APPLICATIONS

Detailed Hydrocarbon Analysis of Refinery Naphtha Streams for Determination of Compound Group-types

Dr. Ramkumar Dhandapani and Tim Nelson
Phenomenex, Inc., 411 Madrid Ave., Torrance, CA 90501 USA

Tim Nelson
Global Marketing Manager
Fuels and Chemicals

Tim is an avid outdoorsman who loves to hike and ski. His most recent exploration is tall ship sailing in our local Pacific Ocean. Tim loves history and everything about the stars and space.

Introduction

Petroleum fuels are required to meet federal and state environmental regulations to mitigate their impact on the environment. In the United States, the refineries use test methods that are approved by the EPA, and in other countries there are similar national regulations to ensure that the required performance criteria are met. There are different regulated test methods to measure the physical characteristics of the fuel as well as its specific chemical components. Depending on global location, spark ignition fuel is called gasoline, petrol, or benzin, and it is distilled from crude oil as part of the naphtha stream (C1-C12). Straight-run product is blended with other processed streams which makes it critical to have a detailed understanding of the hydrocarbon components for a consistent product.

There are hundreds of chemical components in spark ignition fuels, and so to make the testing and regulation manageable they are measured in categories by chemical group-type. These category group-types are based on molecular similarities that give them common performance behaviors. These tests are referred to as Detailed Hydrocarbon Analysis (DHA) which includes several test methods that measure different hydrocarbon subset or group-type categories. DHA identifies the important individual components in spark ignition fuels and other refinery light hydrocarbon process streams. Common refinery naphthas are virgin, alkylate, reformate, FCC and Coker, and finished spark ignition fuels. This technique is sometimes also referred to as PONA, PIONA, or PIANO analysis since specific test methods are measuring the group-type paraffins, isoparaffins, olefins, naphthenes, aromatics, and oxygenates. The DHA analysis helps optimize the production processes in addition to meeting the regulatory requirements.

Many of the DHA test methods utilize gas chromatography to separate and measure the group-type components. This technical work describes the use of a Zebron™ ZB-DHA-PONA GC column which contains a 100 % Dimethylpolysiloxane phase that is specially designed to provide excellent peak symmetry and resolution of hydrocarbon components for a true boiling point separation of complex mixtures in spark ignition fuels.

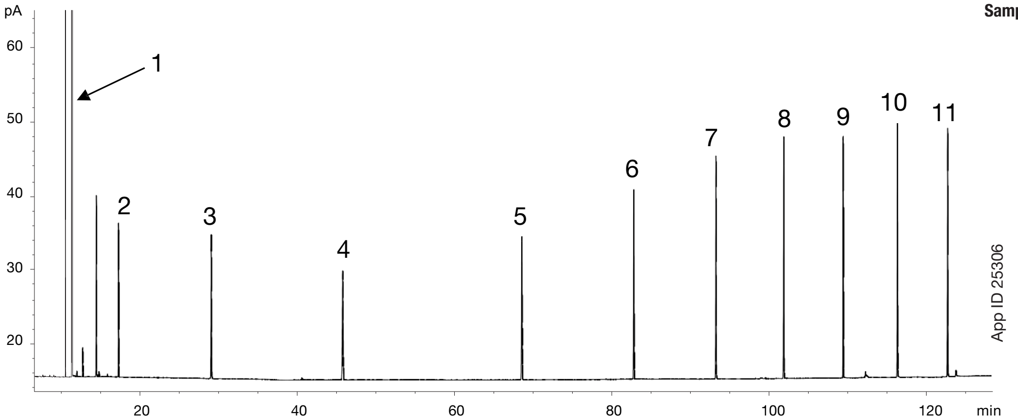
GC Conditions for All Analyses

Column: Zebron™ ZB-DHA-PONA
Phase: 100 % Dimethylpolysiloxane
Dimensions: 100 meter x 0.25 mm x 0.50 µm
Part No.: 7MG-G042-17
Injection: Split 40:1 @ 300 °C, 0.2 µL
Recommended Liner: Zebron*PLUS* Straight Z-Liner™
Carrier Gas: Helium @ 1.55 mL/min (Constant Flow)
Oven Program: 35 °C for 14 min, to 60 °C at 1.1 °C/min. for 19 min, to 280 °C at 2 °C/min. for 5 min
Detection: Flame Ionization (FID) @ 320 °C

