Application Note SI-01295

Detailed Hydrocarbon Analysis of Spark Ignition Engine Fuels by GC using ASTM D 6729

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Introduction

This application note covers the determination of individual hydrocarbon components of spark ignition engine fuels. The method is commonly referred to as detailed hydrocarbon analysis, or DHA. It is also applicable to mixtures containing oxygenate blends (MTBE, ETBE, TAME, ethanol, etc) with boiling ranges up to 225 °C and other light liquid hydrocarbon mixtures typically encountered in petroleum refining operations, such as blending stocks (naphthas, reformates, alkylates, etc). Individual component concentrations and precision are determined in the range of 0.01 to approximately 30 mass%. Interfering co-elution of olefins above C7 is possible, especially for samples containing significant amounts of olefins. Therefore, samples that contain an olefin concentration greater than 25 % are not well suited to this analysis.

Instrumentation

Technique: Varian 450-GC Gas Chromatograph
Injector: 1177, split/splitless, 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

Column: Varian CP-Sil PONA CB™, 100 m x 0.25 mm x 0.5 µm (pn: CP7530)

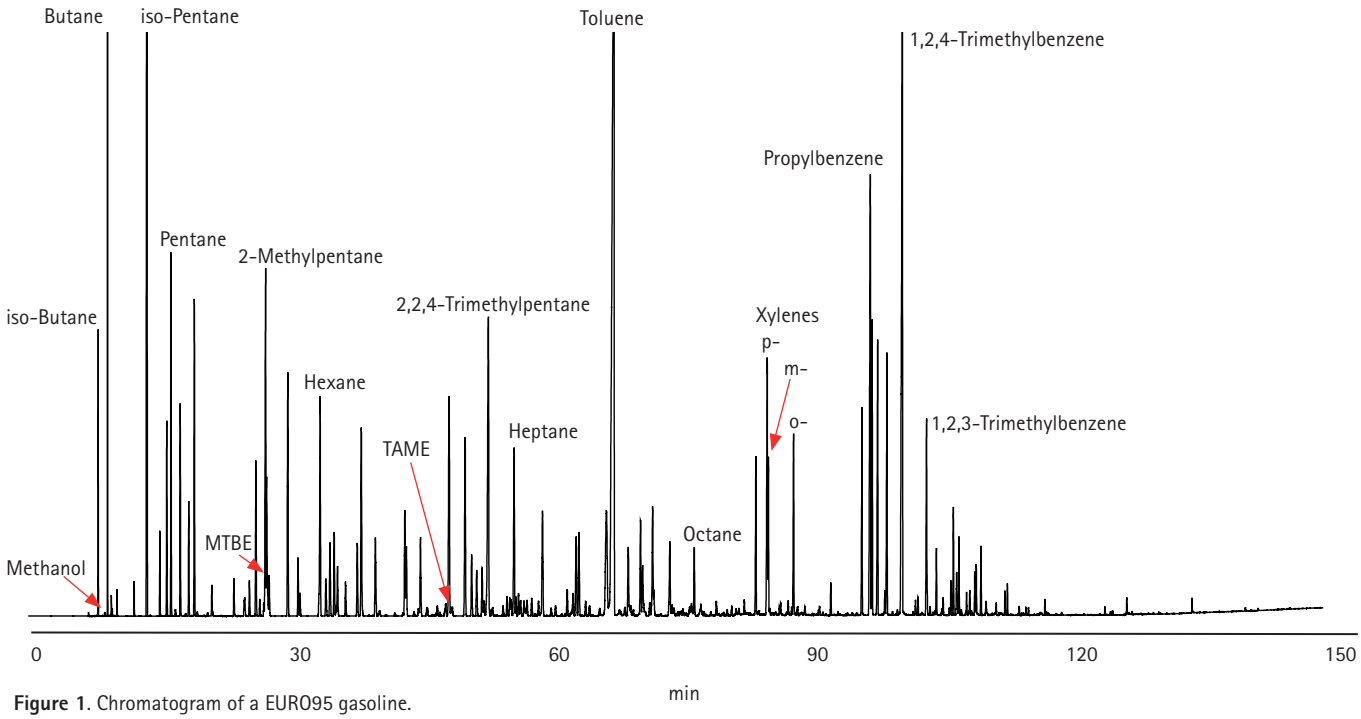

Figure 1. Chromatogram of a EURO95 gasoline.

