Performance Characteristics of a Comprehensive Two-Dimensional Gas Chromatography-High Resolution Time-of-Flight Mass Spectrometry System (GC×GC-HRTOFMS) Utilizing Chemical Ionization

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Introduction

• Comprehensive two-dimensional gas chromatography (GC×GC) is a powerful tool which leads to dramatically improved separation for complex samples. This technique generates very narrow chromatographic peaks, requiring a high speed detection system to accurately represent the chromatographic separation in two-dimensional space. When combined with a rapid acquisition High Resolution Time-of-Flight Mass Spectrometer (HRTOFMS), the resulting accurate mass data provides additional information for compound identification.

• A soft ionization source, which generates mostly molecular or quasi molecular ions, further enhances the information available by allowing for the unambiguous, or nearly unambiguous, identification of the elemental composition of compounds of interest. Conventional Electron Ionization (EI) sources used for MS detection systems generate multiple fragment ions and can limit the formation of the parent ion of interest. Incorporating Chemical Ionization (CI) can greatly assist in maintaining the molecular or quasi molecular ion relative to the typically used EI source. This work demonstrates the performance of a GC×GC-HRTOFMS with a CI source.

• The LECO Pegasus® GC-HRT 4D supports standard CI reagent gases, including methane, isobutane, and ammonia, while also allowing for custom gases to be chosen. To assist in optimization of the ion source, both automated and manual reagent gas flow optimizations are available. In addition, the instrument allows for simple exchange of the ion source between CI and EI.

• The data presented includes: Benzophenone standards to demonstrate the instrument's performance regarding detection limit, linear dynamic range, precision, resolution, and mass accuracy. A 10% Diesel sample is also included to demonstrate the two-dimensional separation capability of the instrument.

Instrument Operation

• Reagent Gas Type: Can select ammonia, isobutane, methane, or other for a custom gas or mixture.

• Reagent Gas Flow Optimization: An automated optimization is available. There are default masses and target ratio values in the automated optimization for ammonia, isobutane, and methane. Values can be changed for greater flexibility, or operator can manually optimize and simply enter the desired reagent gas flow.

• Ionization Method: When a CI Source is installed, an operator can select EI or CI Ionization. EI Ionization can be useful for leak checking or for a quick comparison to CI data without replacing the ion source. Note: EI data collected with a CI Source will have less sensitivity than EI data collected with an EI Source.

• Automated Instrument Optimization: Depending on the reagent gas type and ionization method, ChromaTOF-HRT® brand software will automatically open and close the reagent gas valve as needed.

Experimental

• Instrument - LECO Pegasus GC-HRT 4D with CI Ion Source
  • Resolving Power: >25,000
  • Data Acquisition Rate: Up to 200 full spectra/second

• Columns: (Restek)
  • First Dimension: 30 m x 250 μm x 0.25 μm Rxi-5 MS
  • Second Dimension: 2 m x 250 μm x 0.25 μm Rxi-17Sil MS (0.6 m in transfer line, 0.45 m in secondary oven)

• GC×GC Conditions:
  • Benzophenone: 60°C (0.20 min) at 60°C/min to 300°C (1.00 min)
  • Secondary Oven: +5°C to GC oven
  • Modulator: +15°C to Secondary Oven
  • Modulation Period: 1.50 second; Hot Pulse Time: 0.45 second

  • 10% Diesel: 40°C (1.00 min) at 9.20°C/min to 320°C (1.70 min)
  • Secondary Oven: 45°C (2.70 min) at 9.20°C/min to 325°C (0.00min)
  • Modulator: +15°C to Secondary Oven
  • Modulation Period: 2.00 second; Hot Pulse Time: 0.60 second

• CI Conditions:
  • Methane Reagent Gas automatically optimized using the CI Gas Flow Optimization = 0.5 ml/min
  • Electron Energy: 140eV
  • Emission Current: 1.0mA
  • Acquisition Range: 50-500 m/z
  • Acquisition Rate: 200 spectra/second

Results and Discussion

• Detection Limit: Benzophenone at 10 pg on column. The chromatographic peaks had an average Full Width Half Height (FWHH) of 0.063 second.

