Fast Determination of Denatured Fuel Ethanol Purity by Two-Dimensional Gas Chromatography

Application

Petrochemical

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Abstract

Two-dimensional gas chromatography not only provides improved resolution, it can also provide much faster analysis times. A two-dimensional gas chromatography system based on a simplified Deans switch design is used to analyze the alcohol content in denatured fuel grade ethanol. By using two short columns of different selectivity, the two-dimensional gas chromatography application completes this analysis 10 times faster than the standard American Society for Testing and Materials D5501 method [1] without the use of cryogenic oven cooling. This easy-to-use system also provides high qualitative and quantitative precision for this measurement.

Introduction

Oxygenated compounds are added to gasoline to improve octane rating and reduce emissions of smog-producing combustion products. Until recently, methyl-tert-butyl ether (MtBE) has been the most widely used oxygenated additive in reformulated gasoline (RFG). However, problems with groundwater contamination by MtBE have led to the designation of ethanol as the preferred gasoline additive.

Fermentation and distillation of biomass is used to produce a fuel grade ethanol that contains 85%–98% ethanol and natural impurities such as water and methanol. Before it can be used as a gasoline additive, fuel ethanol is denatured with approximately 2 to 5 vol% of natural gasoline to make it unsuitable for beverage use. This final product is known as denatured fuel ethanol. ASTM Specification D4806 outlines the performance requirements for denatured fuel ethanol [2].

The overall purity of denatured fuel ethanol must be measured by gas chromatography (GC) to meet the ASTM specifications and to determine the amount of methanol impurity present in the material. Since methanol is also an oxygen containing species, its concentration must be determined since it can affect the resulting properties of the RFG. However the natural gasoline denaturant complicates these measurements because it is difficult to separate methanol and ethanol from the hydrocarbons present in the natural gasoline. ASTM method D5501 uses GC with a 150-meter methyl silicone capillary column and subambient oven temperatures to separate the methanol and ethanol from the low-boiling hydrocarbons [1]. While this approach is effective, the run times are in excess of 40-minutes and the method requires the use of a cryogenic coolant.

Two-dimensional gas chromatography (2-D GC) offers another solution to this analysis that is also faster. By combining two short columns of different selectivity, complete separation of the

polar alcohol from the nonpolar hydrocarbons can be made in much less time than is needed with a single, long column. The primary column can make a fast, yet incomplete separation of the target compounds from the majority of compounds in the matrix. As the target compounds and any interference elute from the primary column, they can be selectively transferred to the secondary column. Complete separation of the target compound from interferences is achieved on this column. This technique has been successfully applied to the analysis of oxygenates and aromatics in bulk gasoline samples [3].

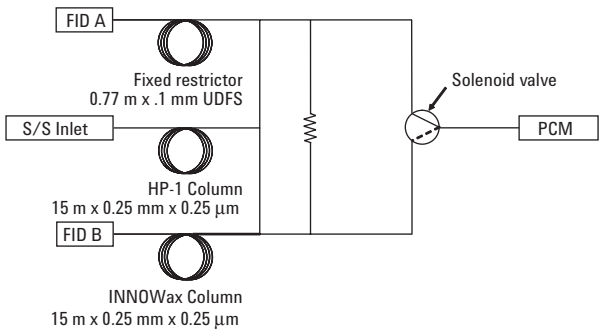

Figure 1. Deans switch configuration for the fast analysis of denatured fuel ethanol with an FID.

Experimental

An Agilent 6890N GC was equipped with a split/splitless injector, a pneumatics control module (PCM), two flame ionization detectors (FIDs) and an automatic liquid sampler. A short, nonpolar HP-1 column was used as the primary column and a polar INNOWax was used as the secondary column. The two columns were linked using a fluidic Deans switch. Figure 1 shows the instrument configuration using this hardware and Table 1 list the details of the hardware configuration.

Determination of electronic pressure control (EPC) pressures, flow rates, and the fixed restrictor dimensions were performed using a Deans switch calculator software program that is specially designed for this system. This calculator program is included with the Deans switch hardware option for the Agilent 6890N GC. All instrument set points required for any successful 6890N based Deans switch application can be quickly and easily determined using this software.

