The Detailed Hydrocarbon Analysis of Individual Components in Oxygenated Gasoline with the DVLS DHA (ASTM D6730) Kit

Introduction

The analysis of individual components in gasoline and its blending stocks is essential for fuel specification and control of gasoline blending. Several methods for Detailed Hydrocabon Analysis are commonly used, such as ASTM D6729, D6730 and D6733. This application note describes the compositional analysis according to ASTM D6730 using the DVLS DHA dedicated kit.

Application Note

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Fuel Specification and test method

Gasoline is blended from several different hydrocarbon streams, such as naphtha, reformate, alkylate. The finished gasoline should meet various quality specifications: reid vapour pressure, octane number and volume percent of hydrocarbon groups such as aromatics and olefins. Knowledge on the individual components helps refiners, blenders and engineers in the field of gasoline blending and process control.
Detailed Hydrocarbon Analysis (DHA) is a well known technique to identify components in complex mixtures and to determine the component concentration in mass%, vol% and mol%.

Application Description

To accurately determine the individual components in oxygenated gasoline Da Vinci Laboratory Solutions developed the DHA D6730 dedicated kit.

The DHA D6730 kit complies with the ASTM standard test method D6730: the Standard Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100 Metre Capillary (with Precolumn) High-Resolution Gas Chromatography.

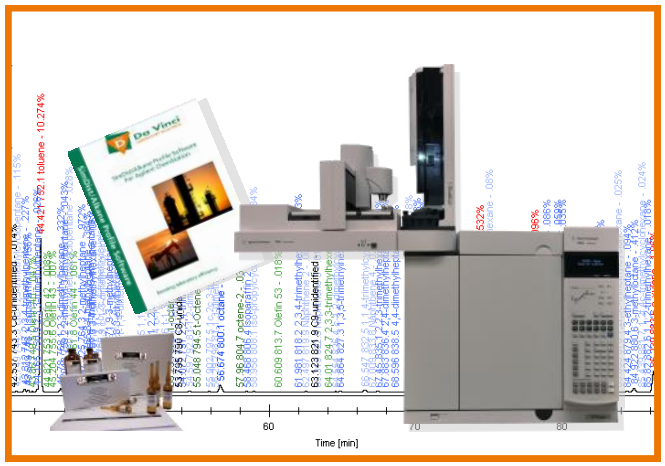


Figure One: a GC configured with the DVLS DHA ASTM D6730 Kit

A representative hydrocarbon sample is introduced into the gas chromatograph (GC) equipped with a capillary column and precolumn. The carrier gas transports the vaporized sample through the column, in which it is separated into the individual components. At the end of the column the components are detected by a flame ionization detector (FID).

The GC is equipped with the DHA ASTM D6730 dedicated kit that includes the following components:

- a GC capillary column
- a Capillary precolumn
- Calibration and validation samples
- PetroReporter sofware to automate data processing and reporting

Boosting laboratory efficiency

Table One lists the system configuration, Table Two shows typical GC operating conditions. Figure Two shows the column configuration of the DHA D6730 application.

GC Hardware	
Gas Chromatograph	Agilent 7890B
Inlet	Split/splitless
Detector	FID
Auto Sampler	Agilent ALS 7693A
Cooling	Liquid Nitrogen
Column	
Precolumn	DB-5 3m, 0.25 mm ID, 1.00 µm phase
Primary column	HP-1 100 m, 0.25 mm ID, 0.50 µm phase

Table One: System configuration of DHA D6730

Analytical Results

The DHA kit includes the DVLS PetroReporter software to automate the data processing of various applications. Due to the universal setup the PetroReporter software can be used for DHA, SimDist and Gas applications.

PetroReporter includes predefined sample settings, component databases and formulas to provide a correct identification.
Each peak is identified using the Kovats Retention Indices (RI). The RI of unknown peaks are calculated from:

- the retention time of the unknown peak
- the retention time of the n-paraffin eluting before and after the unknown peak.

The calculated RI is matched against a database in the software to identify the component. The concentration of each component in mass % is determined by normalization of the peak areas after correction with detector response factors.
Unknown components are reported as a total unknown mass %.
The DVLS DHA D6730 application fully complies with the ASTM D6730 method.

