



ASTM D6729, Determination of Individual components in spark ignition engine fuels by 100 metre capillary high resolution gas chromatography

KEY WORDS: DHA, D6729, gasoline, spark ignition engine fuels.

INTRODUCTION

Scion Instruments offers the solution for detailed hydrocarbon analysis (DHA). Spark ignition engine fuels consists out of hundreds of hydrocarbon compounds, with this method according to ASTM D6729 these components can be distinguished and analysed.

The ASTM D6729 describes a standard test method for individual components in spark ignition engine fuels by high resolution gas chromatography. The ASTM6729 in comparison to the ASTM6730 does not use a pre column for pre-selection of the components.

Figure 1 shows the SCION Instruments 4X6 GC's which this method is applicable to.



Figure 1. SCION Instruments 4X6 GC

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RESULTS AND DISCUSSION

The DHA ASTM D6729 is specific for detailed individual carbon identification in spark ignition engine fuels and oxygenate blends (MTBE, ETBE, ethanol, etc) with boiling ranges up to 225°C in the concentration range from 0.01 to 30 mass %.

The majority of the hydrocarbons present in the different blends will be determined but there are a few critical compounds that have the capability of co-elution, these are the critical separations. These components are:

- 1-Methylcyclopentane – Benzene
- m-Xylene - p-Xylene
- n-Tridecane - 1-Methylnaphthalene

The Scion instruments 4X6 GC's are fine tuned in accordance with the ASTM method to ensure all specification criteria are met, or exceeded. For even better separation ASTM D6730 is recommended. Figure 2 shows the critical separation of these critical components using a column evaluation mix.

When the sample contains a higher amount of olefins some interfering co-elution may occur, therefore it is stated that this method is less suitable when the sample contains a mass over 25 % of olefins.

The primary identification tool of this application is done with Kovats index. Using this index makes it easier to compare data between multiple systems. This method converts retention time to system independent numbers.

Another advantage of this index is that there are only two physical properties that determine this factor, solubility and the n-alkanes. While in comparison, retention times are dependent on six physical properties.

$$I_i = 100 \times \left[n + (N - n) \frac{\log(t_i - t_0) - \log(t_n - t_0)}{\log(t_N - t_0) - \log(t_n - t_0)} \right]$$

I_i = Kovats retention index peak i .

n = Carbon number n -alkane peak heading i .

N = Carbon number n -alkane peak after i .

t_i = Retention time i .

t_0 = air peak, void time.

Table 1. Analytical conditions

Injector	Splitless 200:1, 250 °C
Column	Scion-DHA
Oven Program	0°C (15 min), 1°C/min to 50°C (0 min), 2°C/min to 130°C (0 min)
Carrier	Helium
Pressure	277 kPa (40 psig, constant pressure)
Detector	FID with ceramic jet, 300°C Air: 300 ml/min, Fuel gas (H ₂): 30 ml/min, Make up (N ₂): 30 ml/min
Inj. Volume	0.2 µl
Autosampler	8400
Software	Compass CDS (with Eclipse plug in)

