

# APPLICATIONS

## GCxGC-VUV and GCxGC-FID Analysis of Gasoline, Middle Distillates and Crude Oil Distillation Cuts using Zebron™ ZB-35HT and ZB-1PLUS GC Columns

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### Introduction

Comprehensive two-dimensional gas chromatography has evolved over its relative short history to be a robust tool used in many markets for routine lab analysis in addition to continuing at its roots as a powerful tool in applications for cutting edge research and development. The petroleum industry was one of its earliest adapters to this technology due to the ability to analyze complex crude oil matrices. One of the most frequent utilizations of this analytical technique is the analysis of middle distillates, such as diesel fuel, heating oil, or jet fuel. In most cases, the GCxGC technique utilizes either flow-based modulation or thermal modulation and for the detection by FID, SCD, or mass spectrometry. Thermal modulation typically utilizes a cryogenic modulator, which is great for highly volatile compounds, but it is expensive because of the liquid nitrogen consumption. Hence the flow-based modulation serves as a reliable modulation for a broad temperature range with an economical advantage which makes it an instrument for the analysis of gasoline samples.

The analysis of gasoline is usually accomplished following the European standard DIN EN ISO 22854 and ASTM D6839. New environmental regulation guided fuel formulations have additives that are deviations from the common composition of gasoline, which can be problematic for existing fuel gas chromatography test methods or even harmful to the applied instrument. The demand for improvements in analyzing fuel has brought the development of new test methods to the fuel market utilizing different equipment and techniques. A promising new technique, ASTM D8071, applies GC-Vacuum Ultraviolet detection (GC-VUV) for the quantitative determination of the content of n-paraffins, iso-paraffins, olefins, naphthenes, aromatics, and oxygenates in common gasoline. In addition, it is possible to detect and identify di-olefins with unconjugated and conjugated double bonds. Low concentrated analytes like di-olefins can clearly be identified using VUV detection and the increased sensitivity can be achieved from the two-dimensional GC separation.

In this presented work, the application of GCxGC-VUV and a possible transition to GCxGC-FID were demonstrated. A reversed phase column combination, consisting of 20 meter Zebron ZB-35HT Inferno™ (1st Dimension) and 5 meter ZB-1PLUS (2nd Dimension), was applied for the analysis of gasoline, middle distillates, and crude oil distillation cuts.

### GC Conditions for All Analyses

#### Column 1: Zebron ZB-35HT

Phase: 35 % Phenyl 65 % Dimethylpolysiloxane  
Dimensions: 20 meter x 0.18 mm x 0.18 µm  
Part No.: [7FD-G025-08](#)

#### Column 2: Zebron ZB-1PLUS

Phase: 100 % Dimethylpolysiloxane  
Dimensions: 5 meter x 0.25 mm x 0.1 µm  
Part No.: [7HG-G031-02](#) (30 meter trimmed to 5 meter)

#### Sample 1: Heating Oil

Injection: Split 1:100 @ 280 °C, 1 µL  
Instrument: 2D GC - Agilent® 7890A modified with SepSolve Analytical's Insight flow modulator  
Carrier Gas (column 1): 0.5 mL/min (constant flow)  
Carrier Gas (column 2): 20 mL/min (constant flow)  
Detector: Agilent Flame Ionization (FID) @ 350 °C, 100 Hz acquisition rate  
Oven Program:  
Column 1: 40 °C for 1 min, to 300 °C @ 2 °C/min, hold for 1 min  
Column 2: 40 °C for 1 min, to 300 °C @ 2 °C/min, hold for 1 min

#### Sample 2: Gasoline

Injection: Split 1:100 @ 280 °C, 1 µL  
Instrument: 2D GC - Agilent 7890A modified with SepSolve Analytical Insight flow modulator  
Carrier Gas (column 1): 0.5 mL/min (constant flow)  
Carrier Gas (column 2): 20 mL/min (constant flow)  
Detector: VGA-100 VUV (VUV Analytics Inc.)  
Oven Program:  
Column 1: 30 °C for 5 min, to 200 °C @ 2 °C/min, hold for 0 min  
Column 2: 30 °C for 5 min, to 200 °C @ 2 °C/min, hold for 0 min

