APPLICATIONS

Orthogonal Selectivity for Separation of Oxygenated Compounds and Hydrocarbons in Alternative Fuels by Two-Dimensional Gas Chromatography using Zebron™ ZB-1701 and ZB-1 GC Columns

Badaoui Omais[1], Vincent Souchon[2], Ramkumar Dhandapani[1], and Tim Nelson[1]
[1] Phenomenex, Inc., 411 Madrid Ave., Torrance, CA 90501, USA
[2] IFPEN, Rond-Point de l'échangeur de Solaize - BP3, 69360 Solaize, France

Introduction

The need to diversify energy sources in the transportation industry has sparked great interest in direct coal liquefaction products. When they are first processed, the properties and composition of these alternative fuel source liquids are far from a traditional petroleum fuel final specification, and therefore, must be upgraded with the addition of gas oil cuts. In fact, the alternative fuel composition consists mainly of aromatic hydrocarbons, cyclic alkanes (naphthenes), heteroatomic compounds, and especially oxygenated species.[1-4] To plan for the refining of the alternative fuel source liquids with their additional petroleum cuts, it is crucial to first analyze their chemical and physical properties. The requirements to improve the fuel molecular characterization concern the hydrocarbons and the many oxygenated compound families, which before the hydrodeoxygenation (HDO) step are present in relatively high concentrations.

Multidimensional gas chromatography is the perfect analytical technique for this challenge. This powerful chromatography tool allows for the analysis of complex samples and offers a high peak capacity by combining two different stationary phases with their synergistically combined individual separation mechanisms.[5,6] The value from these coupled systems is the detailed analysis of extremely complex samples and speciation of hundreds of components. It is important to have the right combination of stationary phases to provide the required orthogonal separation of the analytes. This study focuses on the speciation of oxygenated compounds in complex hydrocarbon matrices using complementary gas chromatography selectivities.

GC Conditions for Analysis

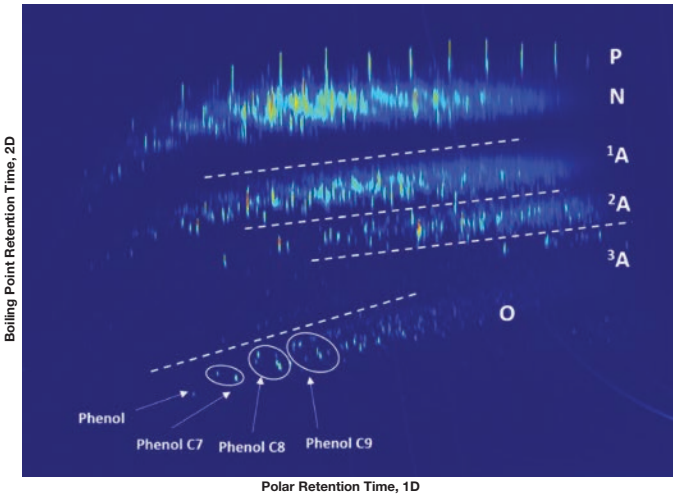
Column 1:	Zebron ZB-1701
Phase:	14 % Cyanopropylphenyl 86 % Dimethylpolysiloxane
Dimensions:	30 meter x 0.25 mm x 0.25 µm
Part No.:	7HG-G006-11
Column 2:	Zebron ZB-1
Phase:	100 % Dimethylpolysiloxane
Dimensions:	1.5 meter x 0.10 mm x 0.1 µm
Part No.:	7TB-G031-02-C (2 meter trimmed to 1.5 meter)
Injection:	Split 100:1 @ 250 °C, 0.5 µL
Recommended Liner:	Zebron PLUS Straight Z-Liner™
Liner Part No.:	AG2-0A03-05
Instrument:	Leco Pegasus 3, Agilent 6890N
Carrier Gas:	Helium @ 1.5 mL/min (constant flow)
Oven Program:	50 °C for 0.3 min, to 300 °C at 2 °C/min
Modulation:	Dual Jet Cryogenic, Liquid Nitrogen
Modulation Period:	7 seconds
Detector:	Flame Ionization (FID) @ 370 °C
Hydrogen:	30 mL/min
Air Flow:	400 mL/min
Sample:	Coal-derived Oil