Table 1. Zebron ZB-DHA-PONA Column Dimensional Options for Detailed Hydrocarbon Analysis (ASTM and alternative methods)

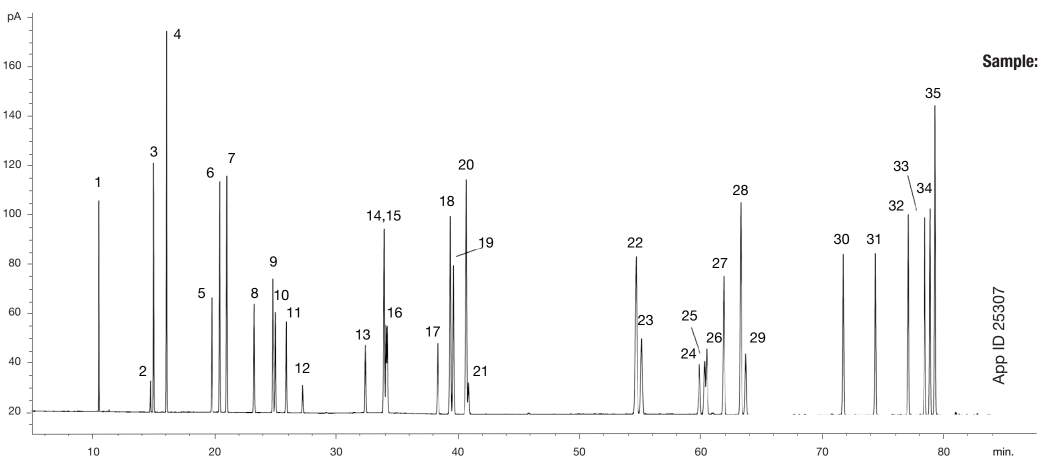
Part Number	Dimensions	Stationary Phase	Benefits
7JE-G042-17	50 meter x 0.2 mm x 0.50 µm	100 % Dimethylpolysiloxane	50 meter column provides shorter run time while the 0.2 µm tighter ID provides higher efficiency.
7MG-G042-17	100 meter x 0.25 mm x 0.50 µm	100 % Dimethylpolysiloxane	100 meter length provides high plate count/efficiency.
7QG-G042-22	150 meter x 0.25 mm x 1.0 µm	100 % Dimethylpolysiloxane	150 meter length with a 1.0 µm thicker film provides better separation of lower boiling fractions and maintains high efficiency from the column length.
7AG-G042-22	5 meter x 0.25 mm x 1.0 µm (tuning column)	5 % Phenyl, 95 % Polydimethylsiloxane	Optional tuning column provides phenyl selectivity in addition to true boiling point separation. This helps in resolving certain aromatics from alkanes and alkenes.

Figure 1.
Separation of Paraffins on a Zebron™ ZB-DHA-PONA GC Column



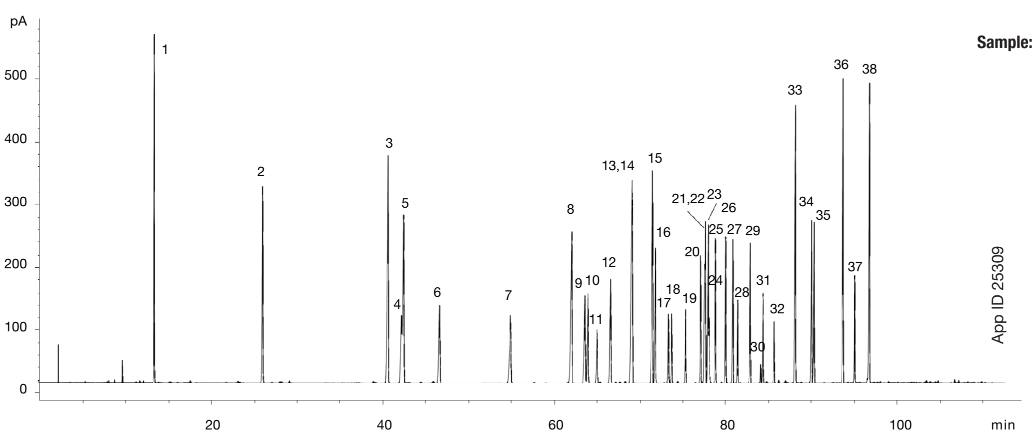
Sample:
1. Pentane
2. Hexane
3. Heptane
4. Octane
5. Nonane
6. Decane
7. Undecane
8. Dodecane
9. Tridecane
10. Tetradecane
11. Pentadecane

