Detailed Hydrocarbon Analysis of Spark Ignition Engine Fuels by GC using ASTM D 6730

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Introduction

Spark ignition fuels are complex mixtures containing hundreds of components. Detailed information on the concentration of these components is important for quality control, controlling refinery processes and evaluation of raw materials. The ASTM D 6730 method describes a GC method for the detailed hydrocarbon analysis (DHA) of gasolines. The method is also applicable to mixtures containing oxygenate blends (MTBE, ETBE, ethanol and so forth) with boiling ranges up to 225 °C in the concentration range from 0.01 to 30 mass%. Some interfering co-elution may occur, especially when higher amounts of olefins are present in the sample. Therefore, the method is less suited for samples containing over 25 mass% of olefins.

Other light liquid hydrocarbon mixtures typically encountered in petroleum refining operations, such as blending stocks (naphthas, reformates, alkylates and so forth) may also be analyzed.

Instrumentation

Technique: Varian 450-GC Gas Chromatograph
Injector: Split/splitless 1177, full EFC control
Column Oven: With cryogenic (CO_2) cooling
Detection: FID with full EFC control
Autosampler: Varian CP-8400 AutoSampler

Software
GC Control and Data Handling: Galaxie™ GC Workstation
DHA Calculations: DHA software fully integrated into Galaxie Workstations

Materials and Reagents

Columns: Varian CP-Sil PONA CB™, 100 m x 0.25 mm x 0.5 µm (pn: CP7530)
Varian CP-Sil 8 CB, 15 m x 0.25 mm x 1.0 µm (a variable length of 1–4 m is used) (pn: CP8521)

