

APPLICATIONS

Orthogonal Selectivity for Separation of Light and Heavy Petroleum Hydrocarbons by 2D GC using Zebron™ ZB-1HT Inferno™ and ZB-35HT Inferno GC Columns

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Introduction

Complex sample mixtures, such as petroleum hydrocarbon fractions, require a detailed separation of the individual organic compound types. A traditional GC approach will lead to multiple coelutions, however in this present work a 2D GC approach was utilized to explore the multi-dimensional separation of complex light and heavier hydrocarbons. The complex hydrocarbon mixture can be thoroughly resolved due to the combination of the high peak capacity in 2D GC, along with the orthogonal selectivity of the Zebron GC columns that provide a complementary selectivity in two-dimensions. This complete resolution includes a range of compounds, for example linear alkanes (paraffins), linear alkenes (olefins), cyclic alkanes, aromatics (one - tetralin ring derivatives), and aromatics (one, two, three, four, and five - benzene ring derivatives). The combination of Zebron ZB-1HT Inferno with ZB-35HT Inferno provides a high temperature capability to further elute all the fractions and to provide a targeted selectivity that separates individual aliphatic and aromatic analytes from each other.

GC Conditions for Analysis

Column 1: Zebron ZB-1HT Inferno

Phase: 100 % Dimethylpolysiloxane

Dimensions: 15 meter x 0.10 mm x 0.10 μm

Part No.: ZFB-G014-02-C (15 m length column, cut from a 20 m column)

Column 2: Zebron™ ZB-35HT Inferno

Phase: 35 % Phenyl 65 % Dimethylpolysiloxane

Dimensions: 5 meter x 0.25 mm x 0.18 μm

Part No.: ZFG-G025-08-C (5 m length column, cut from a longer one)

Injection: Split 20:1 @ 250 °C, 1 μL

Recommended Liner: Zebron PLUS Straight Z-Liner™

Part No.: AG2-OA03-05

Instrument: 2D GC - Agilent system 7890A modified with gas phase Microfluidics

Carrier Gas (column 1): Hydrogen @ 1 mL/min (constant flow)

Carrier Gas (column 2): Hydrogen @ 2.4 mL/min (constant flow)

Detector: Flame Ionization (FID) @ 360 °C, 100 Hz acquisition rate

Oven Program for Figure 1

Column 1: 100 °C for 10 min, to 400 °C @ 2.2 °C/min, hold for 20 min

Column 2: 100 °C for 10 min, to 360 °C @ 2.2 °C/min, hold for 20 min

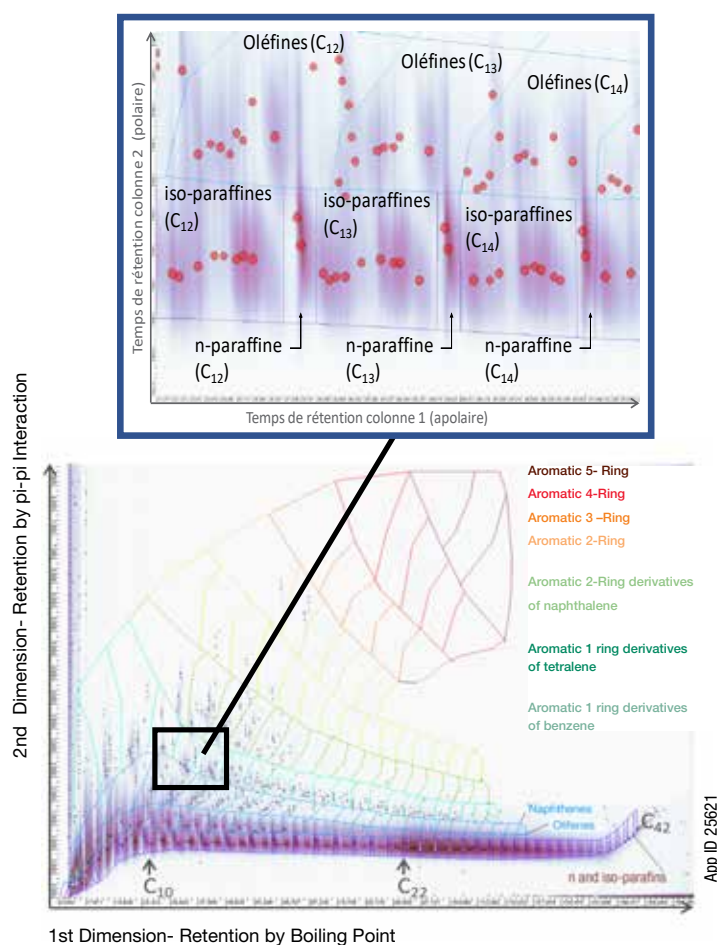
Oven Program for Figure 2.