#### Sample 3: Light Crude Oil Distillation Fraction

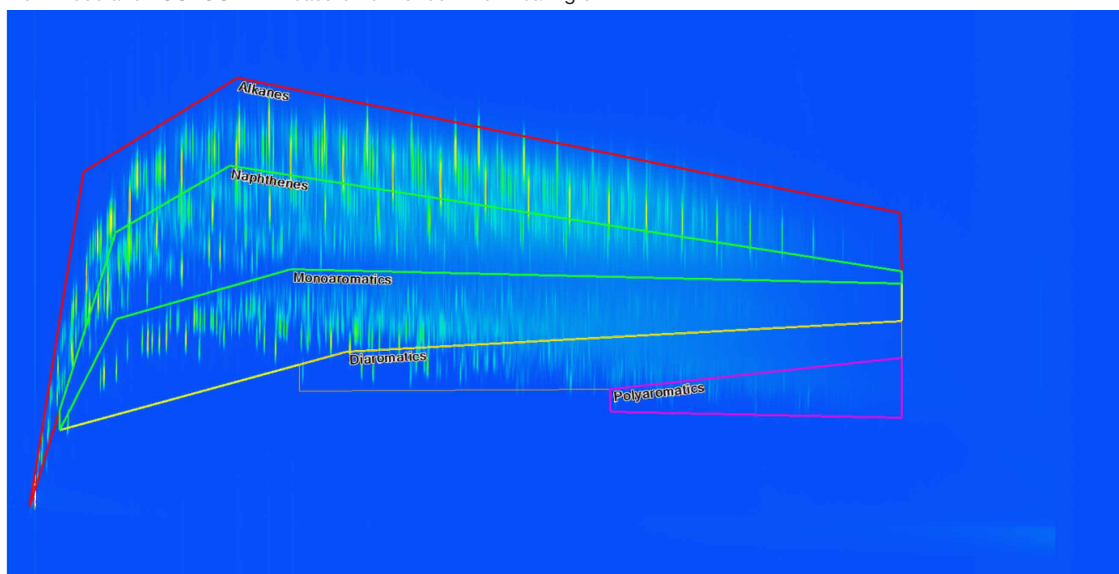
Injection: Split 1:100 @ 280 °C, 1 µL  
Instrument: 2D GC - Agilent 7890A modified with SepSolve Analytical Insight® Flow Modulator  
Carrier Gas (column 1): 0.5 mL/min (constant flow)  
Carrier Gas (column 2): 20 mL/min (constant flow)  
Detection: VGA 100 VUV (VUV Analytics Inc.)  
Oven Program:  
Column 1: 30 °C for 5 min, to 200 °C @ 2 °C/min, hold for 0 min  
Column 2: 30 °C for 5 min, to 200 °C @ 2 °C/min, hold for 0 min

## Results and Discussion

The reversed phase column combination, consisting of 20 meter Zebron™ ZB-35HT Inferno™ (1st Dimension) and 5 meter ZB-1PLUS (2nd Dimension), was first applied for the development of a GC×GC-FID analysis method of middle distillates. **Figure 1** shows the chromatogram of a common heating oil sample along

with a rough classification by substance groups. The more detailed classification by carbon number is given in **Table 1**. Classifications by carbon number are not displayed for reasons of clarity and comprehensibility.