A sample of denatured fuel ethanol containing 0.3 vol% methanol, 95.2 vol% ethanol and 4.0 vol% natural gasoline was prepared using absolute ethanol. The water content of this sample was not measured. A denaturant blank sample was prepared containing 4.0 vol% natural gasoline in isooctane. These samples were used to determine the heart-cut times for the 2-D GC method.

Instrument conditions for this analysis are listed in Table 2. The sample is injected into the split/splitless inlet and is separated on the 15-meter HP-1 primary column. With the solenoid switch in the “off” position, the HP-1 column effuent is directed to FID A. Just before the methanol and ethanol peaks elute from the HP-1 column, the solenoid is automatically set to the “on” position and the HP-1 column effuent is redirected to the INNOWax column. After the ethanol peak has been cut to the INNOWax column, the solenoid valve is set back to the “off” position. The separation of the alcohol peaks from the hydrocarbons is then completed on the INNOWax column and detected on FID B.

Table 1. Agilent 6890 Hardware Configuration for 2-D GC

Standard 6890N GC hardware	
G1540N	Agilent 6890N Series GC
Option 112	Capillary split/splitless inlet with EPC control
Option 210 (2 of each)	FID with EPC control
Option 309	Pneumatics control module with EPC control
SP1 2310-0129	General purpose Deans switch kit, factory installed (may be ordered as an add-on kit for existing 6890 GC Agilent part no. G2855A)
G2613A	Agilent 7683 Autoinjector
Columns	
Primary column	HP-1 column, 0.25 µm film, 15 m × 0.25 mm id (Agilent part no. 19091S-931)
Secondary column	INNOWax column, 0.25 µm film, 15 m × 0.25 mm id (Agilent part no. 19091N-131)
Fixed restrictor*	Deactivated fused silica tubing, 0.38 m × 0.1 mm id (Agilent part no. 160-2635-10)
Data system	
G2070A	Agilent Multitechnique ChemStation
Other consumables	
Agilent part no. 5181-1267	10 µL Fixed tapered needle autoinjector syringe
Agilent part no. 5183-4647	Inlet liner optimized for splitless operation
Agilent part no. 5183-4759	Advanced green septa

*The Deans switch calculator was used to determine the correct EPC pressures for column flows and the dimensions of the fixed restrictor.

Table 2. Instrument Conditions

Split/Splitless injection port	
Temperature	225 °C
Pressure*	25 psi helium
Split ratio	600:1
Injection size	0.2 µL
HP-1 column flow	2.0 mL/min, constant pressure mode
Pneumatics control module (PCM)*	19 psi helium, constant pressure mode
INNOWax column flow	3.0 mL/min
FID temperatures	250 °C
Oven temperature program	70 °C for 3 min, 25 °C/min to 225 °C

*These pressures were calculated using a custom Deans switch software program to achieve the necessary column flow rates.

Results and Discussion

ASTM method D5501 can easily separate methanol and ethanol from the hydrocarbons in the gasoline denaturant. This method achieves the required chromatographic resolution by using a large number of chromatographic plates provided by the very long capillary column and the subambient oven temperatures. Figure 2 shows a typical denatured fuel ethanol analysis using this method. Although the methanol and ethanol separation is completed in 12 minutes, the time required to elute all of the gasoline components can extend to 60 minutes.

