APPLICATION NOTE

Gas Chromatography

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GC-FID: Sensitive Routine Analysis of Commercial Flex Fuel Gasoline (E85) by ASTM Method D5501-20

Introduction

Since the early 2000's, the US Environmental Protection Agency (EPA) has implemented a series of initiatives to promote the introduction and use of renewable fuels, with a target of 136 billion liters of renewable fuel to be blended with gasoline by 2022[1]. So far, ethanol is the main renewable fuel used for transportation in the US[2,3].

During this same period, the production of vehicles running high-ethanol-content gasoline blends, known as flex fuels, has increased. Such fuels have garnered attention due to their reduction in greenhouse gas emissions (at least 40% in comparison to gasoline)[4], as well as their reduced volatility/vapor loss during transport and storage when compared to traditional high-petroleum gasoline blends[5]. Before their use, flex fuels need to be analyzed to determine the amount of ethanol and methanol they contain, to support the assessment of product quality for determination of their final use.

ASTM Method D5501[6], last updated in 2020, provides guidelines for analysis of flex fuels using a 150-meter Detailed Hydrocarbon Analysis (DHA) analytical column. Flex fuels are permitted to contain between 51% and 83% w/w ethanol, whereas methanol content cannot exceed 0.6% w/w. The wide range of target analyte concentrations necessitates a robust calibration procedure. The long analytical column allows for enhanced resolution of methanol from co-eluting C4 hydrocarbon isomers.

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This application note shows the performance of the PerkinElmer GC 2400™ System for the analysis of E85 according to ASTM Method D5501. The GC 2400 System provides ideal separation efficiency and quantitative repeatability for ASTM Method D5501-20 analysis. PerkinElmer SimplicityChrom™ Chromatography Data System (CDS) Software and the detachable touchscreen interface allow for intuitive, high-throughput laboratory workflows and the real-time monitoring of data , anywhere the operator is connected to the VPN. The PerkinElmer Elite DHA-150 column provides an inert separation environment and excellent peak shape for polar hydrocarbon analysis.

PerkinElmer GC 2400 System.

Experimental

Table 1: GC Parameters.

GC Parameters		
Instrument	PerkinElmer GC 2400 System	--
Injector	Capillary Split/Splitless (CAP) with Autosampler	--
	Advanced Green Inlet Septum	N9306218
	Green FocusLiner	N6502041
	5 uL Autosampler Syringe	N6402186
Detector	Flame Ionization Detector (FID)	--
	Grade 5 Hydrogen, 35 mL/min	--
	Grade 5 Air, 400 mL/min	--
	Grade 5 Nitrogen, 25 mL/min	--
Gas Filters	Triple Filter (Hydrogen & Nitrogen)	N9306110
	Moisture/Hydrocarbon Trap (Air)	N9306117
Analytical Column	PerkinElmer 150 m x 0.25 mm x 1.0 µm	N6107239
	Graphite/Vespel Ferrules, 0.4 mm I.D.	09920104
Software	SimplicityChrom CDS Software	--

Table 2: Measurement conditions.

Conditions	
Carrier	Grade 5 Hydrogen, linear velocity control at 21 cm/sec
Septum Purge	3 mL/min
Split	300 mL/min
Injection Volume	0.5 µL
Injector Temp.	250 °C
Detector Temp	300 °C
Oven	60 °C for 15 min, 30 °C/min to 250 °C, hold for 23 min

Calibration standards spanning 20%-99% w/w ethanol, 0.1% - 0.6% w/w methanol, and 0.5%-10% w/w heptane were purchased from Spectrum Quality Standards (Houston, TX), with heptane as the representative hydrocarbon standard. Isooctane diluent was purchased from VWR (Radnor, PA). E85 gasoline was purchased from a local gas station in Stamford, CT.

Following triplicate blanks, calibration standards were analyzed and the measurements were performed for repeatability. Linear regression was performed for the three analytes. The calibration curve was considered linear if the correlation coefficient, R^2, satisfied the criterion $R^2 \geq 0.995$ over the range analyzed. After calibration, a fourth blank was employed prior to the E85 sample. The E85 sample was run as a neat solution and the measurement was performed five times.

Method detection limit (MDL) analysis was performed in accordance with USEPA guidelines[3]. In brief, an ethanol standard was prepared at an estimated concentration of 10x the anticipated MDL by diluting the lowest concentration calibration standard in isooctane. The prepared ethanol standard was analyzed seven times. The MDL was calculated using the following formula:

$$MDL_{ethanol} = SD_{ethanol} * \text{Student's t}$$

where SD is the standard deviation of the seven ethanol standard trials and the value of Student's t is 3.14, which corresponds to the one-handed t-test value at 6 degrees of freedom and 99% confidence.

The calibration procedure was successful, with R^2 meeting the criterion for each analyte regression, as shown in Figure 1. Figure 2A shows a calibration standard chromatogram. The barely detectable methanol peak highlights the vast difference in calibrated concentrations between methanol and ethanol. Figure 2B shows the E85 flex fuel sample chromatogram. ASTM Method D5501-20 warns that small, polar organic compounds, such as methanol and ethanol, are prone to significant peak tailing. In our case, Figure 2C demonstrates no observable peak tailing for these compounds. The Elite DHA-150 column provides an inert flow path, creating excellent gaussian peak shapes for small polar organic compounds that do not differ significantly in appearance from neighboring nonpolar gasoline hydrocarbons.