Conditions

Sample Size: 1 µL
Carrier Gas: Helium, 45 psi
Injector: 1177, 250 °C, split 200 mL/min
Detection: FID, 300 °C
Temperature: 0 °C (15 min), @ 1°C/min to 50 °C, @ 2°C/min to 130 °C, @ 4°C/min to 270 °C (10 min)

Results and Discussion

A calibration mixture containing n-alkanes was used to calculate the Kovats indices of all components in the sample. These indices are compared with known indices in the database and peaks assigned accordingly. A more detailed view of a part of the chromatogram is shown in Figure 2.

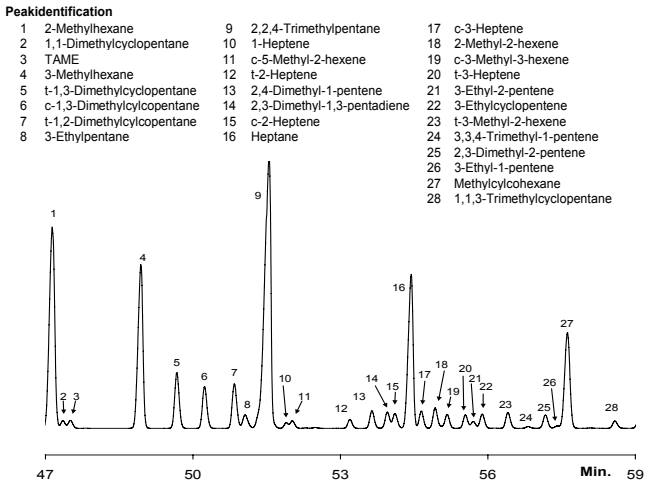

Figure 2. Detailed view of the gasoline chromatogram of Figure 1.

This results in a detailed hydrocarbon analysis report shown in Table 1.

Table 1. Detailed hydrocarbon analysis report.

DHA

Analysis according to ASTM D6729

Sample Info	N.A.		
Sample Type	Sample		
Date Analysed	05 Jan 2006, 00:27:23	Date Printed	31 Jan 2006, 14:45:32
Analyst	Coen	Vial	1
Data File	\GC-DATA\DHA Software test\ASTM D6729 COEN\EURO15_1.DATA		
Method	\DHA Software test\ASTM D6729 COEN\ASTM D6729 COEN.dha		
Description	EURO15_1		
Instrument	Varian 450 DHA		

Detailed Hydrocarbon Analysis

ID	RT	CRT	Index	Name	Area	Area Pecent	Weight Percent	Volume Percent
1	6.69	6.69	300.16	propane	47.317	0.007	0.009	0.013
2	7.78	7.78	354.29	iso-butane	4776.456	0.709	0.925	1.207
3	8.52	8.47	385.03	methanol	113.174	0.017	0.053	0.049
4	8.83	8.83	400.02	butane	35205.549	5.223	6.332	7.950
5	9.26	9.26	407.93	t-2-butene	420.326	0.062	0.087	0.110
6	9.37	9.37	410.01	neo-Pentane	151.352	0.022	0.027	0.032
7	9.90	9.90	419.29	c-2-butene	596.877	0.089	0.124	0.151
8	11.82	11.82	449.19	cyclobutane	866.582	0.129	0.117	0.085
9	13.29	13.11	466.68	iso-pentane	71515.343	10.609	11.873	13.922
10	14.70	14.70	486.03	1-pentene	2605.578	0.387	0.451	0.515
11	15.49	15.49	494.88	2-methyl-1-butene	6216.386	0.922	1.075	1.202
12	15.97	15.97	499.99	pentane	13097.790	1.943	2.175	2.523
13	16.46	16.46	504.20	2-methyl-1,3-butadiene	206.768	0.031	0.043	0.048

All components are reported with retention time, peak area, peak area%, weight% and volume%.

