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APPLICATIONS

Group-Type Analysis of Petroleum Products by GC × GC using Zebron® ZB-1HT Inferno™ and ZB-50 Complementary Selectivity GC Columns

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He has a PhD in Analytical Chemistry and over 15 years experience in chromatographic method development and troubleshooting. Ramkumar loves to write poems, read Shakespeare, and attend Shakespeare plays.

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Introduction

Precise characterization of petroleum-derived fuels is important for the oil industry and environmental monitoring alike. However, it is a tedious and difficult task to identify each of the thousands of individual components present in these complex samples. Group-type analysis using comprehensive two dimensional gas chromatography (GC×GC) offers significant advantages over conventional chromatography, with its vastly expanded peak capacity along two dimensions and the added benefit of highly structured groupings of compounds for simple classification of hydrocarbons. To separate complex species by GC×GC, it is essential to have a highly efficient column dimension and a complementary column selectivity. High temperature resistance and flexibility of the GC column tubing are an added advantage for GC×GC. In addition, complementary selectivities like Zebron ZB-1HT Inferno, which is a high temperature capacity non-polar 100% dimethypolysiloxane based stationary phase, and Zebron ZB-50, which is a higher-polar 50% phenyl phase, together offer improved separation for group type analysis. Here we demonstrate the use of reverse fill/flush flow modulation with complementary set of column chemistry for robust, repeatable and affordable GC×GC, combined with simple, yet effective, data processing workflows for group-type analysis.

GC Conditions for Analysis

- Samples: Crude oil (undiluted)

- GC×GC: INSIGHT™ flow modulator (SepSolve Analytical)

- Column set: Zebron ZB-1HT Inferno and ZB-50 (Phenomenex) in both "normal" and "reversed" phase configurations

- Software: Instrument control and data processing was performed using ChromSpace®

GC x GC Normal Phase		GC x GC Reversed Phase	
Column 1:	Zebron ZB-1HT	Column 1:	Zebron ZB-50
Column 2:	Zebron ZB-50	Column 2:	Zebron ZB-1HT

Detector:	FID
Carrier Gas:	Hydrogen
Flow:	40 mL/min; Air flow: 400 mL/min; Temperature: 300 °C

Figure 1.
The valve-based INSIGHT modulator uses reverse fill/flush dynamics, which provides increased peak capacity and improved peak symmetry compared to forward fill/flush devices
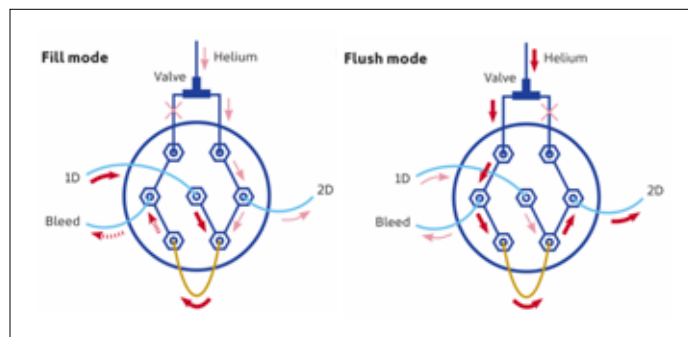
Figure 2.
GC × GC-FID color plots for the separation of the same crude oil using two different column sets

"Normal" phase (ZB-1HT & ZB-50)

Second Dimension Retention Time, Zebron ZB-50
^2t_R (secs)

First Dimension Retention Time, Zebron ZB-1HT
^2t_R (mins)

"Reversed" phase (ZB-50 & ZB-1HT)

Second Dimension Retention Time, Zebron ZB-1HT
^2t_R (secs)