• Linear Dynamic Range: Figure 1 is the calibration curve of Benzophenone. Samples were collected in triplicate to determine the linear dynamic range of Benzophenone from 10 pg (the detection limit) to 10,000 pg on column. The correlation coefficient [r]=0.99416.

• Resolution and Mass Accuracy: Figure 2 at the top shows chromatographic overlays of injections of Benzophenone at 500 pg on column. The precision of the injections was 4.3% RSD Area. The average chromatographic FWHH of the peaks is 0.074 second. The average resolution was 27,996 and Average Mass Accuracy was 0.53 ppm. The bottom are sample spectra comparing the Electron Ionization (EI) and Chemical Ionization (CI) of Benzophenone. The CI spectrum demonstrates the greater abundance of the [M+H]+ Ion.

• Diesel Example: Figure 3 is an example of Diesel Sample collected in GC×GC with Chemical Ionization. The top is a contour plot showing the chromatographic separation in two dimensional space. The contour plot is plotting the Total Ion Chromatogram (TIC) with the peak markers (black dots) on. The area in red near the bottom of the plot are the most intense peaks, the n-alkanes. The bottom figures are example spectra of the C20 n-alkane with the EI spectrum on the left and CI spectrum on the right. Identification of n-alkanes based on EI mass spectral data alone can be problematic because of their tendency to fragment, resulting in small or non-observable molecular ions. Soft ionization used in CI results in a [M-H]+ species for the n-alkanes. The expected m/z value for C20 n-alkane is 281.32028, which agrees well with the observed m/z value of 281.32030. Table 1 summarizes the mass accuracy of some of the n-alkanes in the 10% Diesel sample.

Conclusion

• Combining comprehensive two-dimensional gas chromatography (GC×GC) with a High Resolution Time-of-Flight Mass Spectrometer and Chemical Ionization is a powerful tool for compound identification. Performance of the LECO Pegasus GC-HRT 4D using Chemical Ionization (CI) was demonstrated using Benzophenone and Diesel.

• GC×GC separation results in narrow peaks, therefore, a high speed detection system is necessary. All of the data presented was collected using an acquisition rate of 200 spectra/second.

• The resolving power, mass accuracy, and detection limit are not dependant upon acquisition speed. Resolution was at 25,000 or greater for all collected data.

