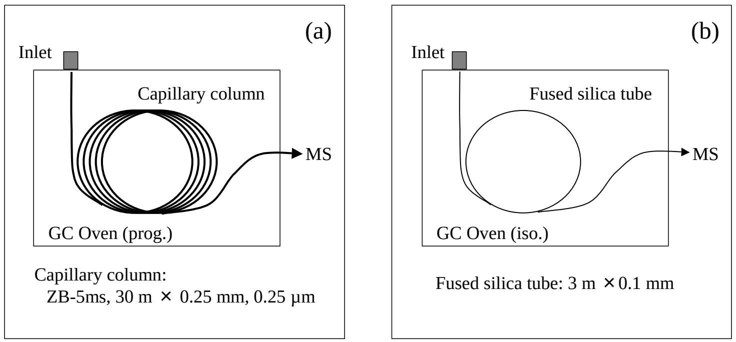



Fig.1 Schematic diagrams of sample introduction system by using GC,
(a) capillary GC/FI. (b) blank tube inlet/FI.

- Short analysis time
- Loss of low boiling point components are minimized compared with probe-based methods, such as FD, DEI, and DCI, in which the sample is deposited on the probe at ambient pressure.
- Loss of high boiling point and trace components is minimized compared to GC/MS methods since there are no interaction with a GC stationary phase.
- GC conditions are not critical; no need to worry about separation parameters.

