

Detailed Hydrocarbon Analysis of Spark Ignition Engine Fuels by GC using ASTM D6729

Application Note

INTRODUCTION

It is vital for quality control purposes that spark ignition engine fuels are analysed via ASTM D6729. This application note covers the determination of individual hydrocarbon component of spark ignition engine fuels, commonly known as detailed hydrocarbon analysis (DHA). The method is applicable to gasolines containing oxygenate blends (MTBE, ETBE, TAME and ethanol), with boiling point ranges up to 225°C and other light liquid hydrocarbon mixtures typically encountered in petroleum refining operations such as blending stocks (naphtha's, reformates and alkylates).

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.

EXPERIMENTAL

A calibration mixture containing n-alkanes was used to calculate the Kovats indices of all components in the sample. Table 1 details the analytical parameters used in this applicationd.

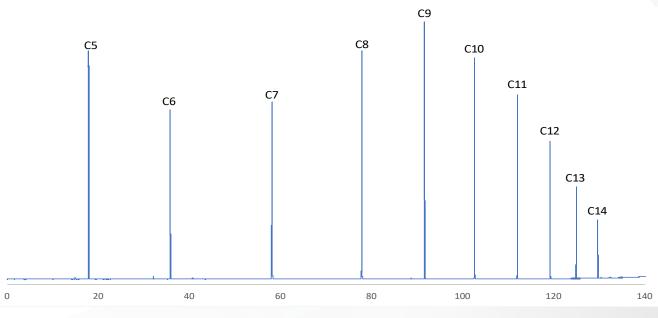
The DHA software, Eclipse, is capable of grouping individual components by hydrocarbon type, including cyclic-, iso-, normal saturates, unsaturates, aromatics and oxygenates. Each group is reported based on carbon number in a weight and volume percent profile.

RESULTS

Once the Kovat indices were generated, they were compared with known indices in the database and peaks were assigned accordingly. Figure 1 shows a C_5-C_{14} (peaks 1-10) n-paraffin calibration standard.

Table 1. Analytical Conditions of GC-MS

Conditions			
Injector	S/SL at 250°C,		
	split 200mL/min		
Column	100m x 0.25m x 0.50µm		
Oven Conditions	0°C (15 min) 1°C/min to 50°C, 2°C/min to 130°C, 4°C/min to 270°C (10 min)		
Carrier	Helium at 43.100 Psi		
Detector	FID at 300°C		
Peak Identification	Unknown hydrocarbons		

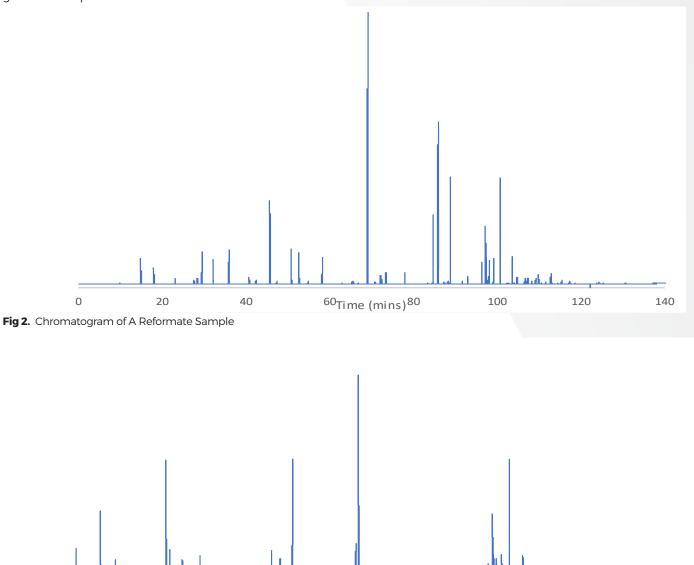


Time (min)





Figure 2 shows the chromatogram of a reformate sample whereas Figure 3 shows the chromatogram of a gasoline sample.