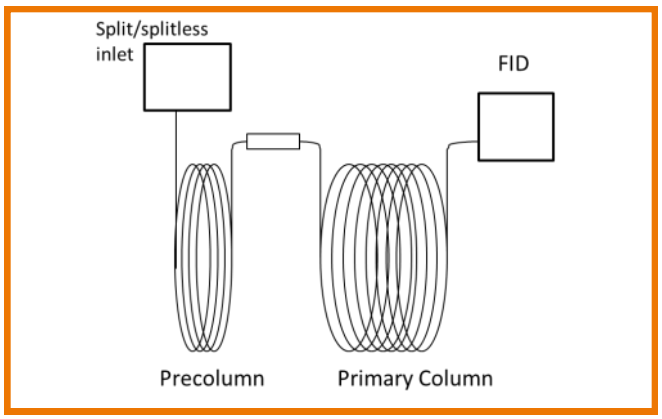


Figure Two: Column Configuration

GC Operating Conditions	
Column Temperature Program	
Initial temperature	5 °C
Initial time	11 min
First program rate	5 °/min
First hold temperature	48 °C
First hold time	55.146 min
Second program rate	1.5 °/min
Final temperature	200 °C
Final hold time	5 min
Injector Parameters	
Temperature	250 °C
Split ratio	150 : 1
Sample size	0.2 µl
Septum purge flow	3 ml/min
Detector	
Temperature	325 °C
Detector gas flows:	
Fuel gas	H_2 at 35 ml/min
Oxidant	Air at 250 ml/min
Make-up gas	He at 20 ml/min
Carrier Gas	
Type	He
Pressure	311.71 kPa
Average linear velocity	28.134 cm/s

Table Two GC Operating Conditions of DHA D6730

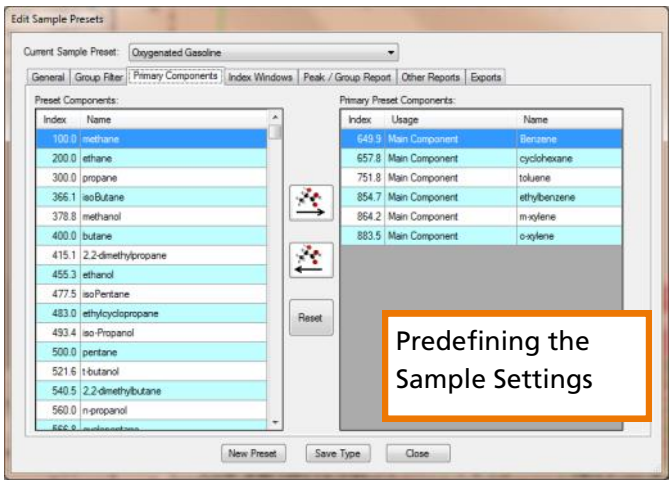
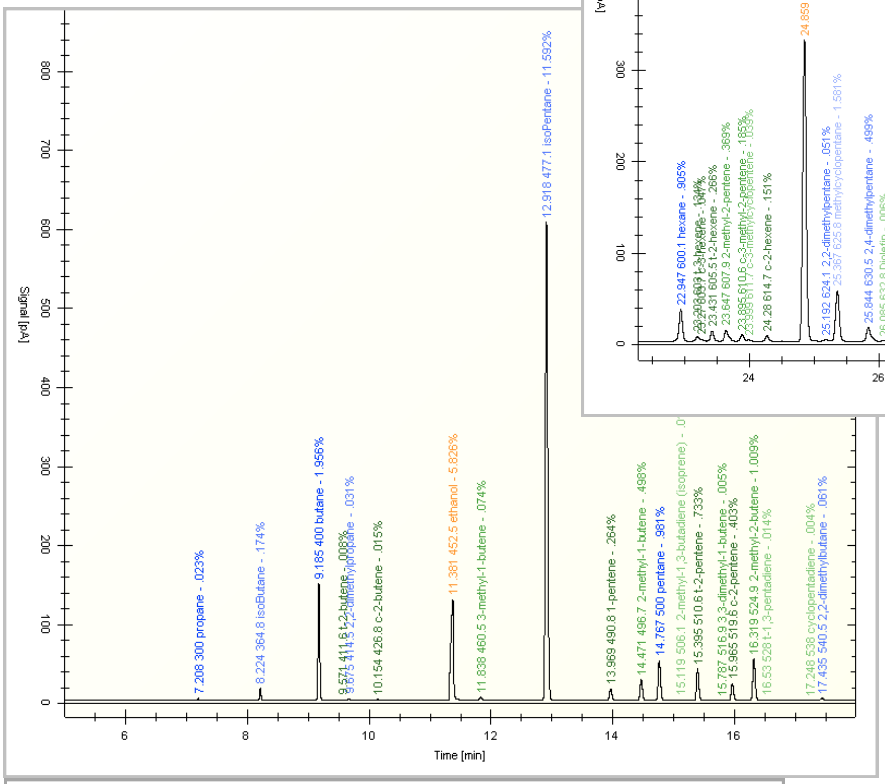
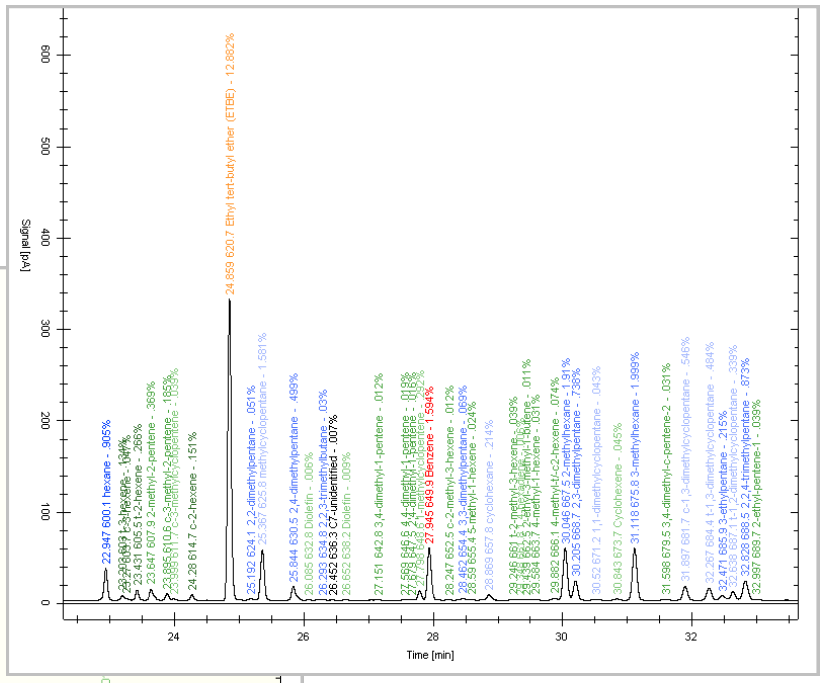