To ensure accurate results, the DHA software calculates peak symmetry. Depending on the peak skewing, a corrected retention time is calculated, as well as 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 by hydrocarbon type. These groups include cyclic-, iso- and normal saturates and unsaturates, aromatics and oxygenates. Each group is reported based on carbon number in a weight and volume percent profile (Table 2).

Table 2. Weight percent profile report.

DHA

Analysis according to ASTM D6729

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Sample Type	Sample							
Date Analysed	05 Jan 2006, 00:27:23					Date Printed	31 Jan 2006, 14:45:32	
Analyst	Coen					Vial	1	
Data File	\GC-DATA\DHA Software test\ASTM D6729 COEN\EURO15_1.DATA							
Method	\DHA Software test\ASTM D6729 COEN\ASTM D6729 COEN.dha							
Description	EURO15_1							
Instrument	Varian 450 DHA							

Weight Percent Profile

	Saturates			Unsaturates					
Carbon	Cyclic	Iso	Normal	Cyclic	N+ Iso	Aromatics	Oxyg	Unknown	Total
1							0.05		**0.05**
2									
3			0.01						**0.01**
4	0.12	0.93	6.33		0.21		0.12		**7.70**
5	0.26	11.90	2.17		3.34		1.49		**22.17**
6	2.07	5.59	1.51		4.41	0.66	0.06		**14.47**
7	2.22	2.27	1.22		3.24	12.41		0.01	**21.75**
8	1.30	8.21	0.38		0.05	3.91		0.13	**13.90**
9	0.13	0.72	0.04		0.01	14.21		0.00	**15.17**
10	0.09	1.18	0.08			2.72		0.19	**4.07**
11		0.03	0.01			0.12		0.09	**0.16**
11+	0.00					0.01		0.12	**0.01**
Total	**6.18**	**30.83**	**11.76**		**11.25**	**34.02**	**1.72**	**0.54**	

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

Table 3. Physical properties report.

DHA

Analysis according to ASTM D6729

Sample Info	N.A.		
Sample Type	Sample		
Date Analysed	05 Jan 2006, 00:27:23	Date Printed	31 Jan 2006, 14:45:32
Analyst	Coen	Vial	1
Data File	\GC-DATA\DHA Software test\ASTM D6729 COEN\EURO15_1.DATA		
Method	\DHA Software test\ASTM D6729 COEN\ASTM D6729 COEN.dha		
Description	EURO15_1		
Instrument	Varian 450 DHA		

Physical Properties Report

%OFF	TBP °C	D86 °C	Property		
IBP	-11.7	36.8	MON Value	97.6	
5%	-0.5	43.5	RON Value	106.5	
10%	27.8	44.8			
20%	27.8	46.4	Reid Vapor P.	13.6	mm Hg
30%	42.0	53.7			
40%	63.3		Net Heat	43.0	kJ/g
50%	80.5	80.9	Gross Heat	46.1	kJ/g
60%	99.2				
70%	110.6	109.9	Density	0.7537	g/ml
80%	133.0	128.8			
90%	164.7	153.0			
95%	169.4				
FBP	193.9	174.8			

The repeatability of the system is determined by analyzing a reference sample multiple times (Table 4). The table depicts a selection of test results. Individual analysis data is includes average and standard deviation (including the ASTM method specified "standard deviation/average" value) as well as physical properties such as MON (Motor Octane Number), RON (Research Octane Number), density, mass% for selected components such as TAME, benzene and toluene, total aromatics and total olefins.

Table 4. Repeatabilty values of a EURO95 gasoline analysis.