Column 1: 40 °C for 8 min, to 360 °C @ 8 °C/min, hold for 5 min

Column 2: 50 °C for 8 min, to 360 °C @ 2.25 °C/min, hold for 27 min

Figure 1.

Gas Oil Petroleum Fraction Separation by 2D GC



App ID 25621

Figure 2.
Heavy Petroleum Fraction Separation by 2D GC

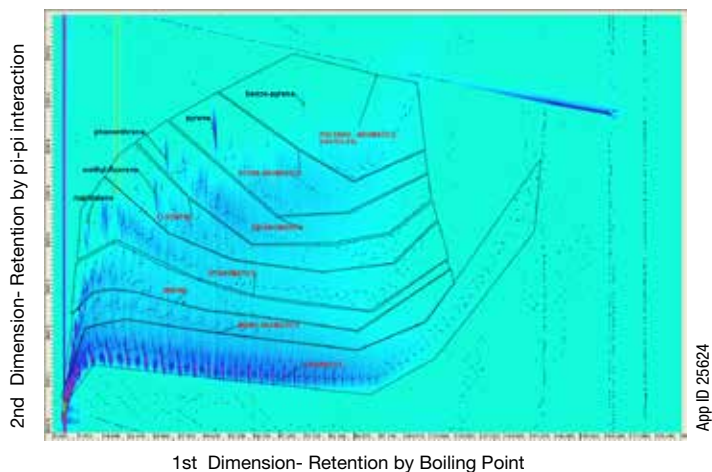
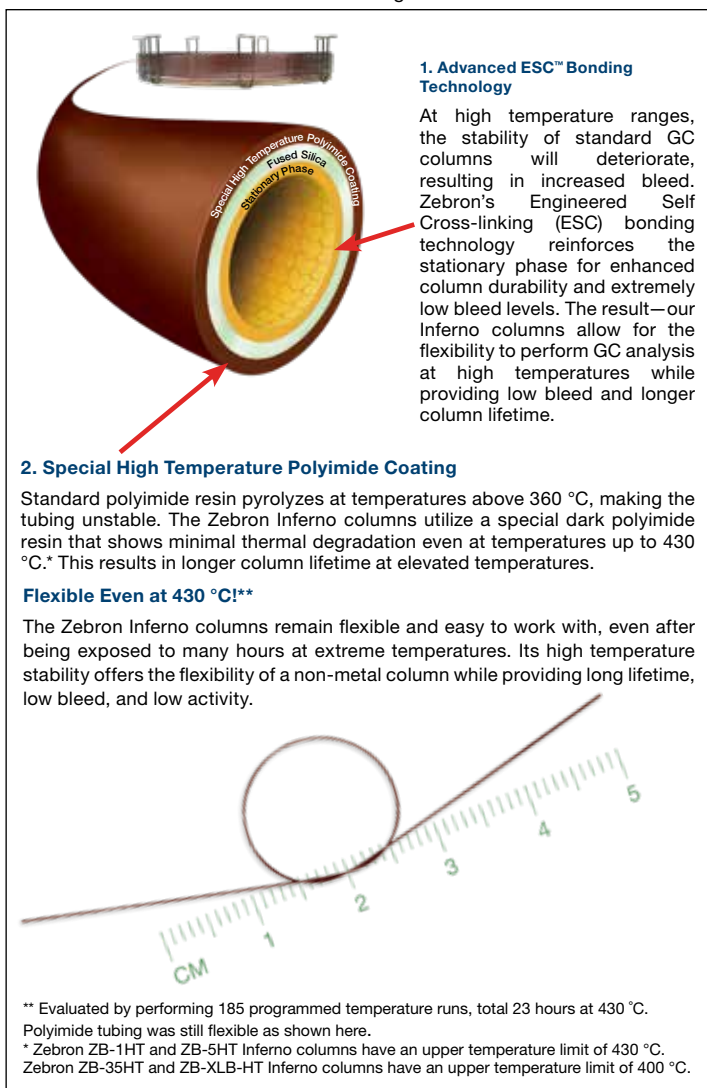


Figure 3.
The Zebtron HT Inferno Technical Advantage



1. Advanced ESC™ Bonding Technology

At high temperature ranges, the stability of standard GC columns will deteriorate, resulting in increased bleed, resulting in increased bleed. Zebtron's Engineered Self Cross-linking (ESC) bonding technology reinforces the stationary phase for enhanced column durability and extremely low bleed levels. The result—our Inferno columns allow for the flexibility to perform GC analysis at high temperatures while providing low bleed and longer column lifetime.