**Figure 1.**  
Flow modulation GC×GC-FID measurement of common heating oil



App ID 25628

**Table 1.**

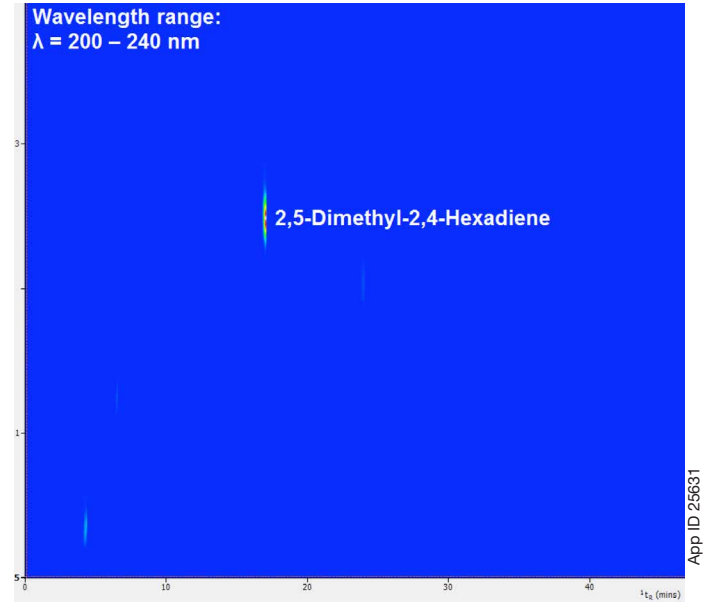
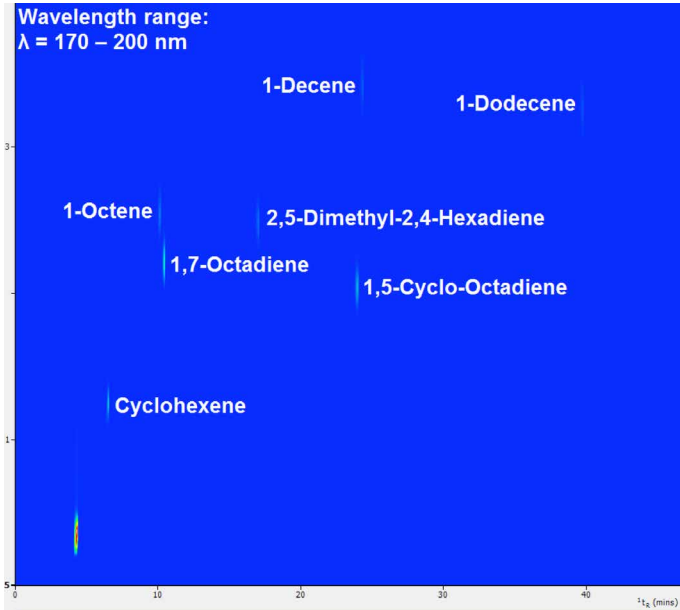
Data evaluation and classification of heating oil sample by substance group and carbon number. Area percentages are considered to be equivalent to weight percentage after validation by representative standard mixtures of paraffins, naphthenes, and mono-, di-, and tri-aromatics.

Weight %	Saturates	Monoaromatics	Diaromatics	Triaromatics	Total
C7	1.04 %	0.05 %	—	—	1.10 %
C8	3.11 %	0.47 %	—	—	3.58 %
C9	6.11 %	1.41 %	—	—	7.52 %
C10	6.42 %	1.58 %	0.03 %	—	8.04 %
C11	6.22 %	2.26 %	0.16 %	—	8.64 %
C12	7.26 %	3.92 %	0.35 %	—	11.53 %
C13	6.98 %	2.08 %	0.63 %	—	9.70 %
C14	7.03 %	1.43 %	0.61 %	0.01 %	9.08 %
C15	5.56 %	1.64 %	0.74 %	0.04 %	7.98 %
C16	6.21 %	0.54 %	0.33 %	0.07 %	7.16 %
C17	5.35 %	0.67 %	0.69 %	0.23 %	6.94 %
C18	4.05 %	1.01 %	0.38 %	0.20 %	5.64 %
C19	2.98 %	0.62 %	0.14 %	—	3.73 %
C20	3.09 %	0.52 %	0.06 %	—	3.67 %
C21	2.26 %	0.32 %	—	—	2.58 %
C22	1.52 %	0.24 %	—	—	1.77 %
C23	0.69 %	0.04 %	—	—	0.73 %
C24	0.45 %	—	—	—	0.45 %
C25	0.14 %	—	—	—	0.14 %
C26	0.05 %	—	—	—	0.05 %
Total	76.51 %	18.82 %	4.12 %	0.55 %	100.00 %