Pegasus GC-HRT 4D

Linear Dynamic Range

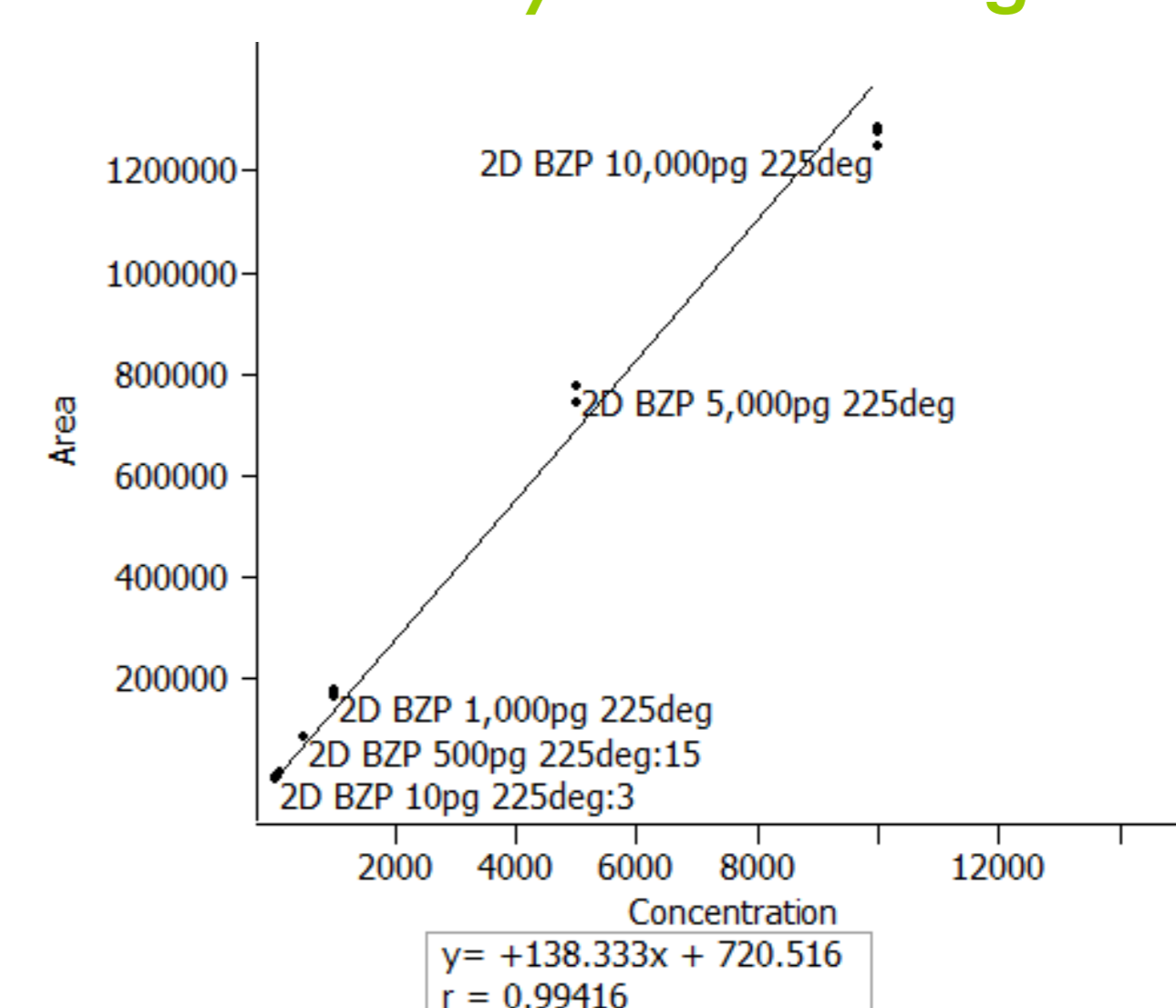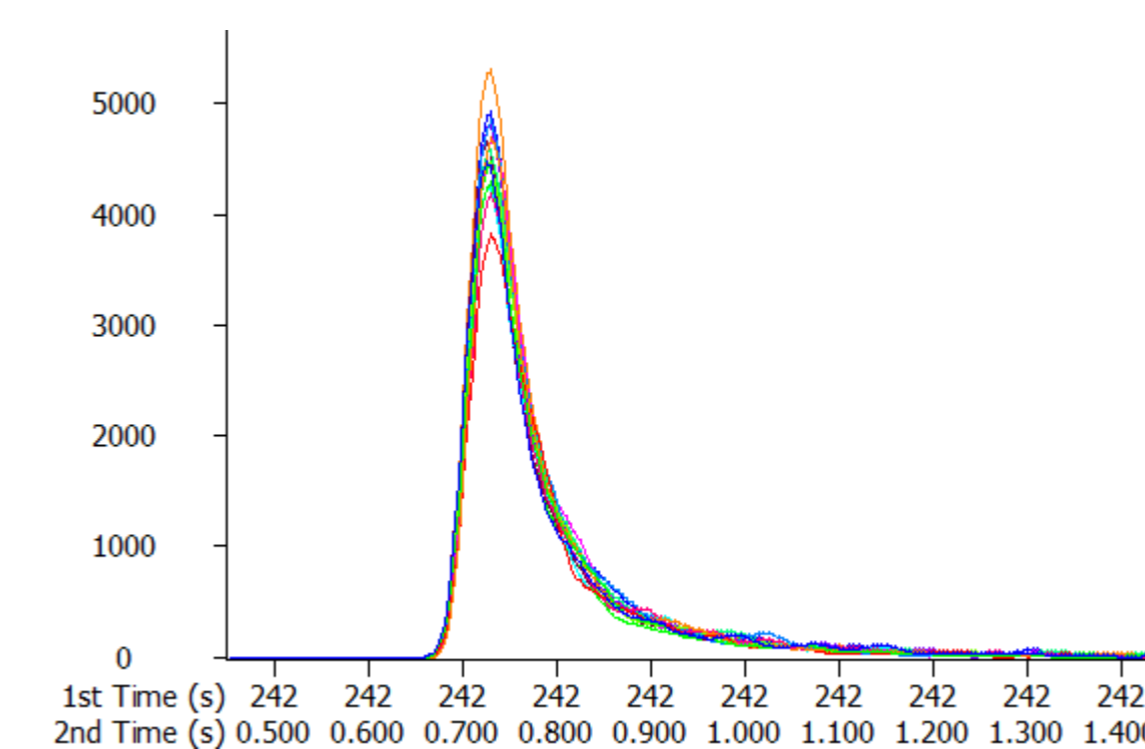y= +138.333x + 720.516
r = 0.99416