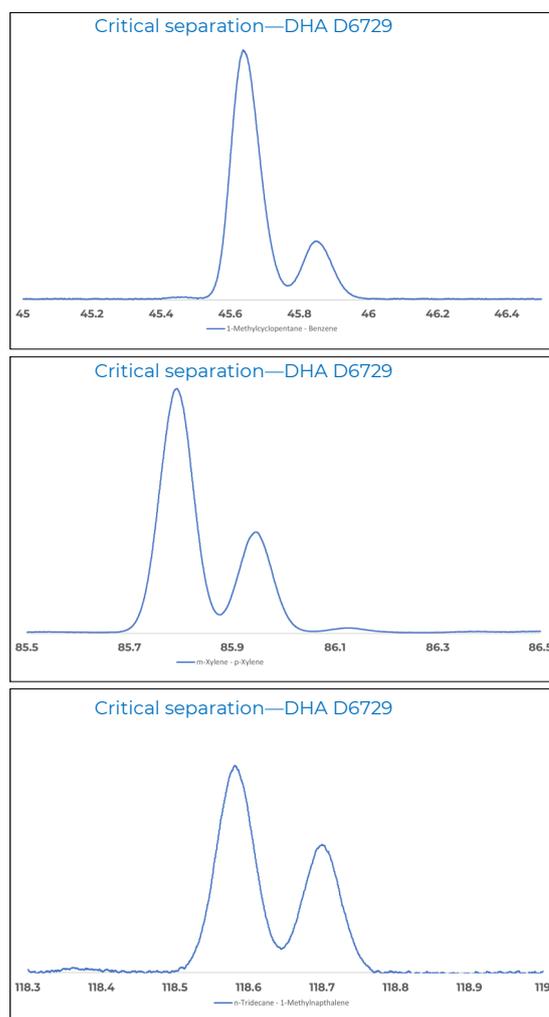


Figure 2: Critical Peak separation of critical components

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To determine the Kovats index a calibration mixture of n-paraffines was injected in the system.

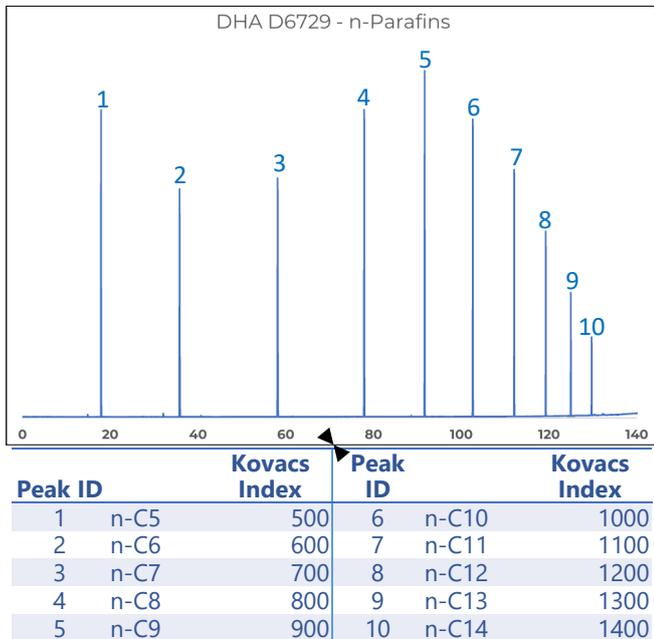


Figure 3: Chromatogram of the calibration mixture to determine the Kovats Index.

The indexes found are compared with known data in the database and the rest of the peaks are signed accordingly.

The next step is to determine the repeatability of seven components by injecting a Reformate sample. The specification set in the ASTM D6729 states that the standard deviation should not exceed 0.1. Table 2 shows an example of a Scion DHA D6729 analyser with excellent repeatability.

Component	Weight Percent					Std Dev
	1	2	3	4	5	
Pentane	2.02	2.04	1.96	1.92	2.07	0.06
Hexane	2.50	2.55	2.45	2.44	2.55	0.05
Benzene	0.51	0.52	0.51	0.51	0.52	0.01
Octane	0.31	0.32	0.32	0.33	0.31	0.01
Ethylbenzene	0.44	0.43	0.44	0.46	0.43	0.01
o-Xylene	0.58	0.57	0.59	0.60	0.57	0.01
1,2,3-Trimethylbenzene	1.48	1.37	1.51	1.49	1.40	0.06

Table 2. Standard deviation of 5 consecutive injections.

A variety of different sample types can be injected in the Scion DHA analyser. Figure 4 shows an example chromatogram of a reformate sample. In the chromatogram a select group of compounds are named but with Eclipse all components are successfully identified.