Results and Discussion

Multidimensional gas chromatography is a powerful separation tool when the correct combination of two different phases together provide thorough orthogonal partition of the components. The configuration depicted in this study is derived from a previous publication.[7] It enables the oxygenates to fully separate from hydrocarbons. In addition, hydrocarbon groups also have great separation including Paraffins, Naphthenes, Mono-aromatics, Di-aromatics, and Tri-aromatics.

Zebron ZB-1701 is a mid-polar selectivity that is composed of 14 % cyanopropylphenyl and 86 % dimethylpolysiloxane, which provides good retention of polar oxygenated compounds. It is then followed with a 100 % dimethylpolysiloxane Zebron ZB-1, which provides complimentary true boiling point selectivity. In GCxGC terminology this is referred to as reversed phase.

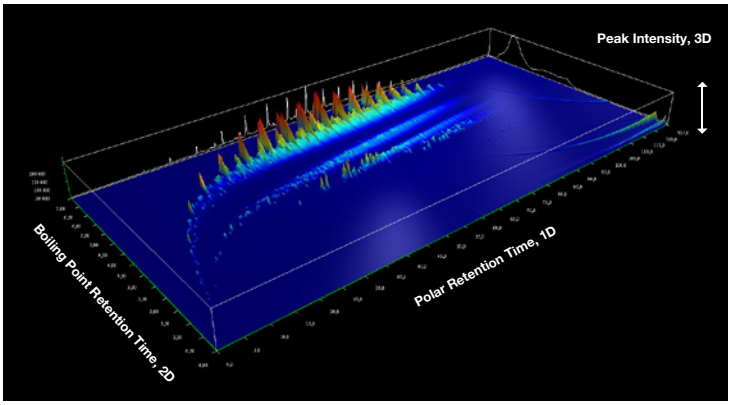
Figure 1.
Two-dimension contour plot of a coal-derived liquid using GC×GC reverse configuration (Zebron ZB-1701 in first dimension and ZB-1 in second dimension)



The identified families are listed as: **P** for Paraffins, **N** for Naphthenes, **1A** for Mono-aromatics, **2A** for Di-Aromatics, **3A** for Tri-aromatics, and **O** for Oxygenated compounds.

In the first dimension, the stationary phase has a high selectivity towards oxygenated compounds, and notably with the phenols. In the secondary dimension, the polar oxygenates are eluted early to completely separate by boiling point from the rest of the analytes in the chromatogram (**Figures 1** and **2**). The two-dimensional chromatogram in **Figure 1** shows that the compounds are separated according to both their polarity and boiling point. As a result, successive elution is seen in the bottom of the chromatogram for phenol, cresols, C2-phenols, C3-phenols, etc. The successful combination in this column set eliminates the need for a sample preparation process to isolate the phenols from hydrocarbons.

Figure 2.
Three-dimension plot of a coal-derived middle distillate using GC×GC (Zebron™ ZB-1701 x ZB-1)



Conclusion

The analysis results obtained using Zebron ZB-1701 and ZB-1 GC columns together enables the GC×GC-FID system to unravel molecular structures of oxygenated compounds in a coal-derived middle distillate. It also shows that oxygenated structures mainly consist of phenolic compounds, and this characterization is crucial to help convert coal-derived oils into alternative fuels.

This study showed that compared to conventional configurations, a reversed configuration involving a highly polar column in the first dimension and a non-polar one in the second enables the separation of oxygenates and hydrocarbons in one single run. In fact, the 2D contour plots obtained under these conditions exhibit good resolution and high space occupation. Nevertheless, in the future there is still an opportunity to separate nitrogenates from oxygenates for improved quantification. Further study is needed to accomplish this, by utilizing either sample preparation or online fractionation in a multi-technical analytical approach with multidimensional gas chromatography.