Figure 2.
Separation of Isoparaffins on a Zebron ZB-DHA-PONA GC Column



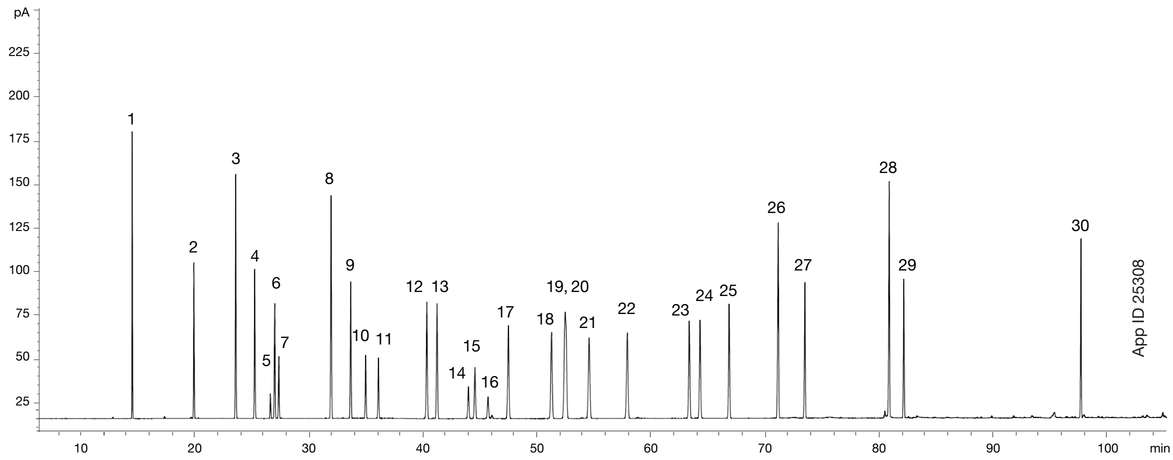
Sample:
1. Isopentane
2. 2,3-Dimethylbutane
3. 2-Methylpentane
4. 3-Methylpentane
5. 2,2-Dimethylpentane
6. 2,4-Dimethylpentane
7. 2,2,3-Trimethylbutane
8. 3,3-Dimethylpentane
9. 2-Methylhexane
10. 2,3-Dimethylpentane
11. 3-Methylhexane
12. 3-Ethylpentane
13. 2,2-Dimethylhexane
14. 2,5-Dimethylhexane
15. 2,2,3-Trimethylpentane
16. 2,4-Dimethylhexane
17. 2,3-Dimethylhexane
18. 2-Methylheptane
19. 4-Methylheptane
20. 3-Methylheptane
21. 3-Ethylhexane
22. 2,5-Dimethylheptane
23. 3,3-Dimethylheptane
24. 2,3-Dimethylheptane
25. 3,5-Dimethylheptane
26. 3,4-Dimethylheptane
27. 2-Methyloctane
28. 3,3-Diethylpentane
29. 3-Methyloctane
30. 2,2-Dimethyloctane
31. 3,3-Dimethyloctane
32. 2,3-Dimethyloctane
33. 3-Ethyloctane
34. 2-Methylnonane
35. 3-Methylnonane