70 Time (mins) 80

90

100

Table 2. Group Report in Mass % of Reformate Sample

110

120

130

140

60

Fig 3. Chromatogram of A Gasoline Sample

20

10

0

The Eclipse data processing software allows reports to be configured depending on the DHA analysis performed. Highly detailed reports are generated with a breakdown of each individual component. The analysis report can be customised to include peak area, peak area % and volume %. Table 2 shows the group report in Mass Percentage (%) for a reformate sample analysed to ASTM D6729 specification.

30

40

50

	n-Paraf	Naph	Arom	Unk	Total
C2	0.00	0.00	0.00	0.01	0.01
C3	0.00	0.00	0.00	0.00	0.00
C4	0.04	0.00	0.00	7.73	7.77
C5	2.04	0.39	0.00	0.01	2.43
C6	6.72	0.77	0.00	0.02	7.51
C7	5.39	0.05	0.02	3.79	9.25
C 8	22.95	4.87	0.02	1.44	29.29
C9	20.63	0.34	6.03	0.22	27.21
C10	1.64	4.89	3.25	2.91	12.68
C11	0.49	0.00	0.04	0.87	1.40
Heavy	0.13	0.01	0.35	1.96	2.45
Total	60.03	11.31	9.71	18.96	100.0

BEYOND MEASURE

To ensure accurate results, the DHA software calculated peak symmetry. Depending on peak skewing, a corrected retention time is calculated.

Repeatability of TAME, benzene, toluene, aromatics and olefins in a gasoline sample were tested using 16 consecutive injections. ASTM D6729 states that repeatability must be less than or equal to 0.1 for the system to be suitable for hydrocarbon analysis. The repeatability is based upon standard deviation/average. Table 3 shows the summarised data for the repeatability study, with figures 4-6 show the repeatability of the 16 injections, in which all pass ASTM specification.

Table 3. Repeatability values of a Gasoline Sample (n=16)

	Mass % TAME	Mass % Benzene		Mass % Aromatics	Mass % Olefins
Average	0.063	0.639	12.525	33.315	13.922
Std Dev	0.0011	0.0190	0.1172	0.9676	1.0168
RSD %	1.8	2.98	0.94	2.90	7.39

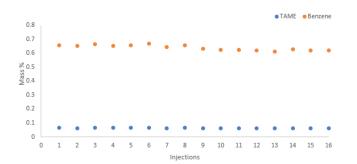


Fig 4. Repeatability data of TAME and Benzene

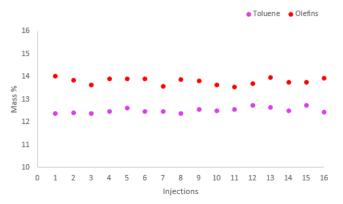


Fig 5. Repeatability data of Toluene and Olefins



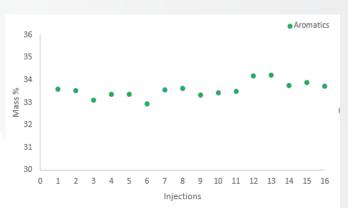


Fig 6. Repeatability data of Aromatics

It is critical to the ASTM D6729 method that three critical pairs are separated. The resolution and associated specifications can be found in Table 4.

Table 4. Resolution and specifications actual values

Critical Pair	ASTM	Resolution
	Specification	Factor
Benzene & Methyl- cyclopentane	>1.0	3.4
m-xylene & p-xylene	>0.4	1.8
n-Tridecane & 1-methyl- naphthalene	>1.0	12.6

CONCLUSION

The SCION Detailed Hydrocarbon Analyser including the DHA software generates excellent results in accordance with the performance requirements of ASTM D6729. Retention time and Kovats indices are used for identification and quantification. The DHA

software also groups the components by type in which they can be represented in either mass % or volume %. The repeatability of the system was excellent, with all components having a standard deviation/average less than 0.1, the specification detailed by ASTM D6729. Additionally, the separation of the critical pairs was exceeded showing excellent resolution of the components.

SCION Instruments HQ

Livingston Business Centre, Kirkton South Road, West Lothian, EH54 7FA, Scotland, UK Tel: +44 1506 300 200 sales-eu@scioninstruments.com www.scioninstruments.com

SCION Instruments NL BV Stanleyweg 4 4462CN, Goes, Netherlands Tel: +31 113 348926 sales-eu@scioninstruments.com www.scioninstruments.com