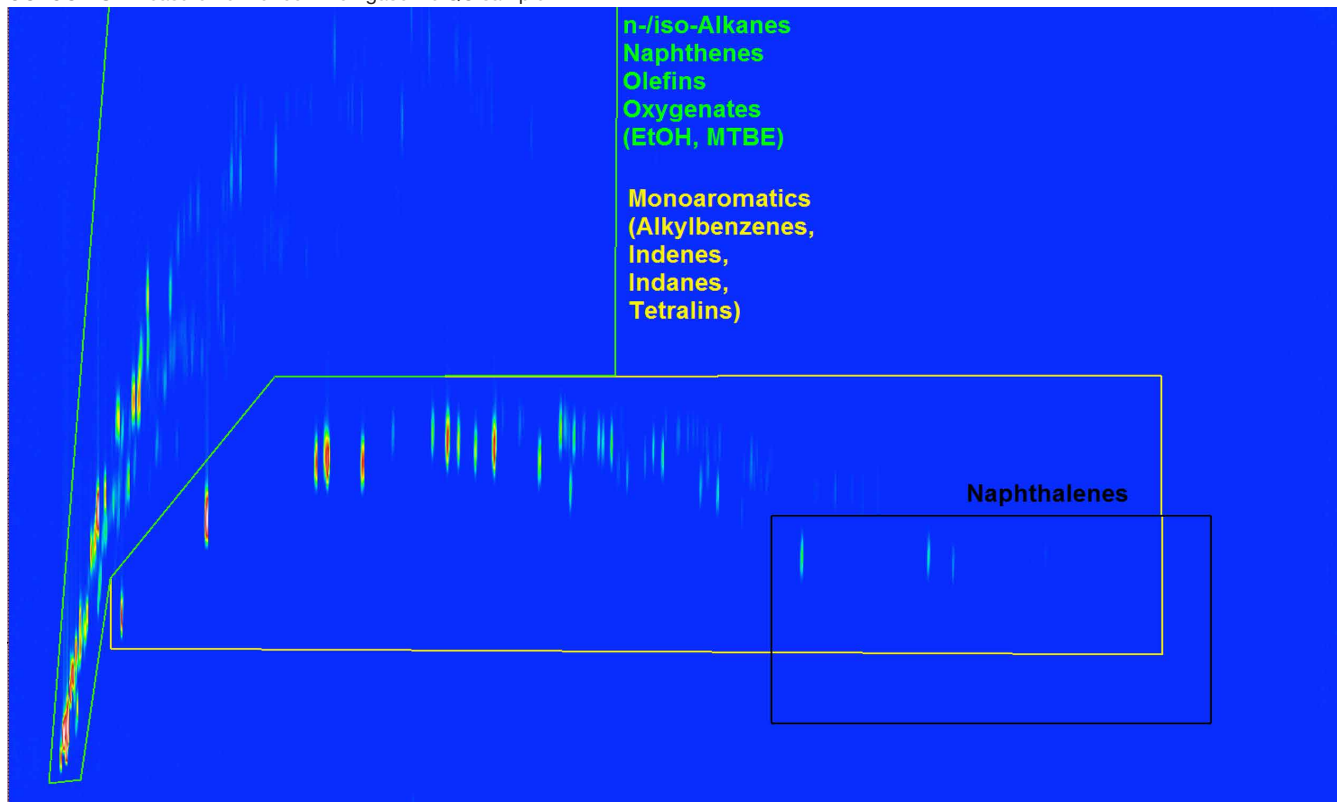
The same setup was used for the analysis of samples in the boiling range of common gasoline. VUV Analytical's VGA-100 had a complete wavelength spectrum from 125–240 nm that was applied for the detection. All raw data were exported from VUVision in CDF format and imported to Chromspace (SepSolve Analytical). Subdivisions were made by wavelength ranges typical for different compound classes, namely n-/iso-alkanes (125–160 nm), naphthenes (140–160 nm), olefins (170–200 nm), aromatics (170–240 nm), and conjugated di-olefins (200–240 nm). Special focus was put on the latter compound class, where it is assumed that these substances cause stability issues and gum formation in gasoline. Currently, no simple analytical technique is available for the determination of the content of di-olefins.