Figure 1. Calibration Curve for the Linear Dynamic Range of Benzophenone 10 pg to 10,000 pg on column in GC×GC and CI mode.

Resolution/Mass Accuracy

• % RSD of Area: 4.3%
• Average FWHH: 0.074 s
• Average Resolution: 27,996
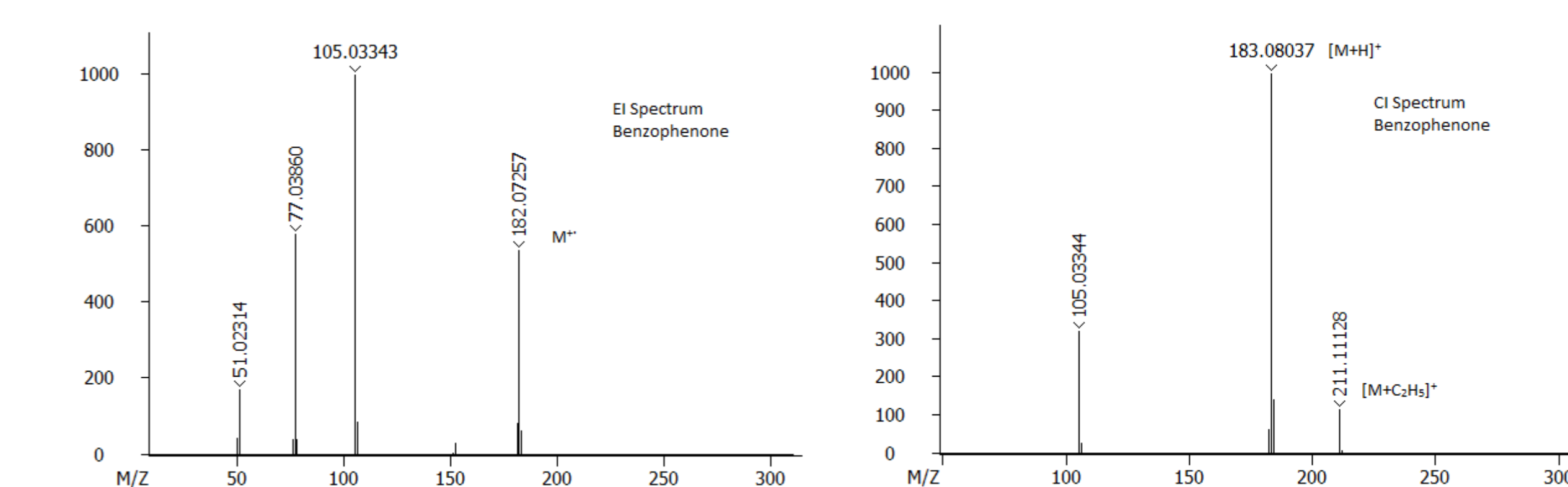• Average Absolute Relative Mass Error 0.53 ppm