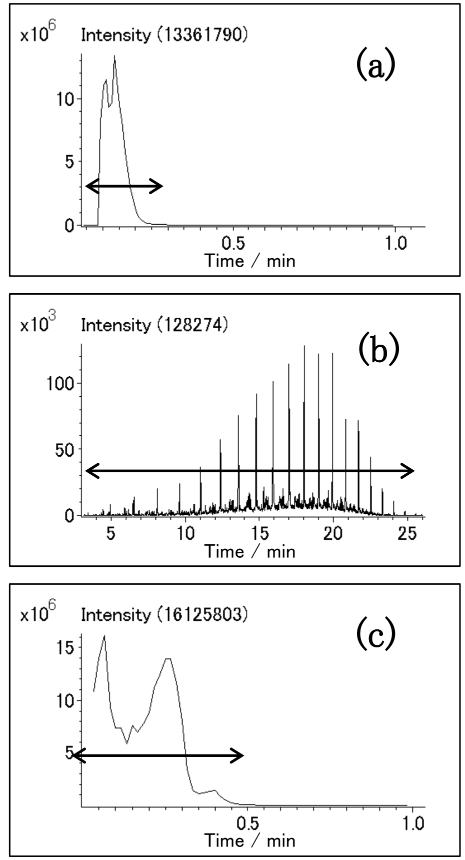



Fig.2 TICs of diesel oil
(a) blank tube inlet/FI,
(b) capillary GC/FI, (c) FD

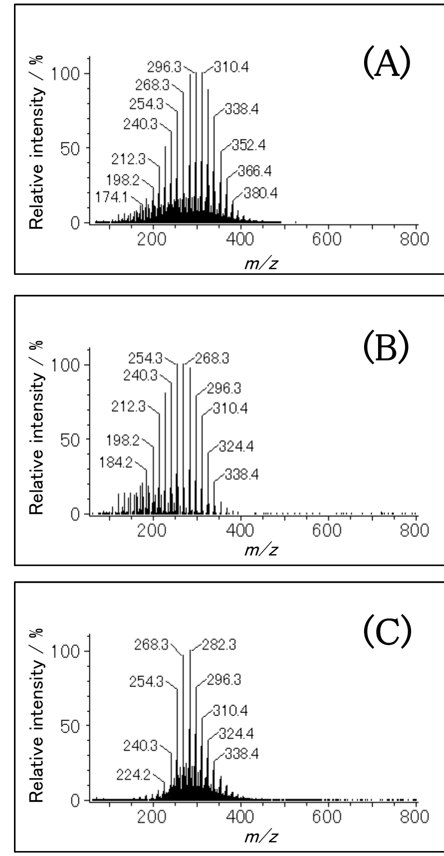
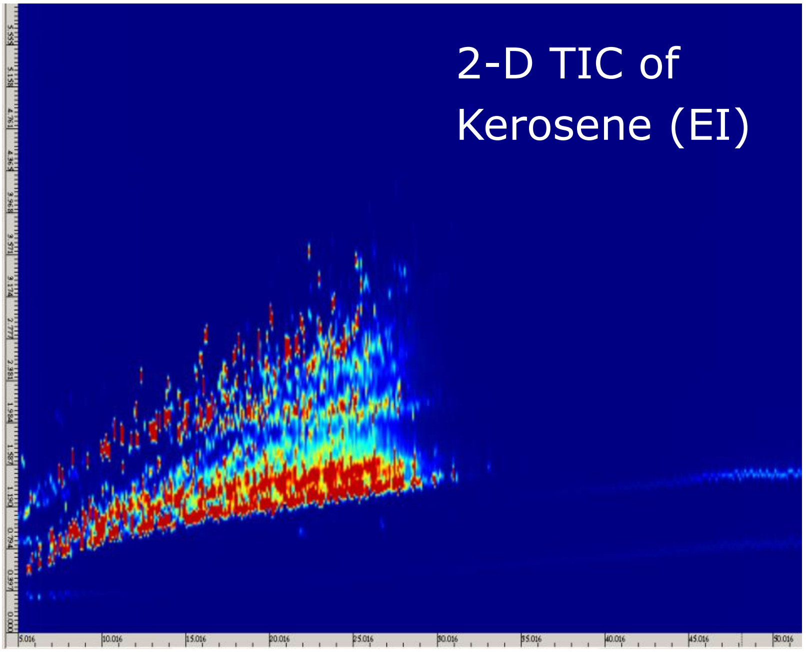
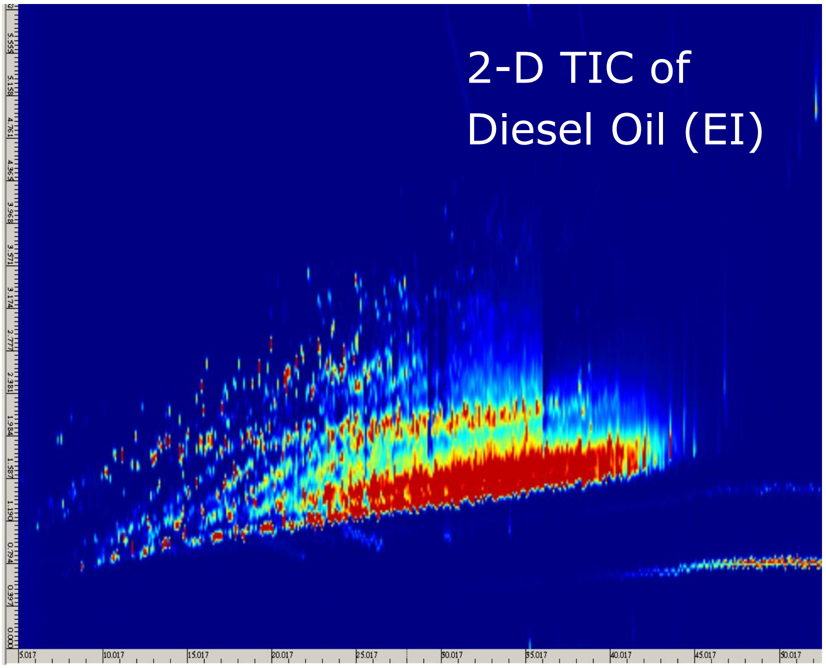



Fig.3 Mass spectra of diesel oil
(A) blank tube inlet/FI,
(B) capillary GC/FI, (C) FD

# GC x GC/EI – Kerosene and Diesel Oil




A time-of-flight mass spectrometer (TOFMS) is the best detector for GCxGC because it is capable of rapid spectral acquisition with no spectral skewing.