For the analysis of gasoline samples, ASTM D8071 is a commonly used method for PIANO analysis. There are two questions that needs to be addressed: 1) Is it possible to achieve a similar analysis based only on chromatographic resolution by the application of GC×GC-FID and 2) is it possible to determine the content of undesired di-olefins either with conjugated or unconjugated double bonds? For this purpose, three samples were analyzed: 1) a mixture of olefins, cyclo-olefins, and di-olefins (**Figure 2**), 2) a quality control sample, and 3) a low boiling distillation cut of light crude oil.

**Figure 2.**  
2D plots of the same flow modulated GC×GC-VUV measurement at the characteristic wavelength ranges of olefins (170–200 nm) and aromatics/di-olefins (200–240 nm)



**Figure 3.**  
GC×GC-VUV measurement of common gasoline QC sample



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In **Figure 2**, all olefin standard compounds were applied with the same concentration. The intensities slightly varied between different kinds of applied n-olefins, cyclo-olefine, and di-olefins in the 170–200 nm olefin range. Only the conjugated double bonds of 2,5-dimethyl-2,4-hexane show a strong absorption in the 200–240 nm aromatic range.

The two-dimensional separation makes it possible to differentiate olefins from aromatic compounds. **Figure 3** shows that the aromatic compounds are well separated from the other compounds. Unfortunately, the pure chromatographic separation is not sufficient to differentiate between iso-alkanes, naphthenes, and olefins. By a visual evaluation of the QC sample's 2D chromatogram at its full wavelength range (**Figure 3**. common gasoline), it is clear that the first question of whether it is possible to achieve a similar anal-

ysis based only on chromatographic resolution by application of GCxGC-FID cannot be answered yet. The applied reversed-phase column combination does not provide an adequate separation of iso-alkanes, naphthenes, and olefins in the range of carbon numbers C4–C9, so that a compound classification based on FID data alone is insufficient. For future method developments, a normal-phase column combination using columns of higher polarity as 2nd Dimension seems more promising. Nevertheless, the application of a VUV detector can provide an assignment to compound classes without full separation based on the different absorption maxima. Unfortunately, a spectral library is not yet available for processing the two-dimensional data within Chromspace and exporting these data results in separated files of the pre-defined wavelength ranges. However, for the purpose of illustration, it is possible to use these wavelength plots for a rough data evaluation.

Figure 4a.