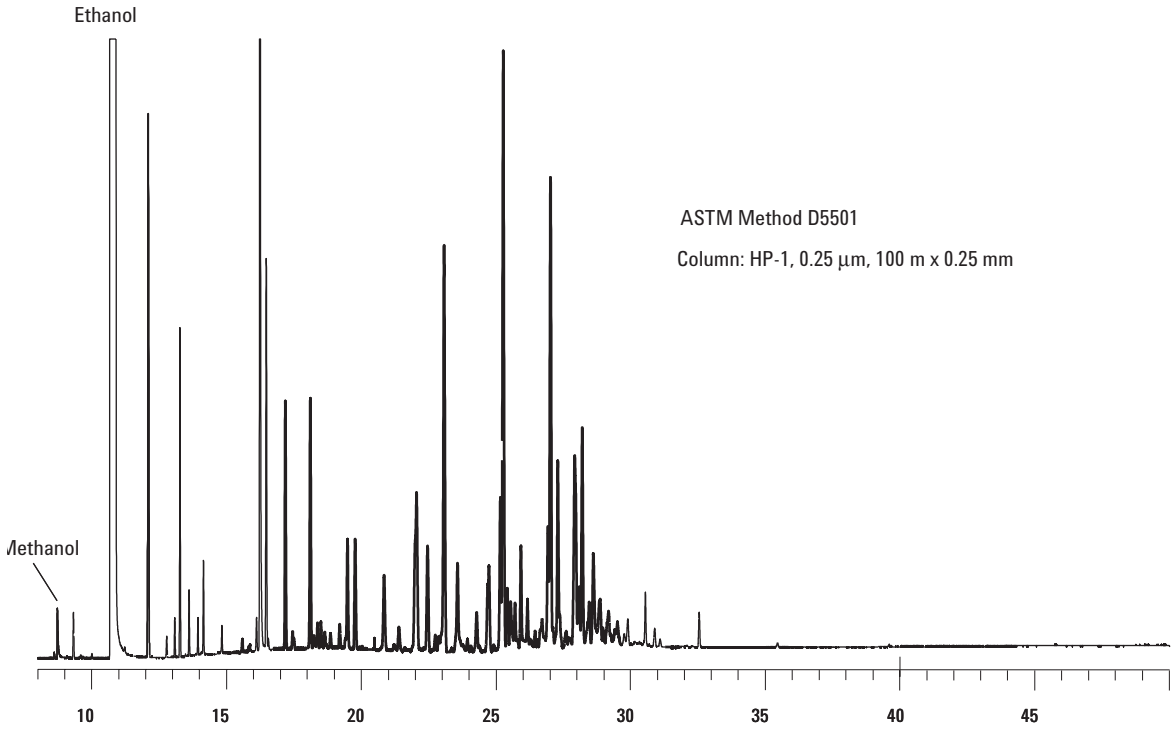

Figure 2. A typical analysis of denatured fuel ethanol using ASTM method D5501. The long column (100 m) and subambient starting temperature (15 °C) contributes to an overall analysis time of 40 minutes or longer.