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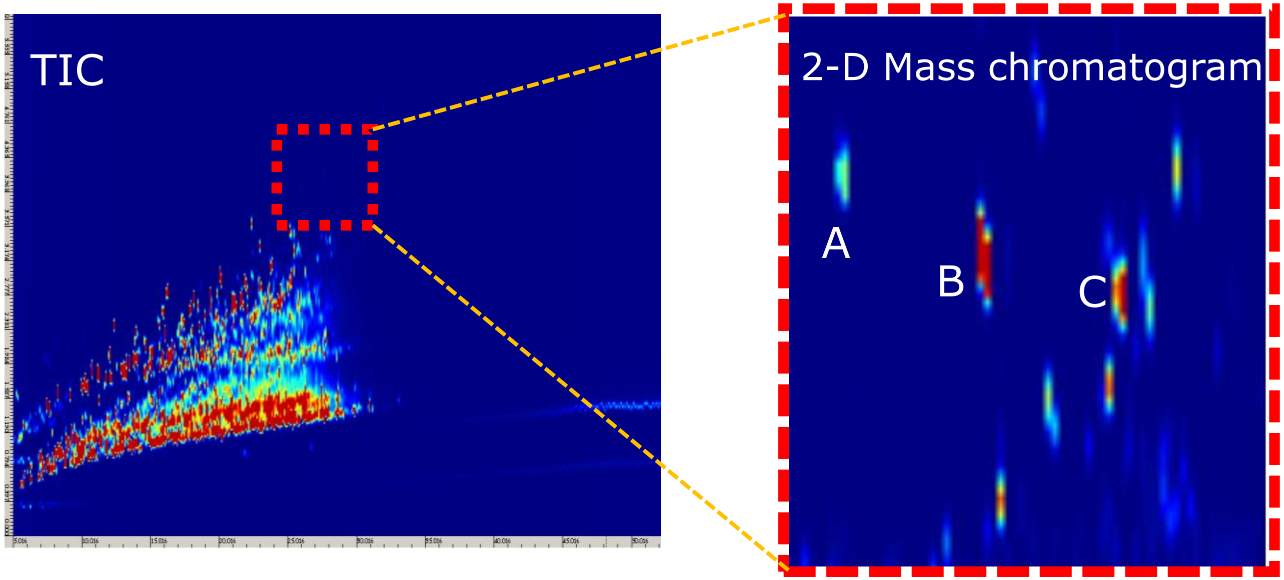
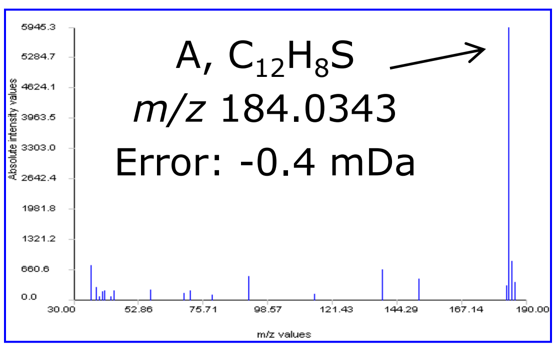
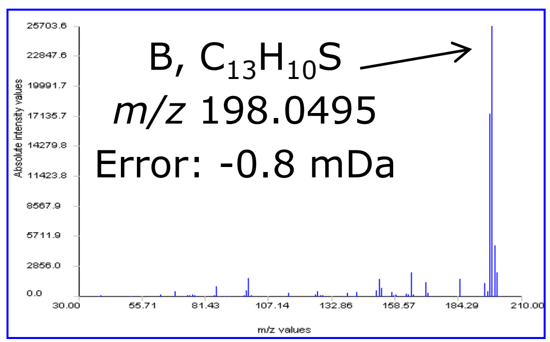
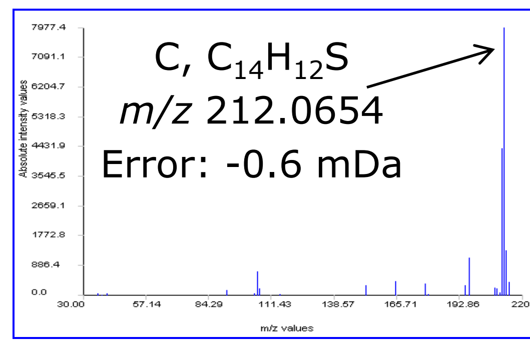
# GC x GC/EI - Dibenzothiophenes in Kerosene