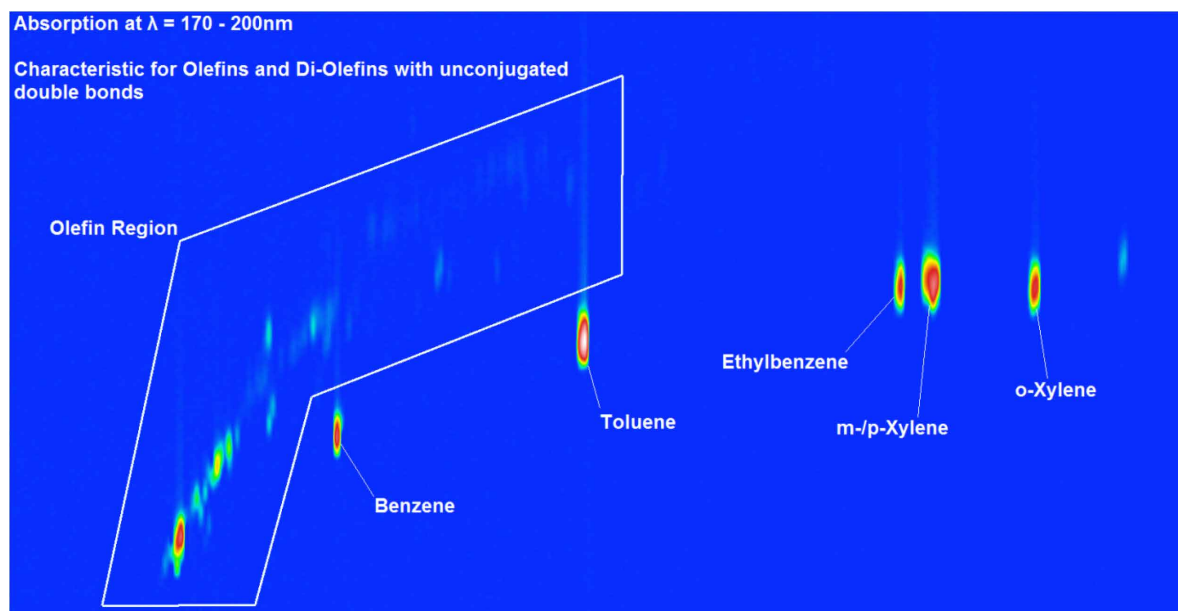
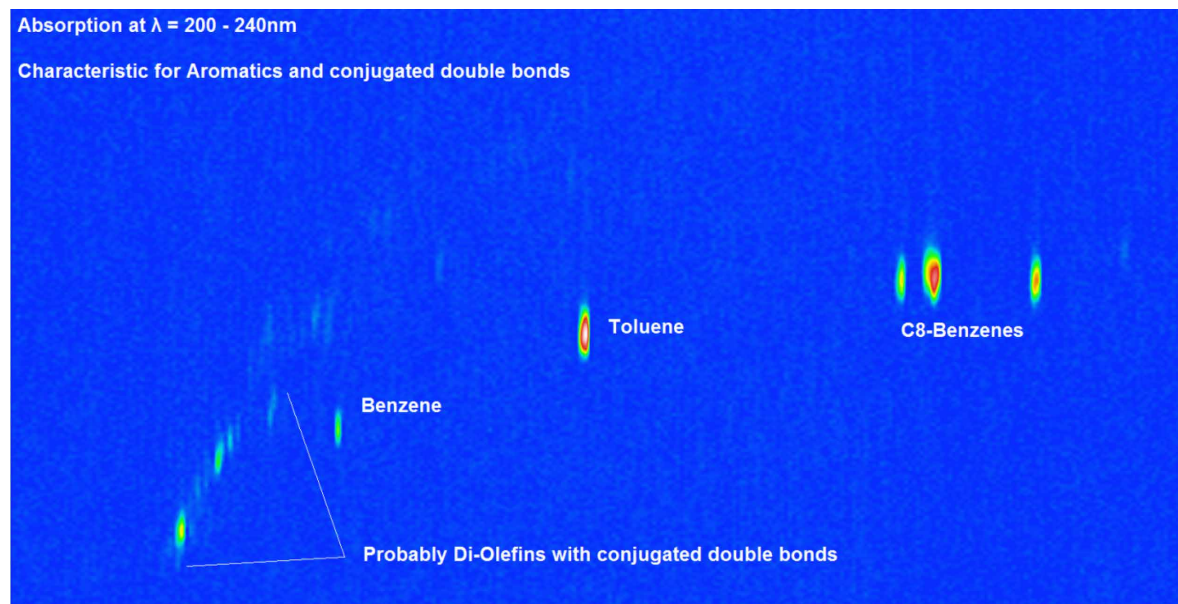


Figure 4b.