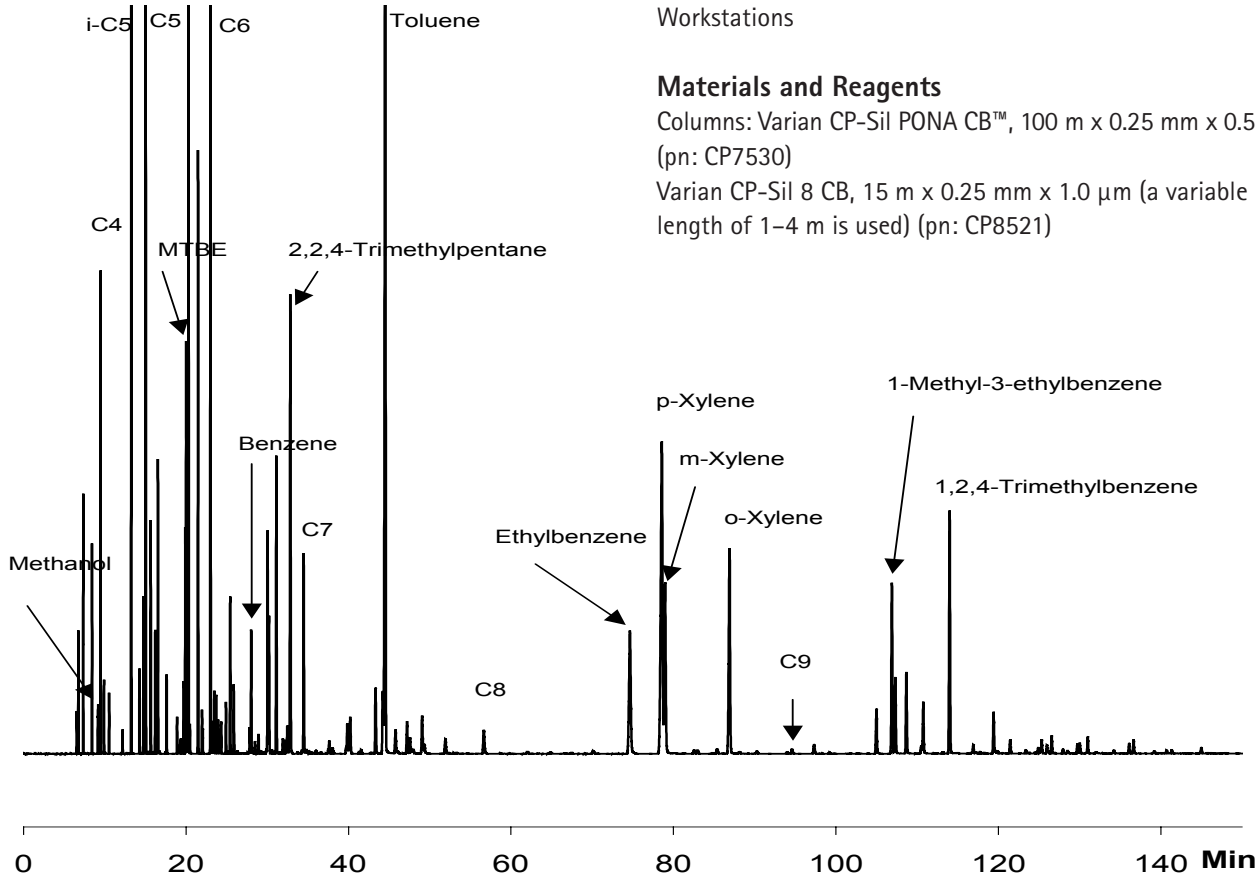


Figure 1. Gasoline analysis.

Conditions

Column temperature program
Initial Temperature: 5 °C (10 min)
First Program Rate: 5 °C/min
First Hold Temperature: 50 °C (~50 min until ethylbenzene has eluted)
Second Program Rate: 1.5 °C/min
Final Temperature: 200 °C (5 min)

Carrier Gas: Helium, ~277 kPa (40 psi)
Split Ratio: 1:150
Sample Size: 0.1–0.2 µL
Injector: 250 °C, split 200 mL/min
Detection: 275 °C, FID

Results and Discussion

A calibration mixture containing n-alkanes is used to calculate Kovats indices of all components in the sample. These indices are compared with known indices in the database and peaks are assigned accordingly. ASTM D 6730 uses an extra pre-column and therefore provides extra selectivity when compared to the ASTM D 6729. This extra selectivity is apparent by some key separations. The following chromatogram sections show these separations in more detail. Figure 2 shows a section of the chromatogram in the pentane-hexane area where the key separation between MTBE and 2,3-dimethylbutane occurs.

1 iso-Pentane
2 Pentene
3 2-Methylbutene
4 Pentane
5 Isoprene
6 t-2-Pentene
7 c-2-Pentene
8 2-Methyl-2-butene
9 t-1,3-Pentadiene
10 2,2-Dimethylbutane
11 Cyclopentene
12 4-Methylpentene
13 Cyclopentane
14 2,3-Dimethylbutane
15 Methyl-t-butylether
16 2-Methylpentane
17 4-Methyl-t-2-pentene
18 3-Methylpentane
19 2-Methylpentene
20 Hexene
21 Hexane

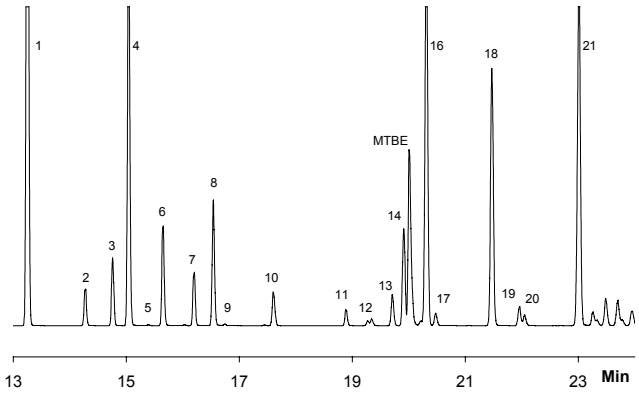
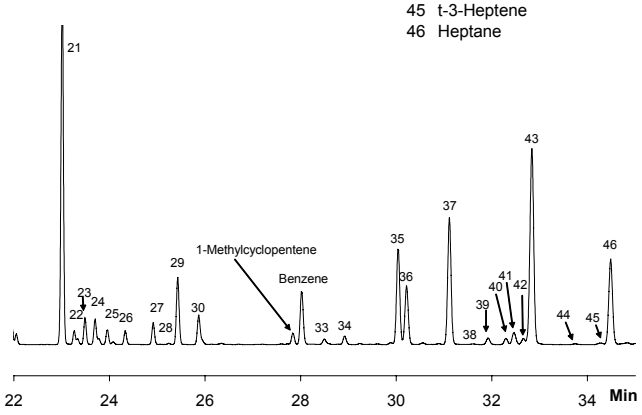


Figure 2. Gasoline analysis of Figure 1. MTBE/2.3 dimethylbutane

separation.