Acknowledgement: This study was run at IFPEN, and we thank them for their collaboration on this project. Phenomenex is not affiliated with IFPEN.

References

1. B. Omais, M. Courtiade, N. Charon, D. Thiebaut, and A. Quignard, 2010, Characterization of oxygenated species in coal liquefaction products: an overview: Energy & Fuels, v. 24, p. 5807-5816.
2. B. Omais, M. Courtiade, N. Charon, D. Thiebaut, and A. Quignard, 2011, Investigating comprehensive two-dimensional gas chromatography conditions to optimize the separation of oxygenated compounds in a direct coal liquefaction middle distillate: Journal of Chromatography A, v. 218, p. 3233-3240.
3. B. Omais, M. Courtiade, N. Charon, J. Ponthus, and D. Thiebaut, 2011, Consider-ations on Orthogonality Duality in Comprehensive Two-Dimensional Gas Chromatography: Analytical Chemistry, v.19, p. 7550-7554.
4. B. Omais, M. Courtiade, N. Charon, D. Thiebaut, C. Roullet, J. Ponthus, and A. Quignard, 2011, Using one and multi-dimensional gas chromatography systems to unravel oxygenated compounds in coal liquefaction naphthas: Journal of Chromatography A. , v. 1226, p. 61-70
5. B. Omais, T. Dutriez, M. Courtiade, N. Charon, H. Dulot, J. Ponthus, and D. Thiebaut, 2011, SFC-GC×GC to analyse matrices from petroleum and coal: LCGC Europe, v. 24, no. 7, p. 352-365.
6. Bertoncini F, Vendeuvre C, Thiebaut D. Interest and applications of multidimensional gas chromatography for trace analysis in the petroleum industry. Oil & Gas Science and Technology-Revue de l'Institut Francais du Petrole 2005; 60:6-937
7. B. Joffres, M.T. Nguyen, D. Laurenti, C. Lorentz, V. Souchon, N. Charon, A. Daudin, A. Quignard, and C. Geantet, 2016, Lignin hydroconversion on MoS2-based supported catalyst: Comprehensive analysis of products and reaction scheme: Applied Catalysis B: Environmental, v.184, p 153–162

Ordering Information

Zebron ZB-1 GC Columns			
ID(mm)	**df(µm)**	**Temp. Limits °C**	**Part No.**
2-Meter			
0.01	0.10	-60 to 360/370	7TB-G031-02-C
10-Meter			
0.53	2.65	-60 to 340/360	7CK-G001-35
15-Meter			
0.25	0.10	-60 to 360/370	7EG-G001-02
0.25	0.25	-60 to 360/370	7EG-G001-11
0.25	1.00	-60 to 340/360	7EG-G001-22
0.32	0.25	-60 to 360/370	7EM-G001-11
0.32	1.00	-60 to 340/360	7EM-G001-22
0.53	0.15	-60 to 360/370	7EK-G001-05
0.53	0.50	-60 to 360/370	7EK-G001-17
0.53	1.50	-60 to 340/360	7EK-G001-28
30-Meter			
0.25	0.10	-60 to 360/370	7HG-G001-02
0.25	0.25	-60 to 360/370	7HG-G001-11
0.25	0.50	-60 to 360/370	7HG-G001-17
0.25	1.00	-60 to 340/360	7HG-G001-22
0.32	0.25	-60 to 360/370	7HM-G001-11
0.32	0.50	-60 to 360/370	7HM-G001-17
0.32	1.00	-60 to 340/360	7HM-G001-22
0.32	3.00	-60 to 340/360	7HM-G001-36
0.32	5.00	-60 to 340/360	7HM-G001-39
0.53	0.50	-60 to 360/370	7HK-G001-17
0.53	1.50	-60 to 340/360	7HK-G001-28
0.53	3.00	-60 to 340/360	7HK-G001-36
0.53	5.00	-60 to 340/360	7HK-G001-39
50-Meter			
0.25	0.50	-60 to 360/370	7JG-G001-17
60-Meter			
0.25	0.25	-60 to 360/370	7KG-G001-11
0.25	1.00	-60 to 340/360	7KG-G001-22
0.32	0.25	-60 to 360/370	7KM-G001-11
0.32	1.00	-60 to 340/360	7KM-G001-22
0.32	3.00	-60 to 340/360	7KM-G001-36
0.53	1.50	-60 to 340/360	7KK-G001-28
100-Meter			
0.25	0.50	-60 to 360/370	7MG-G001-17

