Analysis of Denatured Fuel Ethanol using ASTM Method D5501-09

Application Note

HPI/Energy/Renewable Fuels

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Abstract

Denatured fuel ethanol is the feedstock used to make different types of high ethanol content motor fuels. Before it can be used, the amount of ethanol and methanol must be measured to assure product quality. ASTM method D5501-09 uses high resolution gas chromatography to perform this analysis. In this paper, the Agilent 7890A GC system was configured to run D5501-09. Excellent system performance and precision were demonstrated using the 7890A GC. Combined with the Agilent MultiTechnique ChemStation, this system offers a complete, automated solution for denatured fuel ethanol analysis.

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Introduction

Ethanol is a key additive in gasoline, serving both as a smog reducer as well as a fuel supplement to reduce the overall use of petroleum. It is relatively easy to produce by fermenting sugars obtained from food crops such as corn and sugar cane. However, the future of ethanol fuel cannot rely on food. To solve this problem, researchers are investigating ways to convert polymeric biomass carbohydrates, such as cellulose, to fermentable sugars. These sugars can then be used as an ethanol fermentation feedstock into the existing production infrastructure.

Whether ethanol comes from food sugars or converted biomass, it is first denatured before use as a motor fuel. Hydrocarbons are common denaturants and ASTM Standard D4806 specifies the types of hydrocarbons that can be used as denaturants [1]. Once the hydrocarbons are added, the product is called denatured fuel ethanol. Commercial fuels are then made by blending denatured fuel ethanol with gasoline. To assure product quality, ASTM has published method D5501-09, which uses gas chromatography to measure the ethanol and methanol content in ethanol fuels [2]. This paper describes the configuration and performance of the Agilent 7890A GC System when running ASTM D5501-09 for the analysis of denatured fuel ethanol.

Experimental

An Agilent 7890A GC System was configured according to D5501-09 and is shown in Table 1. The operating conditions for this method are shown in Table 2. Prior to sample analysis, the GC inlet splitter linearity was checked to assure there was no sample discrimination. A splitter linearity mix was prepared using the procedure described in ASTM Practice D4307 [3]. Ten hydrocarbons ranging from C_5 to C_{11} were gravimetrically blended and the final weight percent of each hydrocarbon in the mix was recorded. This mix was run using the GC conditions shown in Table 2. Calibrations for ethanol, methanol and hydrocarbons were performed using standards obtained from Spectrum Quality Standards, Sugarland, TX USA. After calibration, a commercial denatured fuel ethanol sample was analyzed to determine the ethanol and methanol content.

Results

The splitter linearity test was performed to assure quantitative transfer of all compounds from the inlet to the column without any boiling point discrimination. The test sample contained saturated hydrocarbons between C_5 and C_{11}, which covers the boiling range typically found in denatured fuel ethanol. Using a relative mass response factor of 1, each hydrocarbon in the splitter linearity mix was quantified using a normalized percent calculation. The D5501-09 method specifies that the measured mass percent of each hydrocarbon must match the known mass percent within ±3% relative difference. Figure 1 shows the chromatogram of the splitter linearity mix and the results that meet the ASTM D5501-09 specification. This shows that optimal split injection, with no discrimination, can be easily achieved using the Agilent 7693A ALS fast injection and the Agilent split optimized inlet liner.

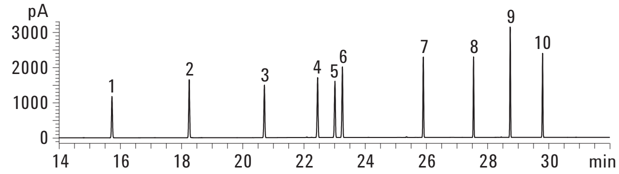
Table 1. The Agilent 7890A GC System Instrument Configuration for ASTM Method D5501