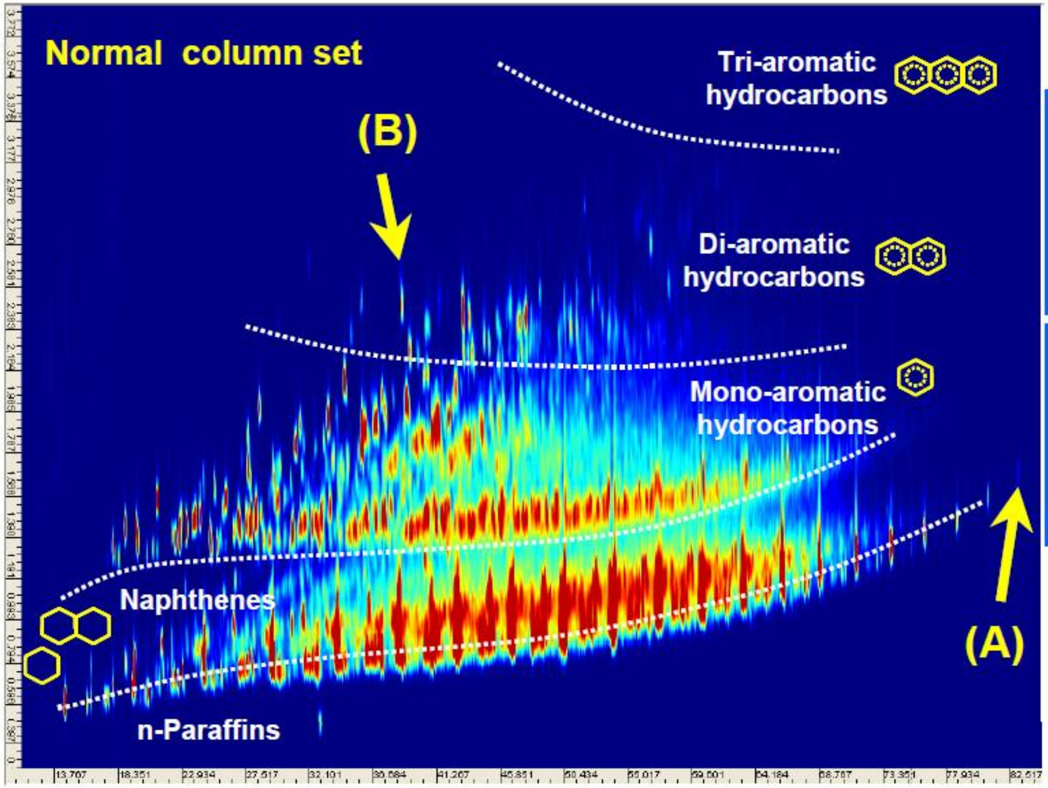


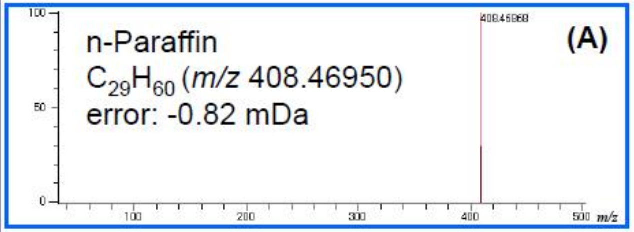



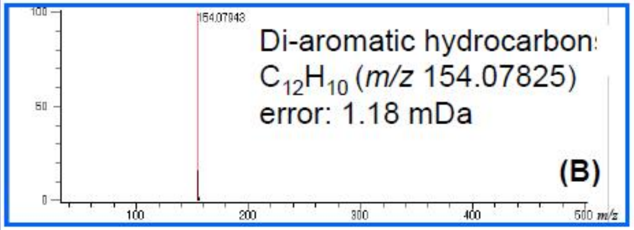



# GC x GC/FI technique with normal column set




GCxGC condition

: $1^{st}$ column : BPX5, 30mx0.25mm, I.D. 0.25um
: $2^{nd}$ column : BPX50, 2mx0.1mm, I.D. 0.1mm
: Oven temp. prog.: 50℃(2min)→3℃/min→300℃

TOFMS condition

: Mass range : *m/z* 35 ~ 500
: Data acquisition speed : 0.04 sec/spectrum
: Ionization mode : FI, cathode voltage -10kV



