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APPLICATIONS

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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.

ASTM D6730 Detailed Hydrocarbon Analysis of Spark Ignition Fuel using Zebron™ ZB-DHA-PONA Gas Chromatography Column

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Introduction

The motor fuel industry continues to make improvements in their formulas to lower emission and to provide higher operational efficiency. In addition, for those same reasons there are new combustion engines that are being designed around alternative formulated fuels. Fuels are composed of very complex matrices that have several hundred different components and there are many different refinery process stream feeds that can be used to blend with the straight run material. The hundreds of different components in the straight run spark ignition fuel are then further complicated exponentially with the numerous different sources of refinery process feed and their hundreds of components, and so it is mandated that the fuel industry use regulated test methods to measure the group type chemical components to make sure that formula guidelines are met. Not only is the component composition needed for the regulatory specifications, but also for the refinery process quality control.

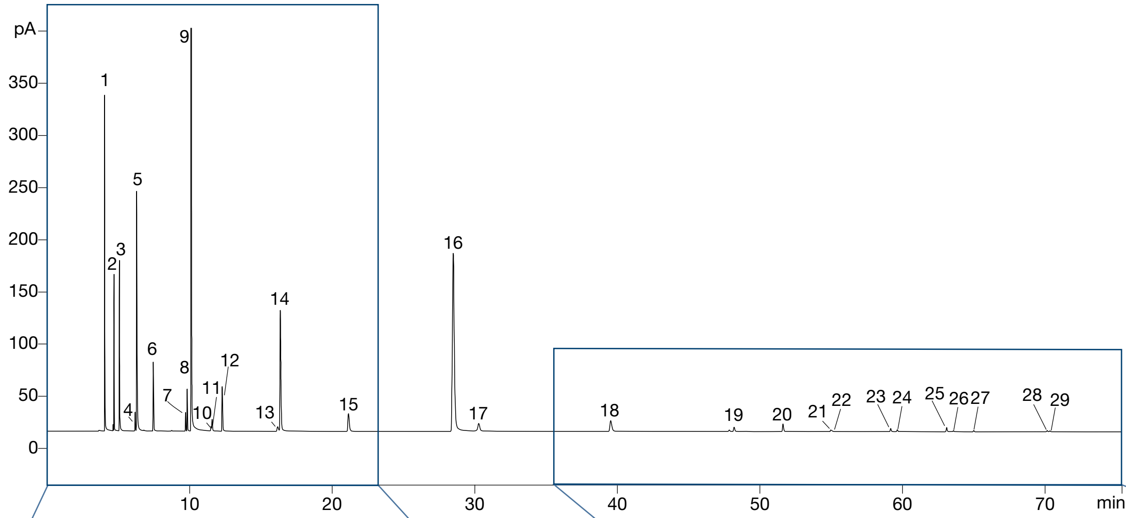
The petroleum fractions in the spark ignition fuel are in the carbon number range of C1 to C12, and the refinery process feedstock are virgin straight run naphtha, along with other blending streams from the FCC, coker, steam cracking, alkylation, and synthetic sources, along with the chemical additives such as oxygenates. Detailed Hydrocarbon Analysis (DHA) are test methods developed specifically to measure the primary chemical group types, such as paraffin, isoparaffin, olefin, naphthenes, and aromatics.

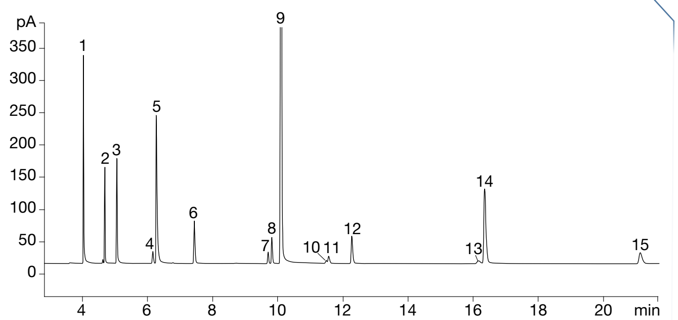
ASTM-D6730-01 is a specific DHA test method for the analysis of hydrocarbon components along with the oxygenated additives that are in spark-ignition engine fuels. This test method covers the determination of individual hydrocarbon components of spark-ignition engine fuels with boiling ranges up to 225 °C. The accuracy for total PONA analysis decreases with higher olefin content and carbon numbers, though the aromatics have reasonable accuracy. A precolumn is used to improve resolution of some key components such as benzene and toluene from paraffins and cycloparaffins.