Results and Discussion

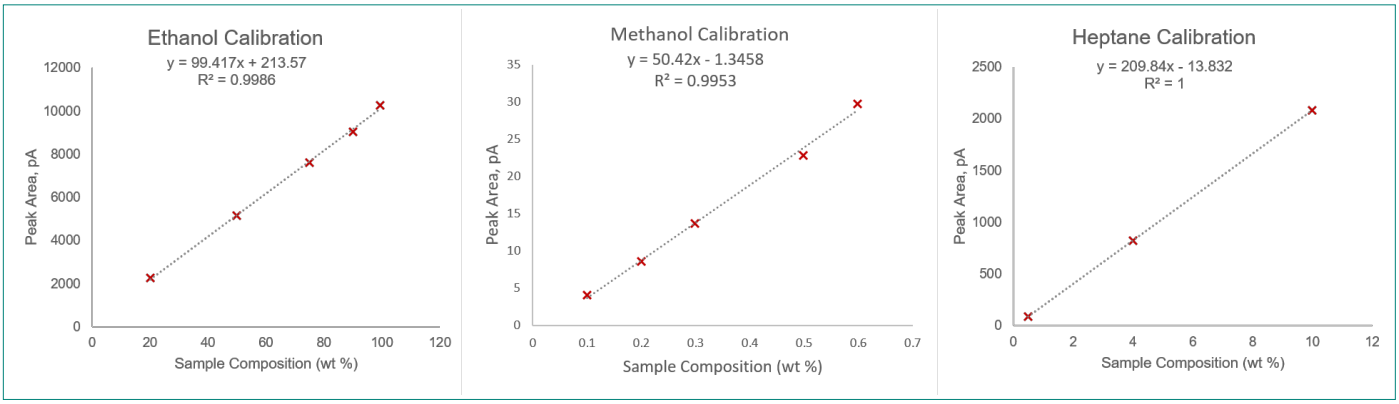

Figure 1. Calibration set results for ethanol, methanol, and heptane. Note: In 3 of the 5 standards, heptane was kept at a 10% concentration; results are presented for this average.

The system displayed good analytical precision. Table 1 shows that ethanol was measured in the flex fuel with 1.15% relative standard deviation (RSD), indicating very high repeatability. The RSD for methanol was slightly greater but still within an acceptable range, a result of its low concentration in the sample. These data demonstrate the robustness of the GC 2400 System for fuel alcohol analysis over a wide range of sample concentrations, making it an ideal solution for ASTM D5501-20 analysis.

Although it is beyond the scope of ASTM Method D5501-20, a method detection limit (MDL) study was conducted to exemplify the wide analytical dynamic range of the GC 2400 System with FID Detector. A standard measured at ~0.03% concentration was analyzed in seven replicates; these results are shown in Table 2. An MDL of 0.0025% was obtained and the upper confidence limit (UCL) and lower confidence limit (LCL) concentrations are shown in Table 3. Considering that this method is capable of quantifying 99 wt% ethanol, it is remarkable that such low detection limits are achievable, spanning over five orders of magnitude difference.

Conclusion

The analysis of Flex Fuels (E85) according to ASTM D5501 is important to determine content of ethanol and methanol in fuels for assessing product quality. The results performed by the GC 2400 System either met or exceeded the requirements of ASTM D5501. The GC 2400 System displayed good analytical precision while demonstrating robustness for fuel alcohol analysis over a wide range of sample concentrations.

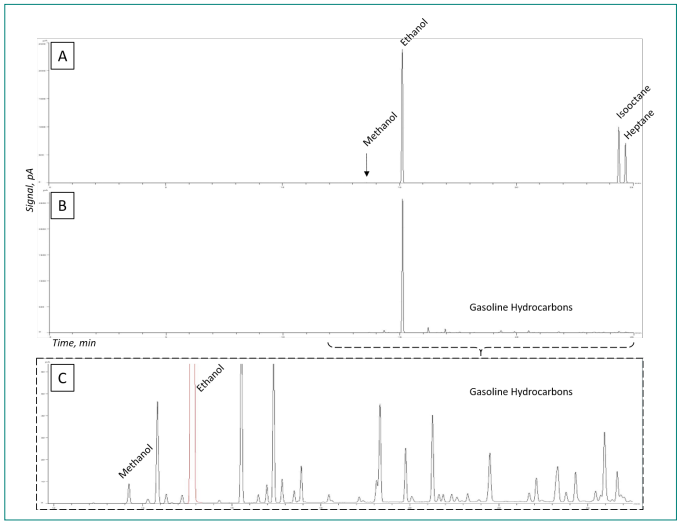

Figure 2. Chromatograms of an analytical standard (A), sample chromatogram (B), and close-up of low-level sample components (C).

Table 3. Repeatability test results from n=5 sample analyses.

Component	Commercial E85 Sample Alcohol Composition (wt %)						
	Run 1	Run 2	Run 3	Run 4	Run 5	*Average*	*RSD*
Ethanol	80.2	78.4	80.1	78.5	80.0	***79.4***	***1.15%***
Methanol	0.56	0.55	0.54	0.51	0.53	***0.54***	***3.63%***

Table 4. MDL concentration results showing high precision at the lowest end of the linear range.

Ethanol MDL Composition (wt %)									
Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Average	SD	RSD
0.030	0.031	0.031	0.030	0.031	0.031	0.029	*0.031*	7.84 E04	2.57%

Table 5. Method detection limit and upper and lower confidence limits.

Ethanol Detection Limits (wt %)		
MDL	LCL	UCL
0.0025	0.0016	0.0054

References

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