Figure Three: Primary Sample Component Setup

Figure Four:
Results of the ASTM D6730 Analysis of an Oxygenated Gasoline





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[Oxygenated Gasoline]
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Sample Preset	Oxygenated Gasoline
Method	D6730.M
Analyst	
Description	
Calibration	C:\Chem32\1\DATA\20130104_GCB_D6730-10\102F0201.D
Bottle	
Sample We	
ISTD Weig	

Group Report in Mass %

	n-Par	i-Par	Olef	Napth	Arom	Oxyg	Unk	Total
C2	0.00	0.00	0.00	0.00	0.00	5.83	0.00	5.83
C3	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.02
C4	1.96	0.17	0.02	0.00	0.00	0.00	0.00	2.15
C5	0.98	11.62	3.17	0.13	0.00	0.00	0.00	15.90
C6	0.97	5.93	2.29	1.93	1.72	0.46	0.00	13.30
C7	1.18	5.86	1.65	2.68	10.82	0.00	0.01	22.19
C8	0.89	5.29	0.27	2.10	10.80	0.00	0.03	19.37
C9	0.30	2.52	0.08	0.84	7.84	0.00	0.03	11.62
C10	0.11	0.74	0.00	0.06	5.80	0.00	0.02	6.74
C11	0.04	0.21	0.00	0.00	0.84	0.00	0.04	1.12
C12	0.03	0.19	0.00	0.00	0.57	0.00	0.26	1.05
C13	0.03	0.01	0.02	0.00	0.00	0.00	0.64	0.70
Total	6.51	32.56	7.50	7.73	38.38	6.29	1.02	100.0