2. Special High Temperature Polyimide Coating

Standard polyimide resin pyrolyzes at temperatures above 360 °C, making the tubing unstable. The Zebtron Inferno columns utilize a special dark polyimide resin that shows minimal thermal degradation even at temperatures up to 430 °C.* This results in longer column lifetime at elevated temperatures.

Flexible Even at 430 °C!***

The Zebtron Inferno columns remain flexible and easy to work with, even after being exposed to many hours at extreme temperatures. Its high temperature stability offers the flexibility of a non-metal column while providing long lifetime, low bleed, and low activity.

** Evaluated by performing 185 programmed temperature runs, total 23 hours at 430 °C. Polyimide tubing was still flexible as shown here.
* Zebtron ZB-1HT and ZB-5HT Inferno columns have an upper temperature limit of 430 °C. Zebtron ZB-35HT and ZB-XLB-HT Inferno columns have an upper temperature limit of 400 °C.

Results and Discussion

A two-dimensional GC analysis of both a gas oil petroleum fraction and a heavy petroleum fraction were performed using a Zebtron™ ZB-1HT Inferno™ coupled to a Zebtron ZB-35HT Inferno on an Agilent 7890A GC system that was modified with a gas phase microfluidics system. The Zebtron ZB-35HT Inferno column with its unique combination of a high temperature capability and a polar selectivity provides a detailed orthogonal separation along with the ZB-1HT that provides a true boiling-point based separation. For this study hydrogen was used as the carrier gas for a faster and more efficient analysis. The FID detector provides a great sensitivity and wider dynamic range for hydrocarbons. A high data acquisition rate of 100 points per second was utilized to capture all the narrow peaks eluting out from the second dimension GC column.

The Zebtron HT Inferno columns have a special high temperature resistant polyimide coating. In addition, this stationary phase has an Engineered Cross-linking™ (ESC™) bonding technology which provides extreme low bleed even at high temperature (**Figure 3**). **Figure 1** shows the carbon range for the gas oil fraction up to C42 and all the compound classes were successfully separated and eluted using this 2D GC Zebtron Inferno HT column set. The use of the Zebtron ZB-1HT Inferno on the first dimension and the Zebtron ZB-35HT Inferno on the second dimension provides a traditional, yet much improved approach in 2D GC. This selectivity combination enables an orthogonal separation of the analytes along both the axes to provide an improved targeted separation. The Zebtron ZB-1HT Inferno separates by boiling point on the first dimension and the Zebtron ZB-35HT Inferno then separates orthogonally with pi-pi interactions on the second dimension.

There is a clear separation of the following classes of compounds along both dimensions:

1. Linear alkanes (n- and iso-paraffins)
2. Linear alkenes (olefins)
3. Cyclic alkanes
4. Aromatics (one-ring, tetralin derivatives)
5. Aromatics (one-ring, benzene derivatives)
6. Aromatics (2-rings, naphthalene derivatives)
7. Aromatics (2-rings, di-benzene derivatives)
8. Aromatics (3-rings)
9. Aromatics (4-rings)
10. Aromatics (5-rings)

In similar fashion, detailed separation of heavier fractions was done by using a 2D GC approach as shown in **Figure 2**. The detailed molecular mapping in **Figures 1** and **2** are crucial to optimize processes in petroleum refining.

Conclusion

2D GC is a versatile technique that resolves complex mixtures. The column combination of the Zebtron ZB-1HT Inferno and the unique Zebtron ZB-35 HT Inferno not only provided a high temperature capability to elute all the fractions, but also provided complementary orthogonal selectivity to separate individual aliphatic and aromatics from each other.

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Ordering Information

Zebtron 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.

Ordering Information

Zebtron ZB-35HT Inferno GC Columns

ID(mm)	df(μm)	Temp. Limits °C	Part No.
15-Meter			
0.25	0.10	40 to 400	7EG-G025-02
0.25	0.25	40 to 400	7EG-G025-11
0.32	0.25	40 to 400	7EM-G025-11
20-Meter			
0.18	0.18	40 to 400	7FD-G025-08
30-Meter			
0.25	0.10	40 to 400	7HG-G025-02
0.25	0.25	40 to 400	7HG-G025-11
0.32	0.25	40 to 400	7HM-G025-11

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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