Standard Agilent 7890A GC System Hardware	
G3440A	Agilent 7890A Series GC System
Option 113	150 psi Split/Splitless Inlet with EPC control
Option 211	Capillary FID with EPC control
G4513A	Agilent 7693 Automatic Liquid Sampler
GC Capillary Column	
Analytical Column	PDMS, 150 m × 0.25 mm id × 1.0 µm film
Data System	
G2070BA	Agilent MultiTechnique ChemStation rev B.04.01
Consumables	
5181-1273	5 µL autoinjector syringe
5183-4647	Single taper split liner with glass wool
5183-4759	Advanced green inlet septa
Calibration Standards	
ETOH5501CAL	D5501 Calibration Set
Spectrum Quality Standards PO Box 2346 Sugarland, TX 77487-2346 USA	

Table 2. GC Operating Conditions for ASTM Method D5501

Split/Splitless Inlet	
Temperature	300 °C
Pressure	Helium at 66 psi
Split ratio	200:1
Septum Purge	3 mL/min
Sample Size	0.5 µL injection
Initial column flow	2.34 mL/min, constant flow mode (24 cm/sec average linear velocity)
FID temperature	300 °C
Oven temperature program	60 °C for 15 min 30 °C/min to 250 °C, hold for 23 min

System calibration for methanol, ethanol and hydrocarbons was done by running seven calibration standards using the GC conditions listed in Table 2. Methanol was calibrated between 0.05 and 0.6 wt% while ethanol was calibrated between 93 and 98 wt%. The calibration for the hydrocarbon



	Compound	Known wt%	Calc wt%	Relative difference (%)
1	n-pentane	6.9	7.0	**2**
2	2,4-dimethylbutane	9.5	9.6	**1**
3	2,4-dimethylpentane	8.5	8.6	**1**
4	3-methylhexane	10.1	10.1	**1**
5	2,2,4-trimethylpentane	9.5	9.7	**1**
6	n-heptane	11.4	11.4	**0**
7	n-octane	10.9	10.8	**1**
8	Nonane	9.6	9.6	**1**
9	Decane	13.3	13.3	**1**
10	Undecane	10.3	10.2	**1**

Figure 1. Analysis of the splitter linearity test mix containing saturated hydrocarbons from C_5 to C_{11}. These results meet the D5501-09 criteria for splitter linearity.

response was done using n-heptane between 1.95 and 7.4 wt%. After the calibration data was collected and the peak integration optimized, the individual response factors (R) for methanol, ethanol and n-heptane were calculated at each calibration level. Using the response factor of n-heptane, the relative response factors (RR) for methanol and ethanol were then determined at each level using the formulas described in ASTM Practice D4626 [4].

The D5501-09 method allows a single level calibration using a standard containing methanol and ethanol amounts expected in the users' samples in order to save time and resources. For this paper, the amount of alcohols in the sample was not known, therefore average RRs were calculated from all seven calibration standards and are shown in Table 3. These average RRs were then used to quantify the alcohols found in the sample of denatured fuel ethanol.

Table 3. Calibration Data for Denatured Fuel Ethanol Analysis

n-Heptane	Methanol	Ethanol
Average RR (1.95 – 7.4 wt%)	**Average RR (0.05 – 0.6 wt%)**	**Average RR (93 – 98 wt%)**
1.00	2.97	2.06

A sample of commercial denatured fuel ethanol was obtained from a producer and analyzed using the Agilent 7890A GC System running ASTM method D5501-09. Five aliquots of the sample were each measured two times for a total of ten runs. An example chromatogram is shown in Figure 2. It is important to optimize the peak integration in order to correctly measure the methanol peak area. Failure to do so could add peak response from nearby C_4 hydrocarbons to the methanol peak resulting in results that are too high. An example of optimized methanol peak integration is shown in Figure 3.