Group Report in Volume %

	n-Par	i-Par	Olef	Napth	Arom	Oxyg	Unk	Total
C2	0.00	0.00	0.00	0.00	0.00	5.51	0.00	5.51
C3	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.03
C4	2.52	0.23						
C5	1.17	14.01						
C6	1.10	6.74						
C7	1.29	6.40						
C8	0.95	5.62						
C9	0.31	2.63						
C10	0.11	0.76						
C11	0.04	0.21						
C12	0.03	0.19						
C13	0.03	0.01						
Total	7.59	36.82						

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[Oxygenated Gasoline]
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Boiling Point Distribution Report

Perc	TBP (mass) [°C]	TBP (vol) [°C]	Perc	TBP (mass) [°C]	TBP (vol) [°C]	Perc	TBP (mass) [°C]	TBP (vol) [°C]
IBP	-10.0	-10.7	34.0	78.2	74.1	68.0	125.7	117.7
1.0	-7.1	-8.4	35.0	78.3	78.0	69.0	136.0	118.7
2.0	-1.4	-4.0	36.0	79.6	78.0	70.0	136.0	119.8
3.0	20.5	20.0	37.0	80.1	78.1	71.0	136.1	125.2
4.0	21.2	20.6	38.0	86.1	78.2	72.0	138.0	131.0
5.0	21.8	21.1	39.0	89.8	78.3	73.0	138.2	136.0
6.0	22.5	21.7	40.0	89.9	79.4	74.0	139.0	136.1
7.0	23.2	22.3	41.0	90.0	80.0	75.0	139.0	136.2
8.0	23.8	22.8	42.0	91.0	80.7	76.0	139.1	138.2
9.0	24.5	23.4	43.0	91.9	89.6	77.0	139.1	139.0
10.0	25.2	23.9	44.0	92.0	89.9	78.0	139.1	139.0
11.0	25.9	24.5	45.0	92.0	89.9	79.0	143.3	139.1
12.0	26.5	25.1	46.0	97.7	90.4	80.0	144.2	139.1
13.0	27.2	25.6	47.0	98.2	91.6	81.0	144.3	141.4
14.0	28.9	26.2	48.0	98.9	91.9	82.0	149.6	143.9
15.0	34.8	26.7	49.0	100.0	92.0	83.0	158.1	144.3
16.0	36.2	27.3	50.0	104.8	93.4	84.0	159.7	146.5
17.0	36.7	28.4	51.0	109.4	98.0	85.0	161.1	156.3
18.0	45.8	34.4	52.0	110.2	98.3	86.0	162.4	159.4
19.0	58.0	36.1	53.0	110.3	98.9	87.0	164.9	160.9
20.0	59.0	36.5	54.0	110.3	100.1	88.0	167.4	162.6
21.0	59.6	37.0	55.0	110.3	105.5	89.0	168.2	165.1
22.0	60.1	57.2	56.0	110.4	109.4	90.0	169.0	167.7
23.0	62.3	58.6	57.0	110.4	110.2	91.0	175.1	168.6
24.0	63.0	59.1	58.0	110.5	110.3	92.0	176.9	173.1
25.0	66.6	59.6	59.0	110.5	110.3	93.0	182.7	176.4
26.0	68.5	60.1	60.0	110.5	110.4	94.0	184.2	182.6
27.0	70.5	62.2	61.0	110.6	110.4	95.0	188.6	185.1
28.0	71.3	62.7	62.0	111.6	110.5	96.0	195.9	189.2
29.0	71.8	63.3	63.0	117.2	110.5	97.0	205.2	197.5

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Detailed Peak Report

#	Index	Time	Area	Mass%	Vol%	Mol %	Name
1	300.0	7.208	1.003E+000	0.007	0.011	0.016	propane
2	364.8	8.225	1.453E+001	0.107	0.143	0.179	isoButane
3	390.0	8.874	1.056E+001	0.075	0.094	0.130	1-butene
4	400.0	9.185	1.882E+002	1.387	1.786	2.313	butane
5	411.6	9.571	8.880E-001	0.006	0.008	0.011	t-2-butene
6	414.5	9.675	3.221E+000	0.024	0.030	0.032	2,2-dimethylpropane
7	426.8	10.154	1.706E+000	0.012	0.015	0.021	c-2-butene
8	454.5	11.494	6.317E-001	0.010	0.009	0.020	ethanol
9	460.5	11.839	8.266E+000	0.059	0.070	0.081	3-methyl-1-butene