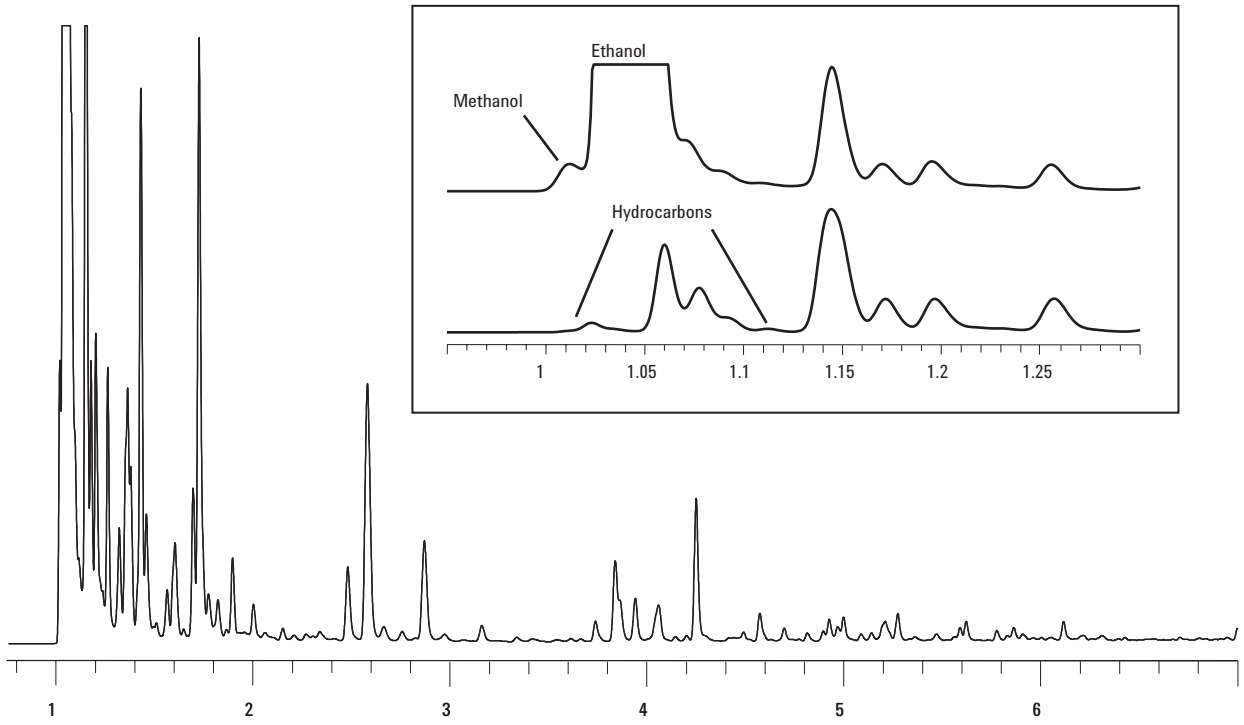

Figure 3. Analysis of denatured fuel ethanol using a much shorter (15 m) HP-1 column. The analysis time is much faster, but the methanol is not separated from the ethanol and there is significant co-elution of the alcohol peaks with hydrocarbons from the natural gasoline. The inset chromatogram shows a comparison of the denatured fuel ethanol sample with a natural gasoline blank.

An easy way to get faster chromatography is to use shorter columns, but one must pay a resolution penalty for the speed gain [4]. See Figure 3. A 15-meter methyl silicone column was used to analyze the fuel ethanol sample in less than 7 minutes. However, the methanol peak is not completely resolved from the ethanol. It also appears that several other compounds are not resolved from the two alcohol peaks. The inset chromatogram in Figure 3 shows a comparison of the denatured fuel ethanol sample with the natural gasoline blank. There are a number of hydrocarbons in the natural gasoline that elute at the same time as the methanol and ethanol with this short capillary column.

Two-dimensional GC can solve this problem by combining two shorter GC columns with different selectivity. For this analysis, a 15-meter HP-1 column was used to perform a preliminary boiling point separation of the alcohols from the bulk of the natural gasoline components. The Deans switch selectively transferred the alcohol peaks and any interferences to a polar INNOWax