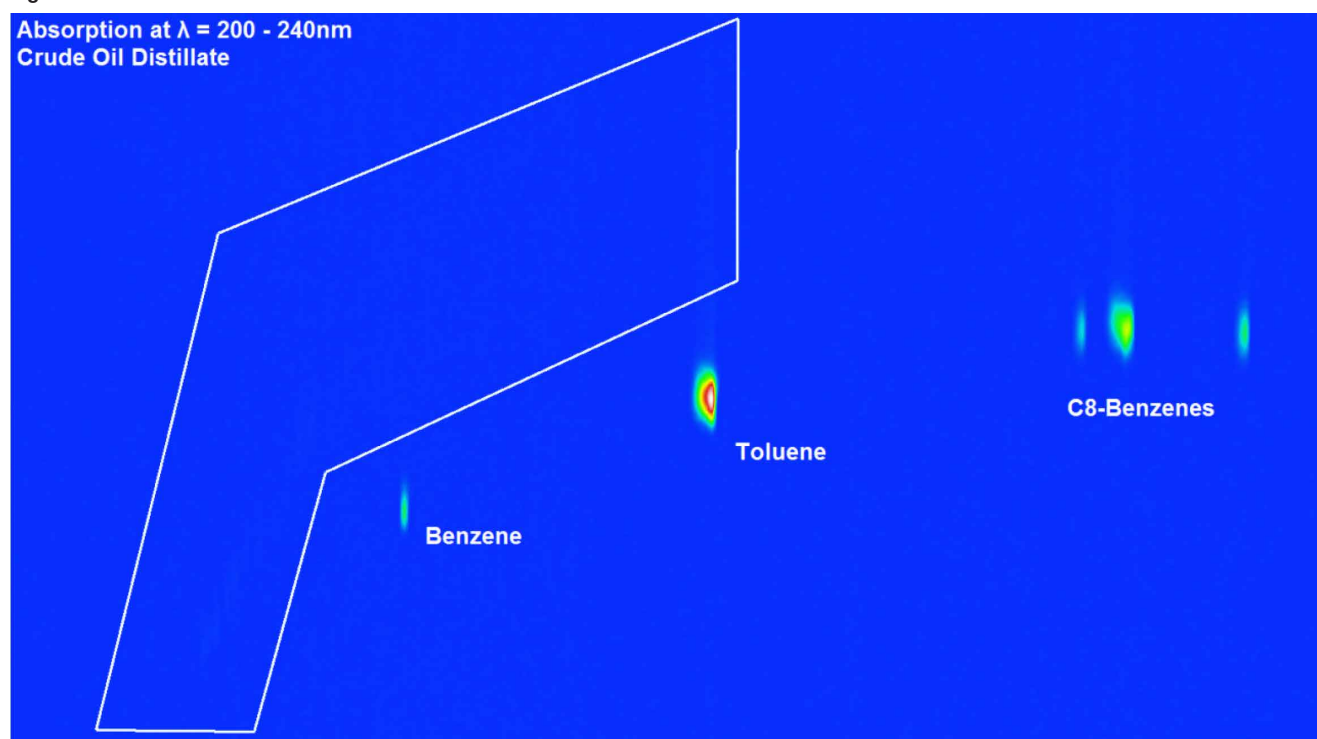




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**Figures 4a** and **4b** show the 2D plots of the same measurement zoomed in at wavelength ranges 170–200 nm for olefin detection (**Figure 4a**) and 200–240 nm for aromatics detection (**Figure 4b**). The di-olefins and olefins with conjugated double bonds show absorption at both wavelength ranges due to their more complex spectra, while olefins and di-olefins with unconjugated double bonds show only weak absorption at 200–240 nm. A plot of the wavelength range, characteristic for aromatic compounds and conjugated double bonds (200–240 nm), of the same measurement shows several peaks with absorption in the chromatographic region of olefins and naphthenes. For comparison, the measurement of a light crude oil distillation fraction is shown in **Figure 4c**. Since crude oils naturally do not contain olefins, it illustrates that the characteristic wavelength range of only aromatic compounds can be found.