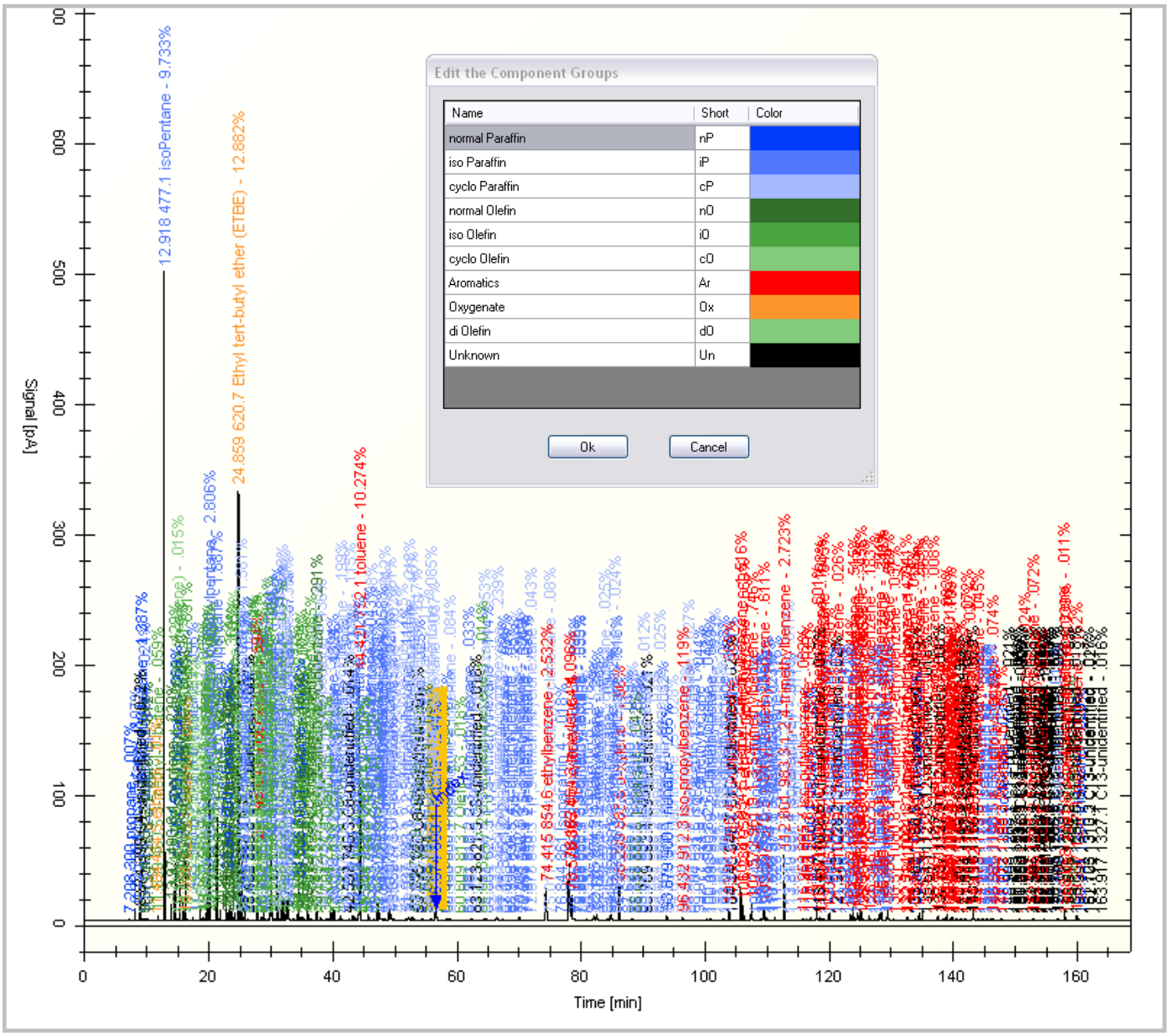

Figure Five: Chromatogram of the complete Oxygenated gasoline analysis according to D6730

Conclusion

The DVLS DHA D6730 kit helps analysts in reporting the individual components in oxygenated gasoline according to ASTM method D6730. The kit includes all components to configure the gas chromatograph with the required hardware, software, calibration and validation samples. The PetroReporter software includes predefined sample settings, component databases and formulas for a correct identification.

References:

ASTM D6730 – 01 (2011) Standard Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100–Metre Capillary (with Precolumn) High-Resolution Gas Chromatography

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