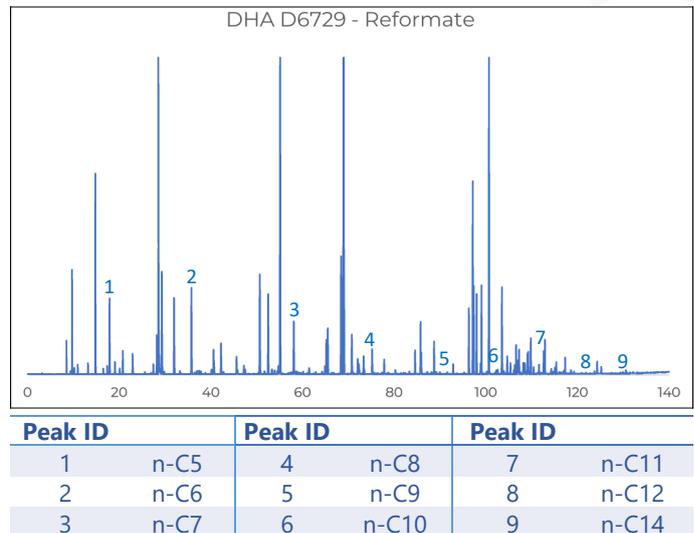


Figure 4: Chromatogram of a Reformate sample.

When analysing all the data the CompassCDS Eclipse plug in will be used. This is an addition to the basic Eclipse and this will provide all the tools to calculate the necessary data. Figure 5 shows an example how the chromatogram will look like and as shown it is also possible to select other ASTM methods.

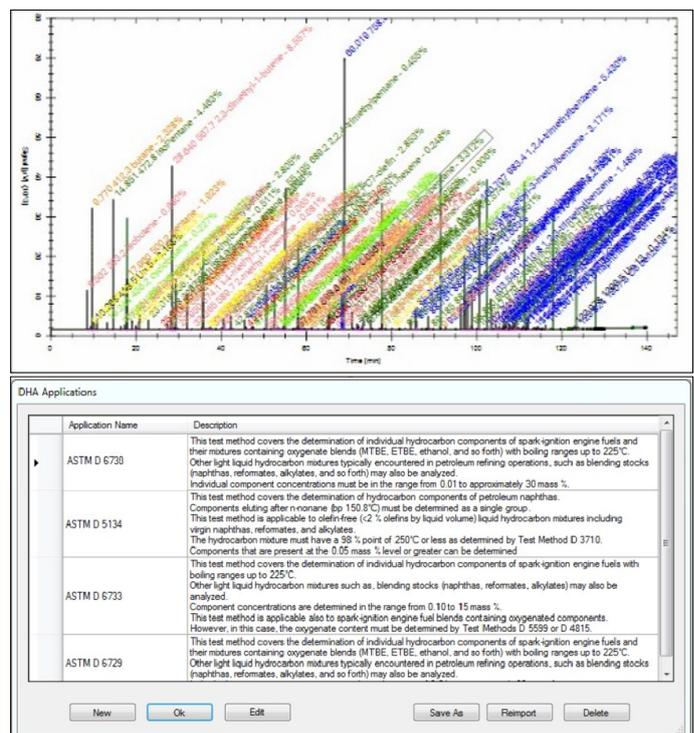


Figure 5: Chromatogram of a gasoline sample using the Compass Eclipse plug in.

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CONCLUSION

Scion Instruments provides a robust, high resolution, complete solution for ASTM D6729 DHA analysis.

The Scion 436 or 456-GC is equipped with industry standard and inert GC hardware. The analyser is easy to service due to great accessibility and minimal downtime.

Another unique feature of the Scion instruments 4X6-GC is the possibility for a dual DHA or even a triple DHA. It is possible to add a channel according to ASTM D6729, D6730, D6733, D5134, Fast DHA or even other analytical channels.

When chosen for a triple channel DHA keep in mind that a XYZ sample like EST Flex or CTC combipal is needed to utilize all the injectors.

Please contact our pre-sales experts for all the possibilities.

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