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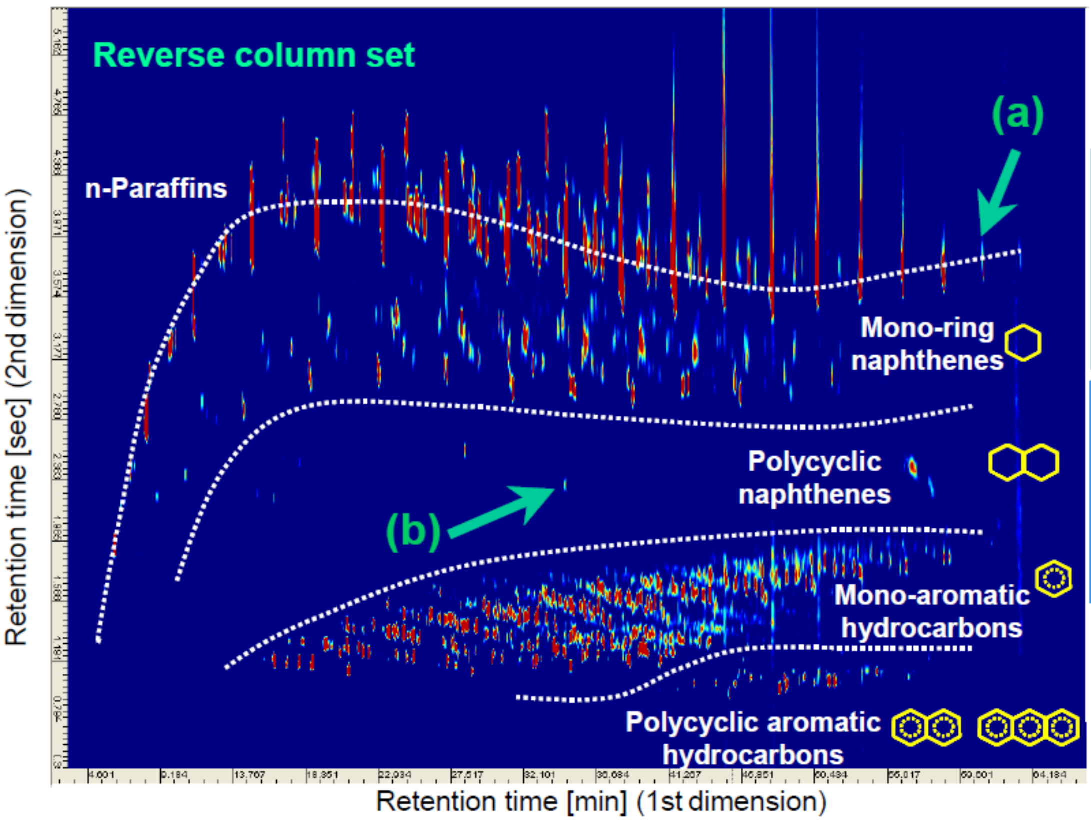
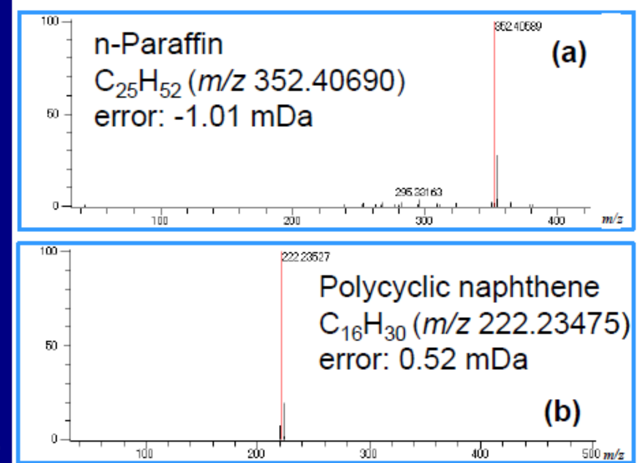
# GC x GC/FI technique with reverse column set




GCxGC condition

: 1st column : DB-WAXETR, 30mx0.25mm, I.D. 0.1um
: 2nd column : DB-1, 1mx0.1mm, I.D. 0.1um
: Oven temp. prog.: 50℃(2min)→3℃/min→300℃

TOFMS condition

: Mass range : *m/z* 35 ~ 500
: Data acquisition speed : 0.04 sec/spectrum
: Ionization mode : FI, cathode voltage -10kV