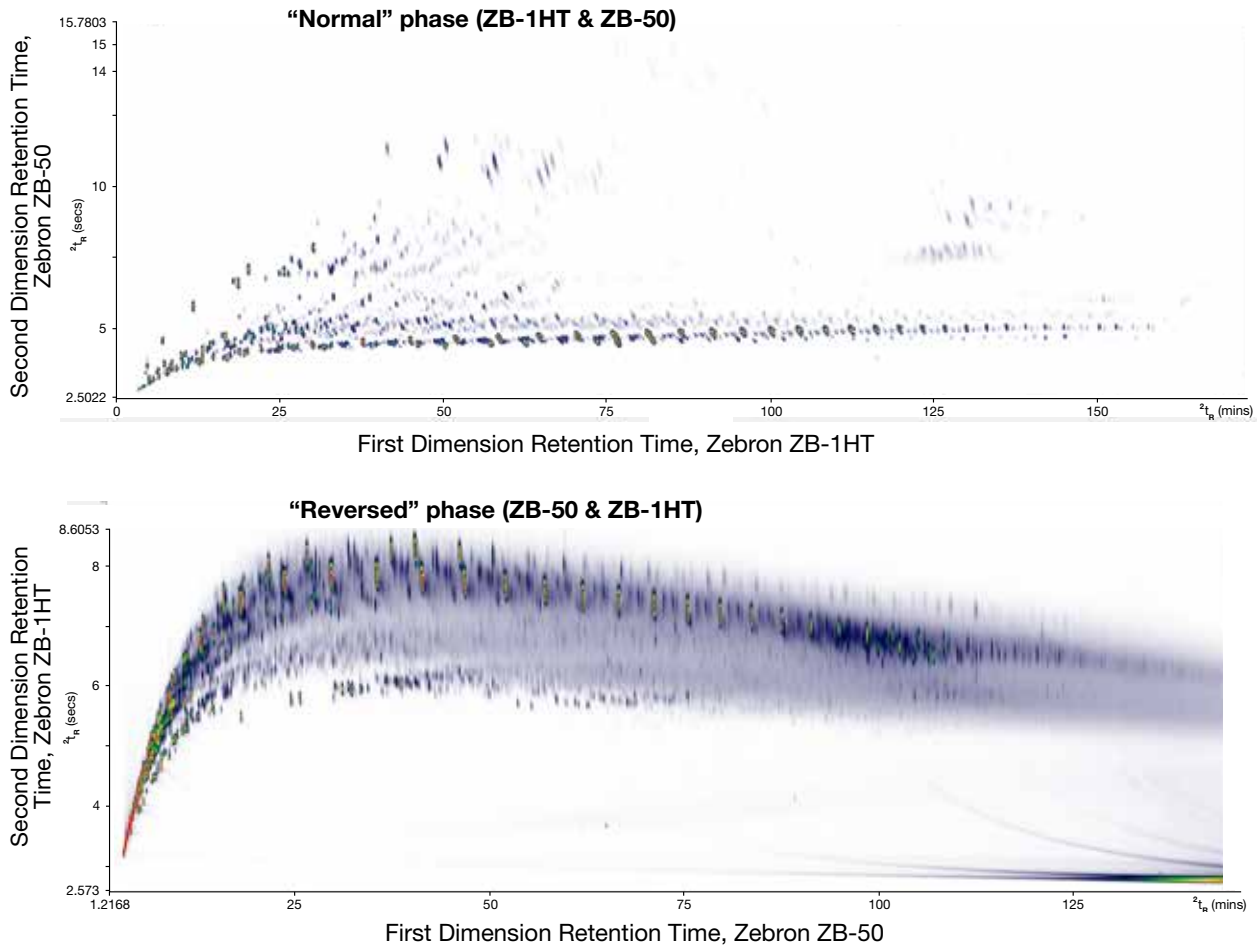First Dimension Retention Time, Zebron ZB-50
^2t_R (mins)