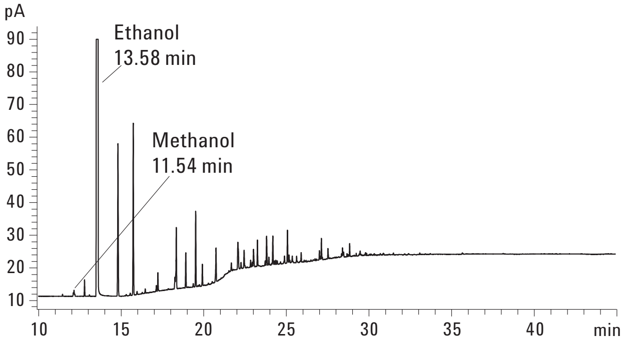


Figure 2. Analysis of a commercial denatured fuel ethanol sample using ASTM method D5501-09.

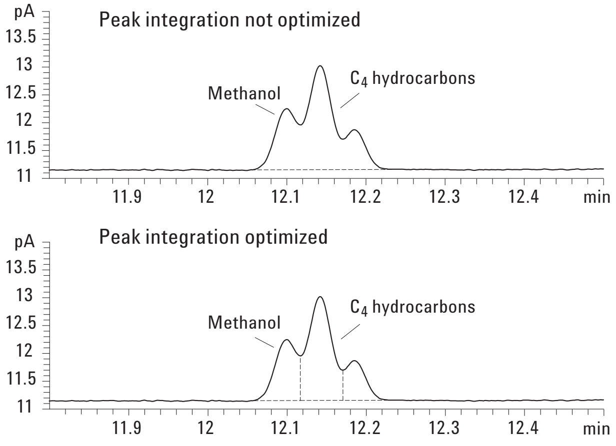


Figure 3. Optimizing the methanol peak integration is important for obtaining correct results.

Quantification of the alcohols in this sample was done using the average RRs calculated in Table 3. For all other peaks in the chromatogram, the n-heptane RR of 1 was used to measure the mass percent. Final reporting of all components was done using a normalized percent calculation as described in the D5501-09 method. The Agilent MultiTechnique ChemStation software can automatically perform both the average response factor calibration as well as the required normalized percent reporting. These results are shown in Table 4. Excellent system measurement precision was obtained for both the low level ethanol content as well as the very high level ethanol content.

Table 4. Results and Precision for the Analysis of Methanol and Ethanol in Denatured Fuel Ethanol.

Run	Methanol	Ethanol
1	0.02	97.81
2	0.02	97.83
3	0.02	97.81
4	0.02	97.82
5	0.02	97.79
6	0.02	97.81
7	0.02	97.78
8	0.02	97.76
9	0.02	97.77
10	0.02	97.74
Avg	**0.02**	**97.79**
Std Dev	**2.18e-4**	**0.03**
RSD	**1.16%**	**0.03%**

Conclusion

The measurement of methanol and ethanol in denatured fuel ethanol can be quite challenging due to the complexity of the hydrocarbon denaturant and the need to quantify near 100% ethanol as well as low level components in the sample. ASTM method D5501-09 uses high resolution gas chromatography to perform this measurement. In this paper, the Agilent 7890A GC Service was configured to run method D5501-09. The system showed no inlet discrimination so that quantitative sample transfer to the column could be made for the wide boiling range components found in denatured fuel ethanol. This was a key factor in the excellent precision shown in this paper. Calibration of a large ethanol concentration as well as a low-level methanol and hydrocarbon concentrations were done using the Agilent MultiTechnique ChemStation. The ChemStation was also able to automate the final calculations and reporting.

References

1. "D4806 - Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel"; ASTM International: 100 Barr Harbor Drive, West Conshohocken, PA, USA, 2010.
2. "D5501-09 Standard Test Method for Determination of Ethanol Content of Denatured Fuel Ethanol by Gas Chromatography"; ASTM International: 100 Barr Harbor Drive, West Conshohocken, PA, USA, 2010.
3. "D4307 - Standard Practice for Preparation of Liquid Blends for Use as Analytical Standards"; ASTM International: 100 Barr Harbor Drive, West Conshohocken, PA, USA, 2010.
4. "D4626 – Standard Practice for Calculation of Gas Chromatographic Response Factors"; ASTM International: 100 Barr Harbor Drive, West Conshohocken, PA, USA, 2010.

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