In Figure 3, the chromatogram continues and shows the elution from hexane through heptane, indicating the critical

21 Hexane
22 t-3-Hexene
23 t-2-Hexene
24 2-Methyl-2-pentene
25 3-Methyl-c-2-pentene
26 c-2-Hexene
27 3,3-Dimethylpentene
28 2,2-Dimethylpentane
29 Methylcyclopentane
30 2,4-Dimethylpentane
31 Methylcyclopentene
32 Benzene
33 3,3-Dimethylpentane
34 Cyclohexane
35 2-Methylhexane
36 2,3-Dimethylpentane
37 3-Methylhexane
38 3,4-Dimethyl-c-2-pentene
39 c-2,3-Dimethylcyclopentane
40 t-1,3-Dimethylcyclopentane
41 3-Ethylpentane
42 t-1,2-Dimethylcyclpentane
43 2,2,4-Trimethylpentane
44 3-Methyl-c-3-Hexene
45 t-3-Heptene
46 Heptane



separation between 1-methylcyclopentene and benzene.

Figure 3. Gasoline analysis of 1-methylcyclopentene/benzene separation from Figure 1.

After normalization a detailed hydrocarbon analysis report is prepared. Table 1 shows part of this report.

DHA

Analysis according to ASTM D6730 DHAX

Sample Info	N.A.		
Sample Type	Sample		
Date Analysed	12 Jan 2005, 03:35:52	Date Printed	26 Jan 2006, 11:18:31
Analyst	ADMINISTRATOR	Vial	5
Data File	\DHA\Example Data\ASTM D6730\DHA 6730 reformate.DATA		
Method	\Varian Galaxie\DHA\Example Data\Methods\astm d6730.dha		
Description	DHA 6730 Reformate		
Instrument	DHA 3800		

Detailed Hydrocarbon Analysis

ID	RT	CRT	Index	Name	Area	Area Pecent	Weight Percent	Volume Percent
1	6.53	6.53	100.00	methane	181.2	0.10	0.134	0.321
2	6.73	6.73	199.17	ethane	619.2	0.35	0.456	0.998
3	7.33	7.33	300.00	propane	1144.6	0.65	0.844	1.217
4	8.42	8.42	354.09	2-methylpropane	1145.4	0.65	0.844	1.094
5	9.16	9.11	384.89	methanol	481.8	0.27	0.857	0.782
6	9.47	9.47	399.79	butane	2798.0	1.58	1.915	2.388
7	9.89	9.89	409.32	t-2-butene	445.9	0.25	0.352	0.442
8	10.00	10.00	411.79	2,2-dimethylpropane	10.2	0.01	0.007	0.008
9	10.51	10.51	422.55	c-2-butene	379.4	0.21	0.300	0.363
10	12.18	12.18	454.41	3-methyl-1-butene	182.9	0.10	0.144	0.166
11	13.24	13.24	472.53	iso-pentane	14772.9	8.35	9.334	10.872
12	14.26	14.26	488.64	1-pentene	682.9	0.39	0.449	0.510
13	14.75	14.75	495.91	2-methyl-1-butene	1148.4	0.65	0.756	0.839
14	15.03	15.03	500.03	pentane	7234.4	4.09	4.571	5.269
15	15.38	15.38	505.41	2-methyl-1,3-butadiene	18.1	0.01	0.014	0.016
16	15.64	15.64	509.33	t-2-pentene	1817.8	1.03	1.196	1.331
17	16.02	16.02	515.00	3,3-dimethyl-1-butene	15.4	0.01	0.009	0.010

Table 1. Detailed hydrocarbon analysis report.