Figure 3.
Separation of Aromatic Compounds on a Zebron ZB-DHA-PONA GC Column



Sample:
1. Benzene
2. Toluene
3. EthylBenzene
4. m-Xylene
5. p-Xylene
6. o-Xylene
7. Isopropylbenzene
8. n-Propylbenzene
9. 1-Methyl-3-ethylbenzene
10. 1-Methyl-4-ethylbenzene
11. 1,3,5-Trimethylbenzene
12. 1-Methyl-2-ethylbenzene
13. 1,2,4-Trimethylbenzene
14. tert-Butylbenzene
15. Isobutylbenzene
16. sec-Butylbenzene
17. 1-Methyl-3-isopropylbenzene
18. 1-Methyl-4-isopropylbenzene
19. 1-Methyl-2-isopropylbenzene
20. 1-Methyl-3-n-propylbenzene
21. 1-Methyl-4-n-propylbenzene
22. n-Butylbenzene
23. 1-Methyl-2-n-propylbenzene
24. 1,2-Diethylbenzene
25. 1,4-Dimethyl-2-ethylbenzene
26. 1,3-Dimethyl-5-ethylbenzene
27. 1,2-Dimethyl-4-ethylbenzene
28. 1,3-Dimethyl-2-ethylbenzene
29. 1,2-Dimethyl-3-ethylbenzene
30. 1,2,4,5-Tetramethylbenzene
31. 2-Methylbutylbenzene
32. trans-1-Butyl-2-methylbenzene
33. n-Pentylbenzene
34. t-1-Butyl,3,5-dimethylbenzene
35. t-1-butyl-ethylbenzene
36. 1,3,5-Triethylbenzene
37. 1,2,4-Triethylbenzene
38. n-Hexylbenzene

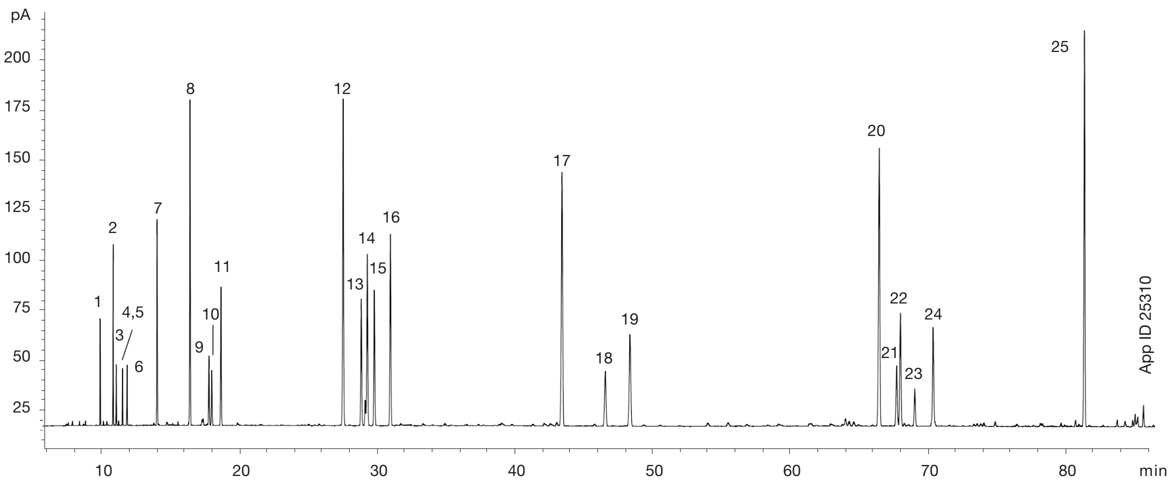
Figure 4.
Separation of Naphthenes on a Zebron ZB-DHA-PONA GC Column



Sample:

1. Cyclopentane
2. Methylcyclopentane
3. Cyclohexane
4. 1,1-Dimethylcyclopentane
5. cis-1,3-Dimethylcyclopentane
6. trans-1,3-Dimethylcyclopentane
7. trans-1,2-Dimethylcyclopentane
8. Methylcyclohexane
9. Ethylcyclopentane
10. ctc-1,2,4-Trimethylcyclopentane
11. ctc-1,2,3-Trimethylcyclopentane
12. cct-1,2,4-Trimethylcyclopentane
13. trans-1,4-Dimethylcyclohexane
14. 1-Ethyl-1-methylcyclopentane
15. trans-1,2-Dimethylcyclohexane
16. ccc-1,2,3-Trimethylcyclopentane
17. Isopropylcyclopentane
18. cis-1,2-Dimethylcyclohexane
19. n-Propylcyclopentane
20. ccc-1,3,5-Trimethylcyclohexane
21. 1,1,4-Trimethylcyclohexane
22. ctt-1,2,4-Trimethylcyclohexane
23. ctc-1,2,4-Trimethylcyclohexane
24. 1,1,2-Trimethylcyclohexane
25. Isobutylcyclopentane
26. Isopropylcyclohexane
27. n-Butylcyclopentane
28. Isobutylcyclohexane
29. t-1-Methyl-2-propylcyclohexane
30. t-1-Methyl-2-(4MP)cyclopentane