**Figure 4c.**



## Conclusion

For the successful separation of a complex matrix in two-dimensional GC, highly efficient column dimensions and complimentary phase selectivity with hyphenated detectors are essential. As individual techniques, Vacuum-Ultraviolet detection and flow modulation GC $\times$ GC are both already versatile instruments, and the hyphenation of both techniques results in a new powerful analytical method. While it is not possible to utilize the full potential with the software's current state, it is evident what opportunities these techniques can provide for the future. This hyphenated technique can help overcome the weaknesses of both instruments specific to the analysis of gasoline. The low concentrated analytes, such as di-olefins, can clearly be identified using VUV detection combined with the increased sensitivity of two-dimensional GC separation. For future investigations and the development of standard methods, this could be the method of choice for a detailed and reliable analysis of olefin and di-olefin content.

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## Ordering Information

### Zebtron™ ZB-1HT Inferno™ GC Columns

ID(mm)	df(μm)	Temp. Limits (°C)	Part No.
<b>5-Meter</b>			
0.53	0.10	-60 to 400/430	<a href="#">7AK-G014-02</a>
<b>10-Meter</b>			
0.32	0.25	-60 to 400/430	<a href="#">7CM-G014-11</a>
<b>15-Meter</b>			
0.25	0.10	-60 to 400/430	<a href="#">7EG-G014-02</a>
0.25	0.25	-60 to 400/430	<a href="#">7EG-G014-11</a>
0.32	0.10	-60 to 400/430	<a href="#">7EM-G014-02</a>
0.32	0.25	-60 to 400/430	<a href="#">7EM-G014-11</a>
0.53	0.15	-60 to 400	<a href="#">7EK-G014-05</a>
<b>20-Meter</b>			
0.18	0.18	-60 to 400/430	<a href="#">7FD-G014-08</a>
<b>30-Meter</b>			
0.25	0.10	-60 to 400/430	<a href="#">7HG-G014-02</a>
0.25	0.25	-60 to 400/430	<a href="#">7HG-G014-11</a>
0.32	0.10	-60 to 400/430	<a href="#">7HM-G014-02</a>
0.32	0.25	-60 to 400/430	<a href="#">7HM-G014-11</a>
0.53	0.15	-60 to 400	<a href="#">7HK-G014-05</a>

Note: If you need a 5 in. cage, simply add a (-B) after the part number, e.g., [7HG-G014-11-B](#). Some exceptions may apply. Agilent 6850 and some SRI and process GC systems use only 5 in. cages.

## Ordering Information

### Zebtron ZB-35HT Inferno GC Columns

ID(mm)	df(μm)	Temp. Limits (°C)	Part No.
<b>15-Meter</b>			
0.25	0.10	40 to 400	<a href="#">7EG-G025-02</a>
0.25	0.25	40 to 400	<a href="#">7EG-G025-11</a>
0.32	0.25	40 to 400	<a href="#">7EM-G025-11</a>
<b>20-Meter</b>			
0.18	0.18	40 to 400	<a href="#">7FD-G025-08</a>
<b>30-Meter</b>			
0.25	0.10	40 to 400	<a href="#">7HG-G025-02</a>
0.25	0.25	40 to 400	<a href="#">7HG-G025-11</a>
0.32	0.25	40 to 400	<a href="#">7HM-G025-11</a>

Note: If you need a 5 in. cage, simply add a (-B) after the part number, e.g., [7HG-G025-11-B](#). Some exceptions may apply. Agilent® 6850 and some SRI and process GC systems use only 5 in. cages.

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