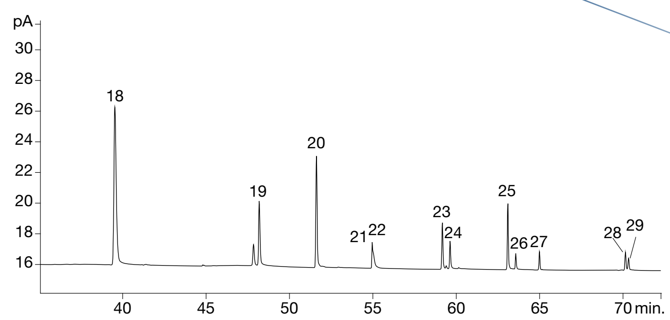
Table 1.
Zebron ZB-DHA-PONA Column Dimensional Options for Detailed Hydrocarbon Analysis (ASTM and alternative methods)

Part No.	Dimensions	Stationary Phase	Benefits
7JE-G042-17	50 m x 0.20 mm x 0.50 µm	100 % Dimethylpolysiloxane	50 m column provides shorter run time while the 0.20 mm tighter ID provides higher efficiency
7MG-G042-17	100 m x 0.25 mm x 0.50 µm	100 % Dimethylpolysiloxane	100 m length provides high plate count / efficiency
7QG-G042-22	150 m x 0.25 mm x 1.0 µm	100 % Dimethylpolysiloxane	150 m 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 m x 0.25 mm x 1.0 µm	5 % Phenyl 95 % Dimethylpolysiloxane	Optional tuning column provides phenyl selectivity in addition to true boiling point separation. This helps resolve certain aromatics from alkanes and alkenes

Figure 1.
Analysis of ASTM D6730 Components by GC-FID on ZB-DHA-PONA & ZB-DHA-PONA-TUNE GC Column





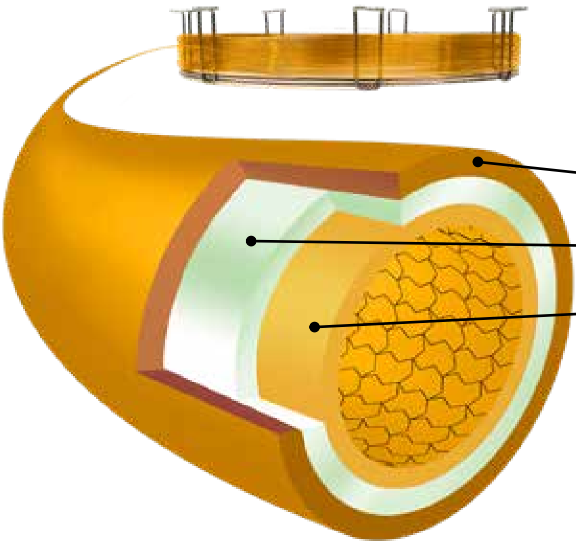


GC Conditions for Analysis:

Column 1 (Tuning): Zebron™ ZB-DHA-PONA-TUNE
Phase: 5 % Phenyl 95 % Dimethylpolysiloxane
Dimensions: 5 meter x 0.25 mm x 1.0 µm
Part No.: 7AG-G042-22
Column 2: Zebron™ ZB-DHA-PONA
Phase: 100 % Dimethylpolysiloxane
Dimensions: 100 meter x 0.25 mm x 0.50 µm
Part No.: 7MG-G042-17
Recommended Column Union: AG0-4716
Injection: Split 150:1 @ 200 °C, 0.2 µL
Recommended Liner: ZebronPLUS Straight Z-Liner ™
Part No.: AG2-0A03-05
Carrier Gas: Hydrogen @ 2 mL/min (Constant Flow Mode)
Oven Program: 30 °C for 8.5 min, to 48 °C at 22 °C/min. for 27 min, to 141 °C at 3 °C/min. for 1 min, to 275 °C at 1 °C/min. for 2 min
Detection: Flame Ionization (FID) @ 275 °C