File	Mon	Ron	Density	Mass% TAME	Mass% Benzene	Mass% Toluene	Mass% Aromatics Total	Mass% Olefins Total
1	94.8	103.0	0.7508	0.064	0.657	12.39	32.59	13.05
2	94.9	103.2	0.7499	0.063	0.653	12.41	32.53	14.17
3	95.2	103.4	0.7484	0.064	0.664	12.39	31.90	14.45
4	95.4	103.7	0.7520	0.064	0.652	12.48	33.36	13.91
5	95.4	103.7	0.7524	0.064	0.654	12.62	33.37	13.93
6	94.4	102.6	0.7495	0.065	0.667	12.48	31.95	13.13
7	94.9	103.3	0.7536	0.062	0.645	12.48	33.57	12.59
8	94.6	102.8	0.7512	0.064	0.656	12.40	32.62	12.89
9	94.4	102.5	0.7522	0.063	0.630	12.57	33.33	12.28
10	96.3	104.6	0.7525	0.062	0.622	12.52	33.42	14.65
11	95.6	104.0	0.7532	0.062	0.624	12.56	33.48	13.55
12	96.2	104.7	0.7565	0.062	0.620	12.74	34.71	13.71
13	96.2	104.8	0.7570	0.061	0.609	12.66	35.22	13.98
14	96.8	105.2	0.7526	0.063	0.628	12.51	33.37	15.76
15	96.9	105.4	0.7566	0.062	0.618	12.75	34.90	15.16
16	96.5	104.7	0.7516	0.062	0.620	12.44	32.72	15.54
Average	95.5	103.9	0.7525	0.063	0.639	12.525	33.315	13.922
St. dv.	0.85	0.94	0.0025	0.0011	0.0190	0.1172	0.9676	1.0168
St. dev (%)	0.89	0.91	0.33	1.8	2.98	0.94	2.90	7.30
St.dev/Av	0.009	0.009	0.003	0.018	0.030	0.009	0.029	0.073

Table 4 indicates the excellent repeatability obtained. The ASTM D 6729 method requires that the standard deviation/ average value be less than or equal to 0.1. The Varian 450-GC based DHA system used to generate data for performs well within ASTM specifications. Figures 3 and 4 depict the repeatability and confidence windows as specified in the ASTM method.

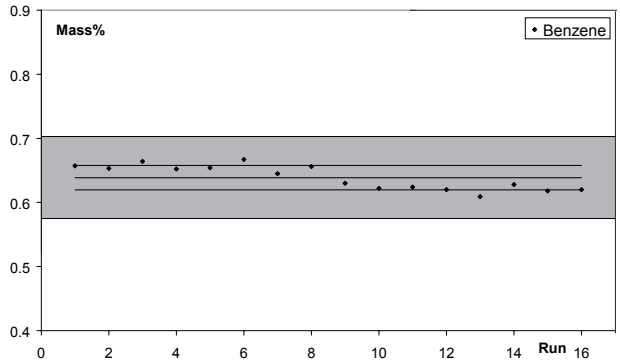

Figure 3. Repeatability values of mass% benzene.

In Figure 4, the mass% of benzene, toluene and total aromatics is shown compared to the average, the achieved standard deviation and the method specified standard deviation.

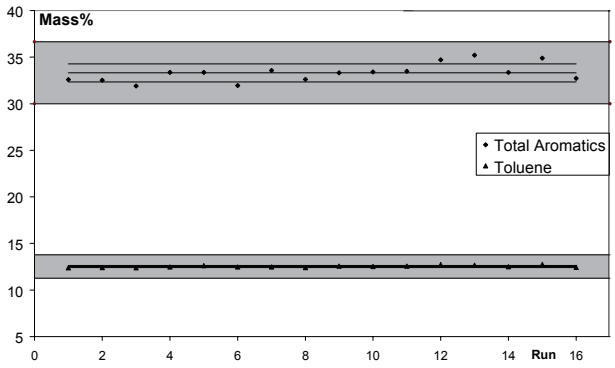

Figure 4. Repeatability figures of mass% tolene and total aromatics.

Conclusion

The Varian 450-GC gas chromatograph and DHA software generate excellent results in accordance with the performance requirements of ASTM D 6729. Mass (m/m) results within 0.001 % are produced as required by the method. By using the density properties of each component, its volume% is calculated and reported. The DHA software also groups the components by type (normal, cyclic, iso-saturated and unsaturated hydrocarbons, aromatics and oxygenates) and can be represented in either mass% or volume%.

Reference

ASTM Standard D 6729-04, "Determination of Invidual Components in Spark Ignition Engine Fuels by 100 Meter Capillary High Resolution Gas Chromatography," ASTM International, West Conshohocken, PA, www.astm.org.

These data represent typical results.
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