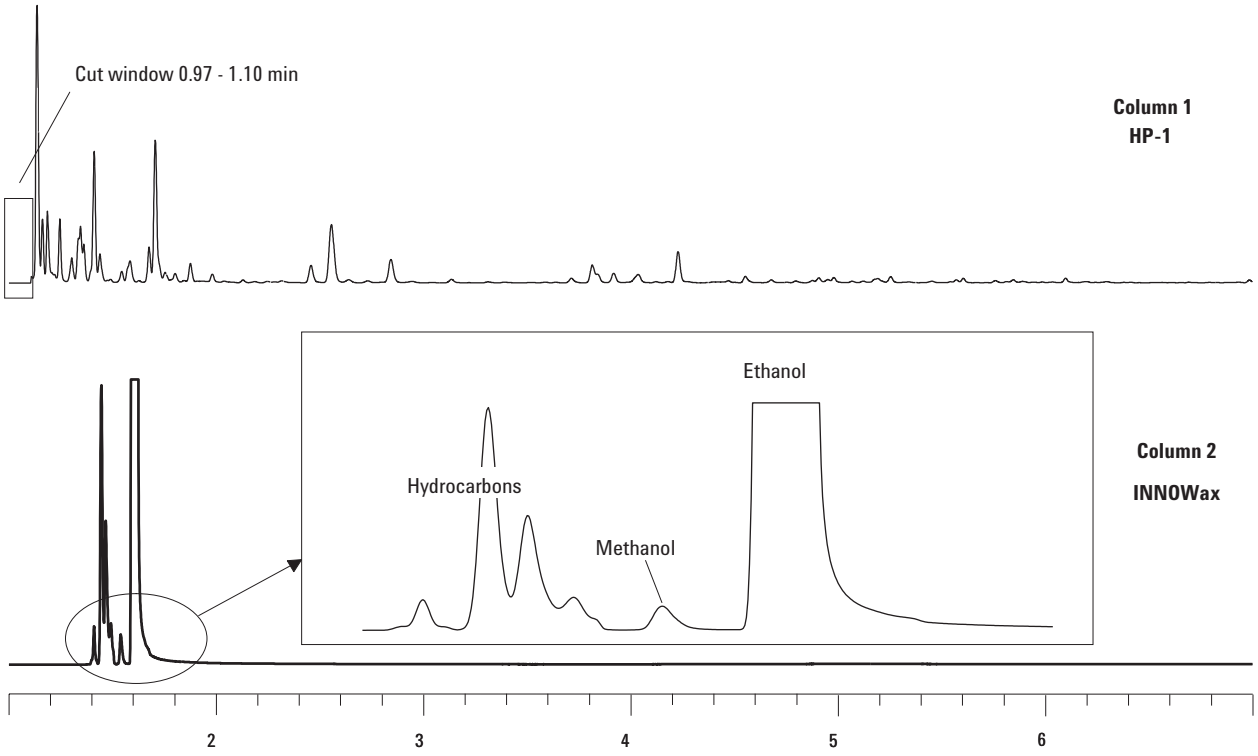

Figure 4. Analysis of denatured fuel ethanol by 2-D GC using a Deans switch to heart cut the alcohol peaks from a 15-m HP-1 column to a 15-m INNOWax column. The heart-cut window is from 0.97 to 1.10 minutes. The chromatographic run is completed in less than 7 minutes using this technique.

column, where the nonpolar hydrocarbons were quickly eluted and the polar alcohols retained and separated. Figure 4 shows the results of this separation using the 2-D GC system. On the HP-1 column, the methanol and ethanol elution time was between 0.97 and 1.10 minutes. This time was use used to heart-cut the alcohols from the HP-1 column to the INNOWax column. The inset chromatogram in Figure 4 shows that the interfering hydrocarbons are separated from the alcohols and the methanol and ethanol are completely resolved.

A sample of the natural gasoline was also run by 2-D GC under the same conditions used for the denatured fuel ethanol analysis. This was done to assure that no other hydrocarbons co-eluted with the alcohol peaks after heart cutting to the INNOWax column. Figure 5 shows that the 2-D GC system using the HP-1 column and the INNOWax column completely eliminated any interference from the gasoline denaturant with the alcohol peaks.

The overall analysis time of this 2-D GC approach is also much faster than the ASTM method. The choice of the INNOWax column was made so that the starting oven temperature could be set to 70 °C, instead of 15 °C used in the original ASTM method. This higher oven temperature allowed the GC recycle time to be approximately 10 minutes shorter, thus reducing the overall run time of the method. The higher temperature also avoids the expense and complication of using cryogens.

The precision of the 2-D GC method was evaluated by running a denatured fuel ethanol sample 30 times over a 5-day period. Table 3 shows the retention time (RT), detector response and volume percent precisions for methanol and ethanol analysis. The high degree of both qualitative (RT) and quantitative precision indicates that the 2-D GC system used for this analysis was stable over extended periods of time.