Figure 3.
Stencil regions to classify the alkyl naphthalenes in crude oil, with an overview of composition provided in the area percent table.
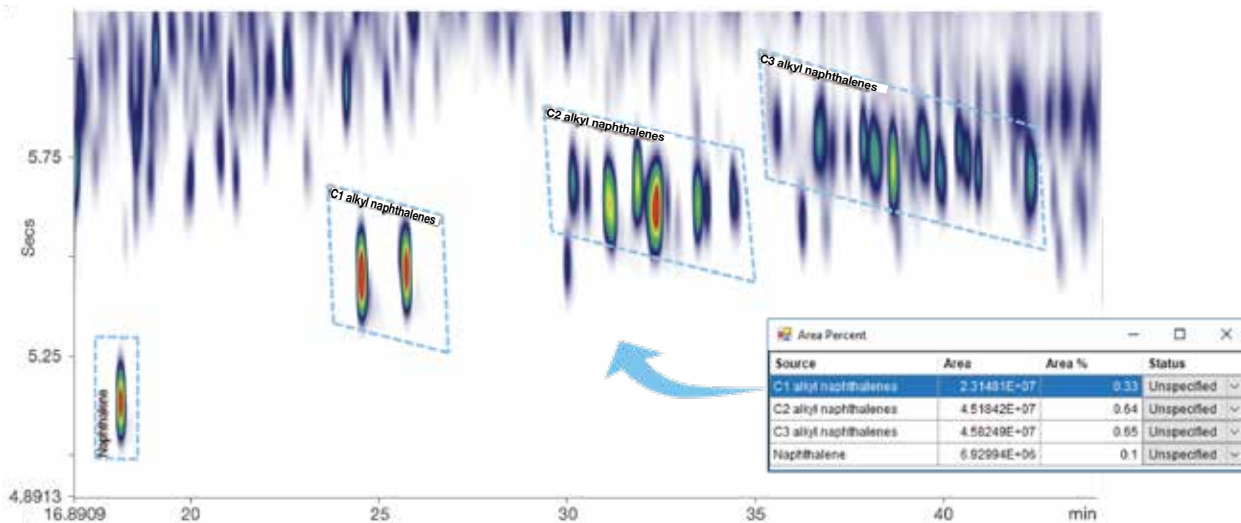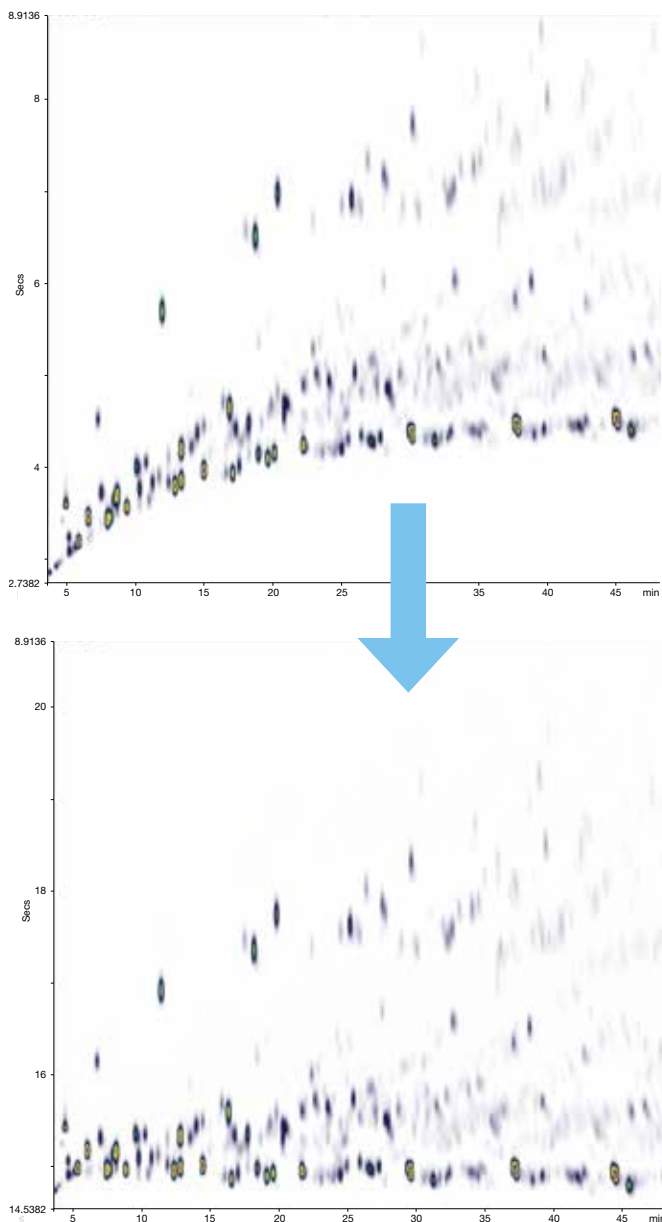

Area Percent			
Source	Area	Area %	Status
C1 alkyl naphthalenes	2.31481E+07	0.33	Unspecified
C2 alkyl naphthalenes	4.51842E+07	0.64	Unspecified
C3 alkyl naphthalenes	4.58249E+07	0.65	Unspecified
Naphthalene	6.92994E+06	0.1	Unspecified

Figure 4.
Alignment tool to allow a homologous series of landmark peaks to be used to "correct" all 2 tR positions