Figure 2. Top: 15 Consecutive injection chromatographic peak overlays of Benzophenone at 500 pg on column in GC×GC and CI mode with precision, resolution, and mass accuracy information. Bottom: Example Mass Spectra of Benzophenone in EI mode (left) and CI mode (right).
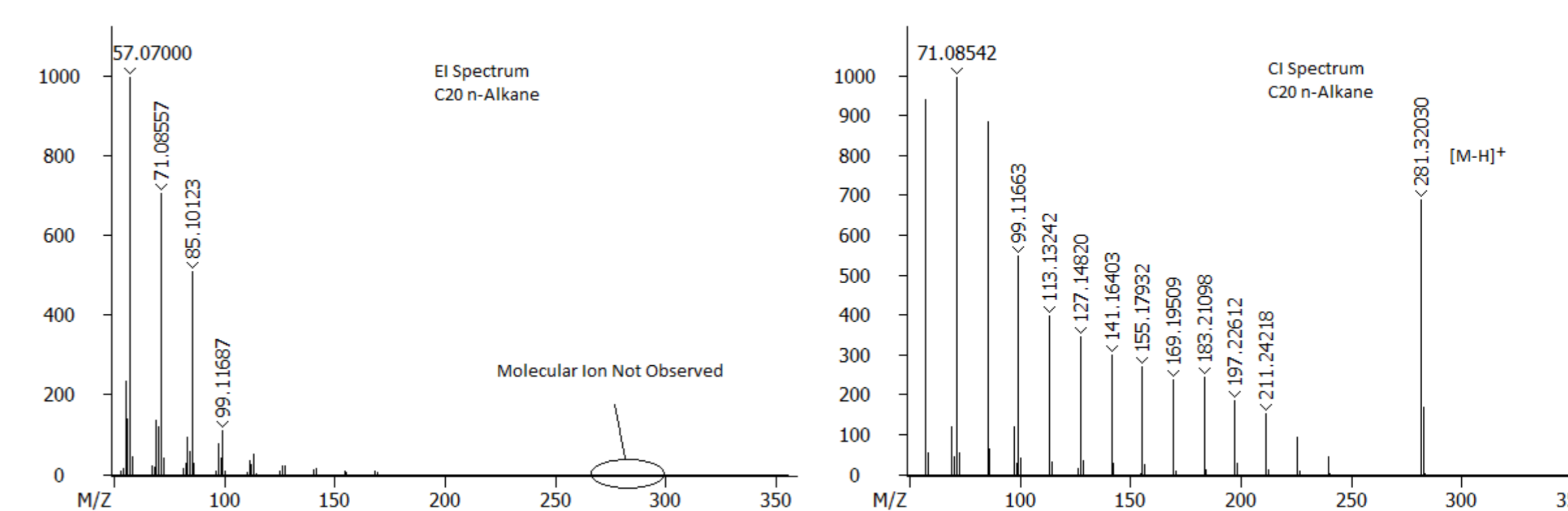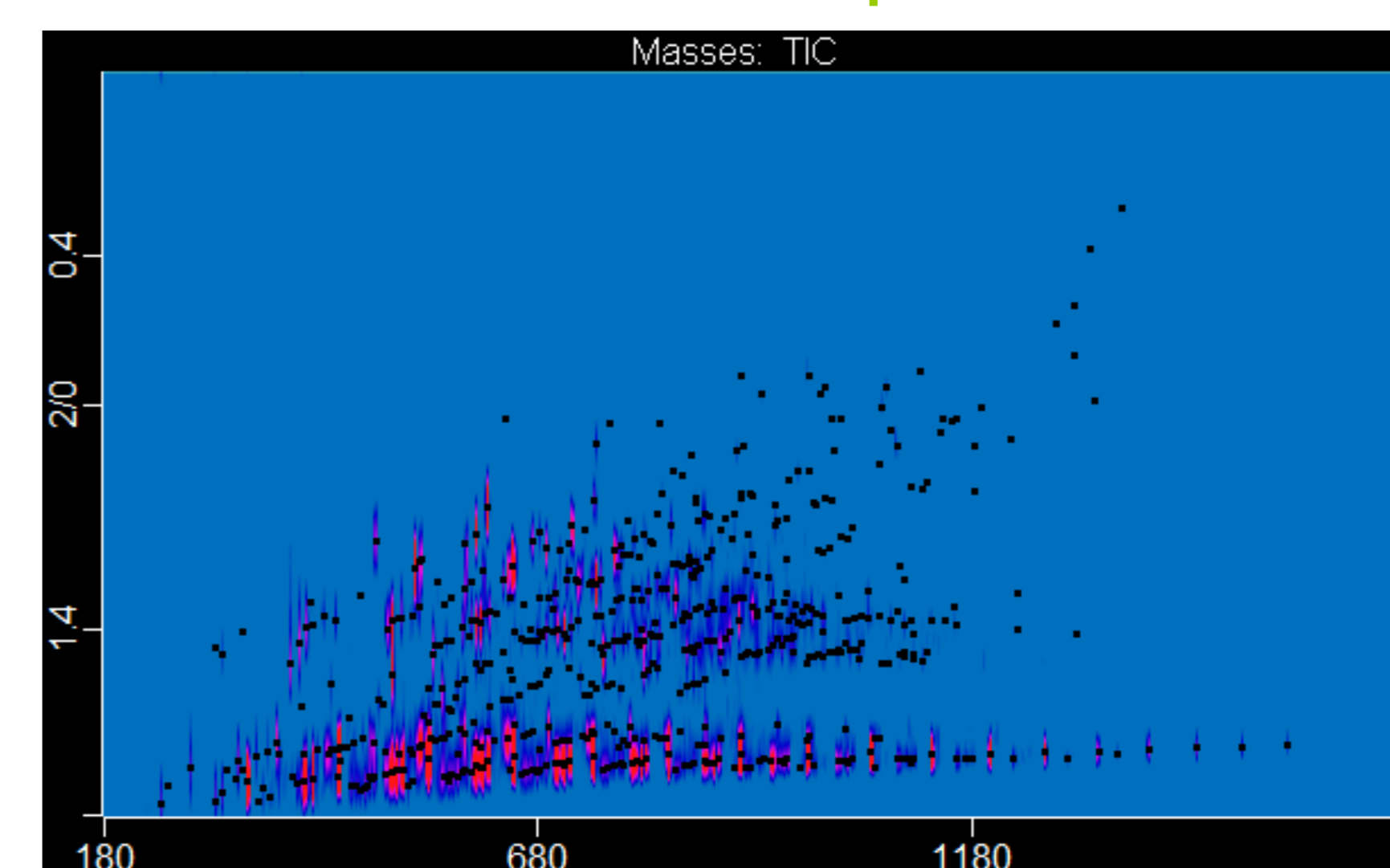
Diesel Sample