Note: If you need a 5 in. cage, simply add a (-B) after the part number, e.g., 7HG-G001-11-B. Some exceptions may apply. Agilent 6850 and some SRI and process GC systems use only 5 in. cages.

Zebron ZB-1701 GC Columns			
ID(mm)	**df(µm)**	**Temp. Limits °C**	**Part No.**
15-Meter			
0.25	0.25	-20 to 280/300	7EG-G006-11
0.32	0.25	-20 to 280/300	7EM-G006-11
30-Meter			
0.25	0.25	-20 to 280/300	7HG-G006-11
0.25	1.00	-20 to 260/280	7HG-G006-22
0.32	0.25	-20 to 280/300	7HM-G006-11
0.32	1.00	-20 to 260/280	7HM-G006-22
0.53	1.00	-20 to 260/280	7HK-G006-22
60-Meter			
0.25	0.25	-20 to 280/300	7KG-G006-11
0.32	0.25	-20 to 280/300	7KM-G006-11

Note: If you need a 5 in. cage, simply add a (-B) after the part number, e.g., 7HG-G006-11-B. Some exceptions may apply. Agilent 6850 and some SRI and process GC systems use only 5 in. cages.

Australia
t: +61 (0)2-9428-6444
auinfo@phenomenex.com

Austria
t: +43 (0)1-319-1301
anfrage@phenomenex.com

Belgium
t: +32 (0)2 503 4015 (French)
t: +32 (0)2 511 8666 (Dutch)
beinfo@phenomenex.com

Canada
t: +1 (800) 543-3681
info@phenomenex.com

China
t: +86 400-606-8099
cninfo@phenomenex.com

Denmark
t: +45 4824 8048
nordicinfo@phenomenex.com

Finland
t: +358 (0)9 4789 0063
nordicinfo@phenomenex.com

France
t: +33 (0)1 30 09 21 10
franceinfo@phenomenex.com

Germany
t: +49 (0)6021-58830-0
anfrage@phenomenex.com

India
t: +91 (0)40-3012 2400
indiainfo@phenomenex.com

Ireland
t: +353 (0)1 247 5405
eireinfo@phenomenex.com

Italy
t: +39 051 6327511
italiainfo@phenomenex.com

Luxembourg
t: +31 (0)30-2418700
nlinfo@phenomenex.com

Mexico
t: 01-800-844-5226
tecnicomx@phenomenex.com

The Netherlands
t: +31 (0)30-2418700
nlinfo@phenomenex.com

New Zealand
t: +64 (0)9-4780951
nzinfo@phenomenex.com

Norway
t: +47 810 02 005
nordicinfo@phenomenex.com

Portugal
t: +351 221 450 488
ptinfo@phenomenex.com

Singapore
t: +65 800-852-3944
sginfo@phenomenex.com

Spain
t: +34 91-413-8613
espinfo@phenomenex.com

Sweden
t: +46 (0)8 611 6950
nordicinfo@phenomenex.com

Switzerland
t: +41 (0)61 692 20 20
swissinfo@phenomenex.com

United Kingdom
t: +44 (0)1625-501367
ukinfo@phenomenex.com

USA
t: +1 (310) 212-0555
info@phenomenex.com

All other countries
Corporate Office USA
t: +1 (310) 212-0555
info@phenomenex.com

www.phenomenex.com

Phenomenex products are available worldwide. For the distributor in your country, contact Phenomenex USA, International Department at international@phenomenex.com

TN70250819_W

Having trouble reproducing this method? We would love to help!
*Visit **www.phenomenex.com/LiveChat** to get in touch with one of our Technical Specialists*