Comprehensive GCxGC analysis requires the use of 2 columns of complementary selectivity to assist in orthogonal separation of the analytes which in this case are Zebron GC columns, ZB-1HT Inferno and ZB-50. The analyte is first retained in one column (x axis) then the INSIGHT™ modulator focuses them into the second column where they are retained and then the ChromSpace software draws the image on a graph. The chromatogram in **Figure 2** shows great distribution of peaks across both axis. This signifies that the two columns selected, ZB-1HT Inferno and ZB-50, provide exceptional selectivity for the orthogonal separation of the complex analyte mixture. The Zebron ZB-1HT Inferno is non-polar and separates by boiling point on one dimension and the Zebron ZB- 50 is a polar 50% phenyl phase that separates with pi-pi interactions in the other dimension.
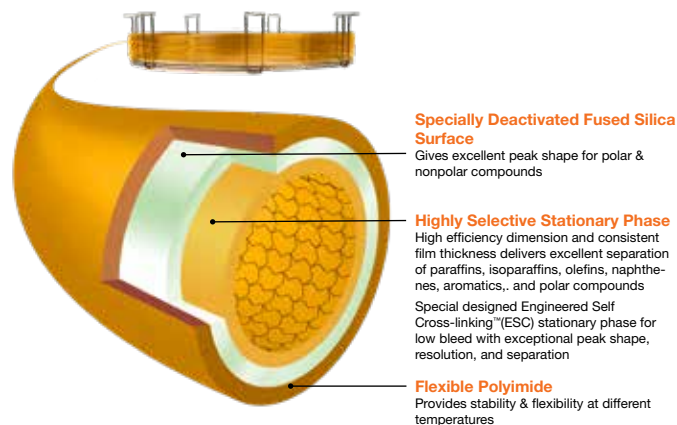
Figure 2 shows the GC×GC–FID separations achieved for the crude oil. Note the wide volatility range from C6-C45+ with excellent peak shape throughout. As illustrated in **Figure 2** they can be run in "normal" phase with the non-polar ZB-1HT Inferno as the first column separating by boiling point and then separating by pi-pi interactions on the second phase with the ZB- 50, or they can be run in "reversed" phase in the opposite arrangement. Reversed phase is popular for the complex oil matrices with many similar boiling point aromatic components since it does a great job in separating them into group-types. ChromSpace incorporates a range of other processing tools which are beneficial for GCxGC analysis of petrochemicals, including an alignment tool to allow a homologous series of landmark peaks to be used to "correct" all second-dimension retention time (2tR) positions. As seen in **Figure 4** this can simplify the application of stencils.

Conclusion
Fast and efficient group-type analysis of complex petrochemicals is possible using flow-modulated GC×GC-FID

- INSIGHT flow modulator offers consumable-free, robust and repeatable GC×GC for a wide range of analytes

- Streamlined data processing workflows in ChromSpace software

- Using two Zebron GC columns, ZB-1HT Inferno and ZB-50, provided complementary orthogonal selectivity to separate individual aliphatics and aromatics from each other

- Reversed phase GCxGC works well to separate the higher boiling point large molecule compounds into group-types

Figure 5.
Zebron GC Column Benefits

Specially Deactivated Fused Silica Surface
Gives excellent peak shape for polar & nonpolar compounds

Highly Selective Stationary Phase
High efficiency dimension and consistent film thickness delivers excellent separation of paraffins, isoparaffins, olefins, naphthenes, aromatics,. and polar compounds

Special designed Engineered Self Cross-linking™(ESC) stationary phase for low bleed with exceptional peak shape, resolution, and separation

Flexible Polyimide
Provides stability & flexibility at different temperatures

Results and Discussion
Precise characterization of petroleum-derived fuels is important, but it can be a tedious and challenging task to identify each of the individual components present in these complex samples. Group-type analysis using GC×GC overcomes these issues by summing the response for hydrocarbons according to their chemical class. Stencils can be saved in ChromSpace software for particular sample types, and then automatically applied to new samples for rapid group-type speciation of the components, as well as reporting of summed peak integrals (**Figure 3**.). The stencil regions are easily drawn around the target class and altered to the desired shape. Stencil regions can even be connected in contiguous meshes to ensure no areas of the chromatograms are overlooked.

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Ordering Information

Zebron ZB-50 GC Columns

ID(mm)	df(µm)	Temp. Limits °C	Part No.
10-Meter			
0.10	0.10	40 to 320/340	7CB-G004-02
0.53	2.00	40 to 320/340	7CK-G004-32
15-Meter			
0.25	0.15	40 to 320/340	7EG-G004-05
0.25	0.25	40 to 320/340	7EG-G004-11
0.32	0.25	40 to 320/340	7EM-G004-11
0.32	0.50	40 to 320/340	7EM-G004-17
0.53	1.00	40 to 320/340	7EK-G004-22
30-Meter			
0.25	0.25	40 to 320/340	7HG-G004-11
0.25	0.50	40 to 320/340	7HG-G004-17
0.32	0.25	40 to 320/340	7HM-G004-11
0.32	0.50	40 to 320/340	7HM-G004-17
0.53	1.00	40 to 320/340	7HK-G004-22
60-Meter			
0.25	0.25	40 to 320/340	7KG-G004-11
0.25	0.50	40 to 320/340	7KG-G004-17

Note: If you need a 5 in. cage, simply add a (-B) after the part number, e.g., 7HG-G004-11-B. Some exceptions may apply. Agilent 6850 and some SRI and process GC systems use only 5 in. cages.

Ordering Information

Zebron ZB-1HT Inferno GC Columns

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

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.

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