The analysis results are presented in weight% as well as volume% to the nearest 0.001 %. To ensure accurate results, the DHA software calculates peak symmetry. Depending on the peak skewing, a corrected retention time is calculated and, subsequently, the corresponding Kovats indices. This is also shown in Table 1 in the CRT (corrected retention time) column.

The DHA software is capable of grouping individual components according to their hydrocarbon type. These groups include cyclic-, iso- and normal saturates and unsaturates, aromatics and oxygenates. Each group is reported according to carbon number and reported in a

weight and volume percent profile report (Table 2).

DHA

Analysis according to ASTM D6730 DHAX

Sample Info	N.A.		
Sample Type	0		
Date Analysed	12 Jan 2005, 03:35:52	Date Printed	26 Jan 2006, 11:18:31
Analyst	ADMINISTRATOR	Vial	5
Data File	\DHA\Example Data\ASTM D6730\DHA 6730 10224924.DATA		
Method	\Varian Galaxie\DHA\Example Data\Methods\astm d6730.dha		
Description	DHA 6730 10224924		
Instrument	DHA 3800		

Weight Percent Profile

	Saturates			Unsaturates					
Carbon	Cyclic	Iso	Normal	Cyclic	N+ Iso	Aromatics	Oxyg	Unknown	Total
1			0.134				0.857		**0.991**
2			0.456						**0.456**
3			0.844						**0.844**
4		0.844	1.915		0.652				**3.411**
5	0.379	9.341	4.571		4.453		3.242		**22.467**
6	1.077	9.864	4.349		2.276	0.694		0.025	**18.592**
7	0.566	5.729	1.524		0.118	12.666			**20.733**
8	0.133	6.942	0.331			14.652			**22.058**
9	0.029	0.412	0.058			8.100		0.088	**8.598**
10	0.185	0.082				1.195		0.116	**1.462**
11						0.122			**0.122**
Total	**2.368**	**33.215**	**14.182**		**7.498**	**37.430**	**4.099**	**0.230**	

Table 2. Weight percent profile report.

In the database, all physical properties of the different sample components are listed. The DHA software uses these properties and combines them with volume% and weight% values in the sample. These combined calculations lead to the properties of the sample reported in the physical properties report shown in Table 3.

DHA

Analysis according to ASTM D6730 DHAX

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Analyst	ADMINISTRATOR	Vial	5
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Method	\Varian Galaxie\DHA\Example Data\Methods\astm d6730.dha		
Description	DHA 6730 reformate		
Instrument	DHA 3800		

Physical Properties Report

%OFF	TBP °C	D86 °C	Property		
IBP	-89.0	9.9	MON Value	95.4	
5%	-0.5	42.6	RON Value	104.2	
10%	27.8	47.7			
20%	36.1	55.1	Reid Vapor P.	24.4	mm Hg
30%	55.2	59.6			
40%	63.3		Net Heat	42.7	kJ/g
50%	68.7	69.3	Gross Heat	46.0	kJ/g
60%	98.4				
70%	110.6	112.8	Density	0.7517	g/ml
80%	136.1	130.4			
90%	144.4	139.0			
95%	164.7				
FBP	188.4	179.8			

Table 3. Physical properties report.

Conclusion

The Varian 450-GC gas chromatograph, Galaxie chromatography and data handling software with a DHA plug-in give excellent results in DHA analysis of gasolines according to the ASTM D 6730 method. Several reports can be produced. The detailed hydrocarbon analysis report gives the weight and volume% to the nearest 0.001 % of the individual components. With the DHA software, grouping of components per type (normal-, iso- and cyclic saturated and unsaturated hydrocarbons, aromatics and oxygenates) can be performed in mass% as well as volume%. In addition, a physical properties report can be generated. This report yields sample information such as boiling point distribution, including initial and final boiling point, MON/RON values, Reid vapor pressure, net heat, gross heat and density.

Reference

ASTM Standard D 6730-01, 2006e1, "Determination of Individual Components in Spark Ignition Engine Fuels by 100 Meter Capillary (with Precolumn) High Resolution Gas Chromatography," ASTM International, West Conshohocken, PA, www.astm.org.

These data represent typical results.
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Application Note SI-01297