Figure 3. Top: Example Two-Dimensional Contour Plot of a 10% Diesel sample in GC×GC and CI mode. Total Ion Chromatogram (TIC) with peak markers are plotted. Bottom: Example Mass Spectra of Eicosane (C20 n-alkane) in EI mode (left) and CI mode (right).

Table 1. Summary GC×GC HR-CI Mass Accuracy Data for n-Alkanes in 10% Diesel Sample

Name	Formula	Species	Expected Ion m/z	Observed Ion m/z	Mass Accuracy (ppm)
Decane	$C_{10}H_{22}$	[M-H]+	141.16378	141.16379	0.07
Dodecane	$C_{12}H_{26}$	[M-H]+	169.19508	169.19518	0.59
Tetredecane	$C_{14}H_{30}$	[M-H]+	197.22638	197.22632	-0.30
Hexadecane	$C_{16}H_{34}$	[M-H]+	225.25768	225.25769	0.04
Octadecane	$C_{18}H_{38}$	[M-H]+	253.28898	253.28926	1.11
Eicosane	$C_{20}H_{42}$	[M-H]+	281.32028	281.32030	0.07
Docosane	$C_{22}H_{46}$	[M-H]+	309.35158	309.35161	0.10
Tetracosane	$C_{24}H_{50}$	[M-H]+	337.38288	337.38303	0.44