Figure 5.
Separation of Olefins on a Zebron ZB-DHA-PONA GC Column



Sample:

1. 3-Methyl-1-butene
2. 1-Pentene
3. 2-Methyl-1-butene
4. 2-Methyl-1,3-butadiene
5. trans-2-Pentene
6. cis-2-Pentene
7. 4-Methylpentene-1
8. 1-Hexene
9. 2-Methylpentene-2
10. trans-2-Hexene
11. cis-2-Hexene
12. 1-Heptene
13. trans-3-Heptene
14. cis-3-Heptene
15. trans-2-Heptene
16. cis-2-Heptene
17. 1-Octene
18. trans-2-Octene
19. cis-2-Octene
20. 1-Nonene
21. trans-3-Nonene
22. cis-3-Nonene
23. trans-2-Nonene
24. cis-2-Nonene
25. 1-Decene

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Results and Discussion

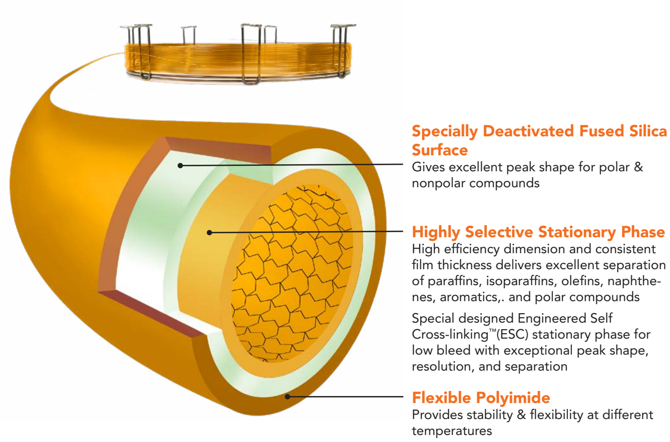
Detailed hydrocarbon analysis involves analysis of a matrix that can contain a variety of compounds including paraffins, isoparaffins, olifins, naphthenes, and related compounds which makes the separation complex. Presented in this tech note is the analysis of PIONA compounds by Zebron ZB-DHA-PONA column which is specially designed for the separation of detailed hydrocarbons. The polymide layer provides temperature stability and flexibility. The middle ultra clean silica layer provides great peak shape for polar and nonpolar compounds. The inner layer of a 100 % dimethylpolysiloxane that delivers great separation of the paraffins, isoparaffins, olefins, naphthalenes, and aromatics (**Figure 6**.)

The Zebron ZB-DHA-PONA column has a special Engineered Self Cross-linking™ (ESC) stationary phase that provides low bleed and exceptional column life. The dimensions used in this test (100 meter length x 0.25 mm ID x 0.50 µm film thickness) are important to provide the ideal separation and resolution. The smaller 0.25 mm diameter along with the column length provides an efficient mass transfer of the complex analytes for great separation and peak shapes. The column's low polar 100 % Dimethylpolysiloxane phase provided great separation for all of the DHA test components (**Figure 1-5**). In Table 1. there is a list of additional column dimensions that can be used for other test methods which will provide optimal separation of detailed hydrocarbons in the refinery naphtha process streams.

Conclusion

The Zebron ZB-DHA-PONA GC column provides the optimal separation of DHA critical pairs with symmetric peaks. The Zebron ZB-DHA-PONA GC column with the 100 % Dimethylpolysiloxane phase is a great selectivity to provide separation of paraffins, isoparaffins, aromatics, naphthalene, and olefins.

Figure 6.
Benefits of ZB-DHA-PONA GC Column



Ordering Information

Zebron™ ZB-DHA-PONA GC Columns

ID (mm)	df (µm)	Temp. Limits °C	Part No.
5-Meter			
0.25	1.00	-60 to 340/360	7AG-G042-22
50-Meter			
0.20	0.50	-60 to 360/370	7GE-G042-17
100-Meter			
0.25	0.50	-60 to 360/370	7MG-G042-17
150-Meter			
0.25	1.00	-60 to 340/360	7QG-G042-22

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

Taiwan
t: +886 (0) 0801-49-1246
twinfo@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

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