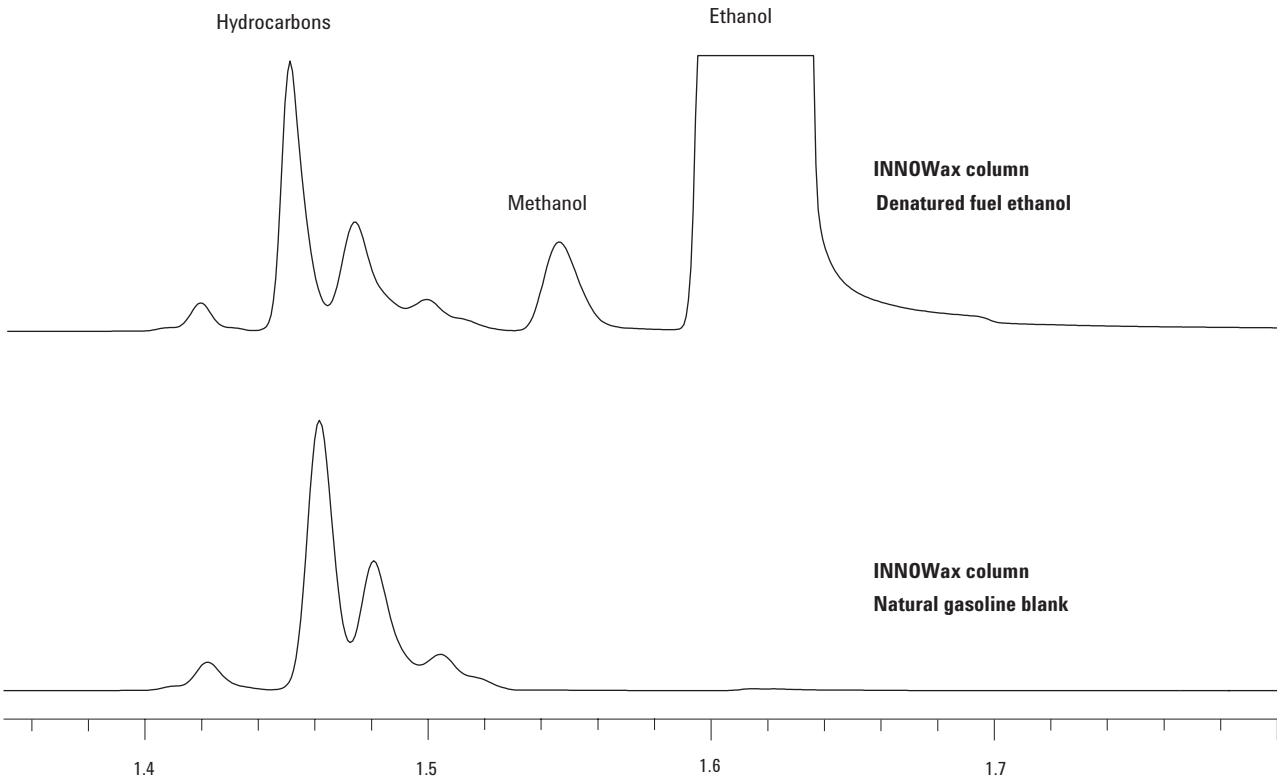

Figure 5. The upper chromatogram shows the analysis of denatured fuel ethanol using the 2-D GC system. The lower chromatograms shows a sample of the natural gasoline denaturant run on the same 2-D GC system. No hydrocarbons in the gasoline blank elute on the INNOWax column at the same time as methanol and ethanol.

Table 3. Measurement Precision for the Analysis of Denatured Fuel Ethanol by 2-D GC

	Methanol			Ethanol		
	RT (min)	**Area counts**	**Vol%**	**RT (min)**	**Area counts**	**Vol%**
Average	1.552	47.92	0.3	1.622	20410.55	95.4
SD	0.0004	0.35	0.002	0.0004	118.93	0.6
%RSD	0.025	0.74	0.7	0.023	0.58	0.6

Conclusion

Two-dimensional GC offers both high resolution of target compounds in complex matrices and a significant improvement in analysis speed when compared to high resolution GC methods that use a single, long capillary column. This is shown for the analysis of ethanol and methanol content in denatured fuel grade ethanol. A 2-D GC system with a simplified Deans switch used two short columns of different selectivity to quickly separate the alcohols in fuel ethanol from the natural gasoline hydrocarbons used as a denaturant. The 7-minute GC analysis time with this system was shown to be nearly 10-times faster than the standard ASTM methodology. The overall run time was also faster since the 2-D method used an initial oven temperature that was well above ambient and did not require cryogenic coolants. This 2-D GC approach also gave precise results over an extended period of time.

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Printed in the USA
April 24, 2003
5988-9460EN

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