Sample:	#	Analyte	Time min.
	1.	Ethanol	4.039
	2.	C5 (n-pentane)	4.696
	3.	2-Methylbutane	5.064
	4.	Tert-Butanol	6.174
	5.	2,3-Dimethylbutane	6.276
	6.	Methyl tert-butyl ether (MTBE)	7.446
	7.	C6 (n-hexane)	9.708
	8.	1-Methylcyclopentene	9.823
	9.	Benzene	10.106
	10.	Cyclohexane	11.493
	11.	3-Ethylpentane	11.568
	12.	trans-1,2-Dimethylcyclopentane	12.278
	13.	C7 (n-heptane)	16.167
	14.	2,3,3-Trimethylpentane	16.355
	15.	Toluene	21.131
	16.	C8 (n-octane)	28.485
	17.	Ethylbenzene	30.269
	18.	2,3-Dimethylheptane	39.526
	19.	p-Xylene	48.182
	20.	C9 (n-nonane)	51.611
	21.	5-Methylnonane	54.958
	22.	1-Methyl-2-ethylbenzene	55.011
	23.	C10 (n-decane)	59.164
	24.	C11 (undecane)	59.628
	25.	1,2,3,5-Tetramethylbenzene	63.09
	26.	Naphthalene	63.568
	27.	C12 (dodecane)	64.984
	28.	1-Methylnapthalene	70.146
	29.	C13 (Tridecane)	70.331

Figure 2.
Benefits of ZB-DHA-PONA GC Column



Flexible Polyimide
Provides stability & flexibility at different temperatures

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

Results and Discussion

The spark ignition fuel matrix contains a variety of compounds including paraffins, isoparaffins, olifins, naphthenes, and related compounds which makes the DHA separation complex. This technical work describes the use of a Zebron™ ZB-DHA-PONA GC column in combination with a 5 meter ZB-DHA-PONA-TUNE column which are specially designed to provide excellent peak symmetry and resolution of hydrocarbon components and oxygenates. The primary ZB-DHA-PONA column's low polar 100 % Dimethylpolysiloxane phase provides very good separation of low and high boiling impurities of complex mixtures in the spark ignition fuels while the 5 m ZB-DHA-PONA-TUNE GC tuning column provides a phenyl selectivity that helps the effective separation of aromatics such as benzene and toluene from hydrocarbons.

The DHA of a 29-component mixture was performed for this technical piece (**Figure 1**). The column efficiency of the Zebron ZB-DHA-PONA far exceeded the ASTM-6730-01 required minimum 400,000 plates for the pentane peak. Zebron ZB-DHA-PONA has a special deactivated fused silica surface that provides excellent peak shape for polar and nonpolar compounds, plus it's stationary phase has an Engineered Cross-linking™ stationary phase designed for lower bleed, which together are wrapped in a flexible polyimide outer coating that can withstand up to 340/360 °C maximum temperature (**Figure 2**). The smaller 0.25 mm inner diameter along with the 100-meter column length provides an efficient mass transfer of the complex analytes for great separation and resolution of critical pairs.

Conclusion

The Zebron ZB-DHA-PONA GC column provides the optimal separation of DHA critical pairs with symmetric peaks and it is suitable for ASTM-D6730-01. The Zebron ZB DHA-PONA GC column with the 100 % Dimethylpolysiloxane phase in combination with ZB-DHA-PONA-TUNE is a great selectivity to provide separation of paraffins, isoparaffins, aromatics, naphthalene, olefins and Oxygenates.

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Ordering Information

Zebron ZB-DHA-PONA GC Columns			
ID(mm)	**df(µm)**	**Temp. Limits °C**	**Part No.**
5-Meter			
0.25	1.0	-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	1.0	-60 to 340/360	7QG-G042-22

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