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APPLICATIONS

Fast Bioethanol Analysis Following ASTM Method D 5501 Using the New Zebron™ ZB-Bioethanol GC Column

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Abstract
Standard fuel ethanol analysis can take up to 40 minutes following ASTM Method D 5501 and Europe prEN 15376. Using a new, innovative stationary phase, the analysis time for this method is reduced to 5 minutes while still providing complete resolution of methanol and ethanol from all denaturant components. This fast analysis time allows the trucks to be tested before leaving the plant and is suitable for analysis following ASTM Method D 5501 and Europe prEN 15376.

Introduction
Political priorities as well as economic interests have fueled a dramatic growth in the biofuels industry, due much in part to research funding and tax incentives. Currently the world's ethanol production is estimated to be over 16 billion gallons a year.[1] With more bioethanol plants planned or under construction than are currently operating, the usage of fuel grade ethanol or gasoline-ethanol blends will increase significantly.

Many plants today require that the ethanol in a denatured fuel sample be analyzed by gas chromatography (GC) prior to transporting the product. The results of this test are required to be with the truck as it leaves the plant. However, due to the long analysis time needed by the method, results often don't ship with the truck, but are faxed ahead to the truck's final destination.

The current analytical procedure for ethanol in a denatured fuel product is covered under ASTM Method D 5501 and Europe prEN 15376. The methodology uses a long (100 or 150 meter) GC column and suggests a program with an analysis time up to 40 minutes to resolve methanol and ethanol from the denaturant, which is typically gasoline. The long run time is necessary to resolve these components because of the complexity of gasoline, which contains thousands of components, many of which can co-elute with methanol and ethanol.

In this application note, we ran bioethanol fermentation samples on both the Zebron ZB-1 and ZB-Bioethanol GC columns. The results were compared for equivalency. We also evaluated the columns' run time to determine the time savings that the new column can provide for an ethanol plant. Results indicate that the Zebron ZB-Bioethanol GC column provides a significant time savings and is suitable for fuel ethanol analysis under ASTM Method D 5501 and Europe prEN 15376.

Experimental Conditions
GC analysis was run on a Shimadzu™ GC-2010 system (Shimadzu Scientific Instruments, Columbia, MD, USA) equipped with a A0C-20i automatic liquid handler and a flame ionization detector. Identical bioethanol samples were run following ASTM Method D 5501 using three GC columns: 1) 100 meter x 0.25 mm x 0.50 µm Zebron ZB-1 GC column (Phenomenex, 7MG-G001-17), 2) 30 meter x 0.25 mm x 1.00 µm Zebron ZB-Bioethanol column (Phenomenex, 7HG-G020-22), and 3) 15 meter x 0.25 mm x 1.00 µm Zebron ZB-Bioethanol column (Phenomenex, 7EG-G020-22).

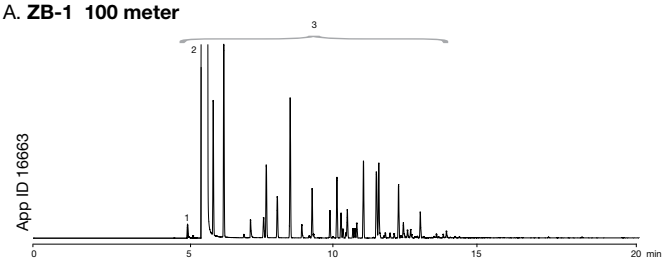
Conditions for injections on
Zebron ZB-1 GC Column

Column:	Zebron ZB-1
Dimensions:	A) 100 meter x 0.25 mm x 0.50 µm
Part No.:	7MG-G001-17
Injection:	Split 50:1 @ 300 °C, 1 µL
Carrier Gas:	Helium @ 35 cm/sec (Constant Flow)
Oven Program:	45 °C for 7 min to 255 °C @ 30 °C/min
Detector:	FID @ 300 °C
Instrument:	Shimadzu™ GC-2010 with Flame Ionization
Sample:	1. Methanol
	2. Ethanol
	3. Denaturant

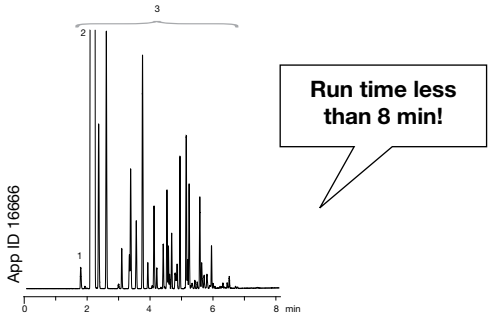
Conditions for injections on
Zebron ZB-Bioethanol GC Columns

Column:	Zebron ZB-Bioethanol
Dimensions:	B) 30 meter x 0.25 mm x 1.00 µm
	C) 15 meter x 0.25 mm x 1.00 µm
Part No.:	B) 7HG-G020-22
	C) 7EG-G020-22
Injection:	Split 50:1 @ 300 °C, 1 µL
Carrier Gas:	B) Hydrogen @ 35 cm/sec (Constant Flow)
	C) Hydrogen @ 25 cm/sec (Constant Flow)
Oven Program:	B) 45 °C for 2.5 min to 255 °C @ 30 °C/min
	C) 55 °C for 1.7 min to 260 °C @ 40 °C/min
Detector:	FID @ 300 °C
Instrument:	Shimadzu™ GC-2010 with a AOC-20i Automatic Liquid Handler

A. **ZB-1 100 meter**



B. **ZB-Bioethanol 30 meter**



C. **ZB-Bioethanol 15 meter**

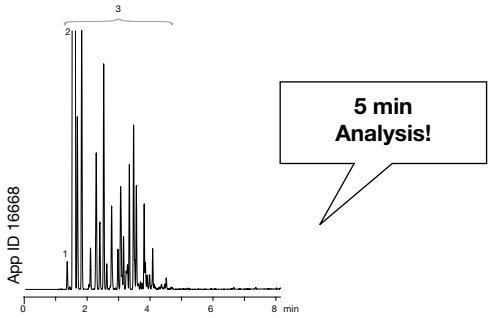


Figure 1.
Comparison of bioethanol analysis on a Zebron ZB-1 versus a Zebron ZB-Bioethanol GC column. Denatured bioethanol sample from corn feedstock was run on a 100 meter Zebron ZB-1 (A), 30 meter ZB-Bioethanol (B), and a 15 meter ZB-Bioethanol GC column (C). All columns provided complete resolution of methanol and ethanol from the gasoline denaturant. The ZB-Bioethanol columns shorten run time down to less than 8 minutes with the 30 meter column and 5 minutes with the 15 meter column.

Results

Field samples supplied by bioethanol plants were compared on both columns. Results show that the Zebron ZB-Bioethanol columns perform bioethanol analysis in less than half the time of standard GC columns (Figure 1). Resolution of methanol and ethanol from a sample denatured with gasoline was achieved in less than 8 minutes with the 30 meter ZB-Bioethanol column, and 5 minutes with a 15 meter ZB-Bioethanol column.

The ethanol and methanol values obtained by the Zebron ZB-Bioethanol GC columns were compared with those obtained using the Zebron ZB-1 GC column (Table 1). Results show very high correlations for all three columns. Less than 1 % relative standard deviation was achieved for both methanol and ethanol.

Run-to-run variability was also evaluated for all three GC columns (Table 2). Three samples of a bioethanol sample were injected into each column. This was repeated two times for a total of three runs. The average and standard deviations of the results were analyzed and showed no significant difference between the runs on each column.

Table 1.
Comparison of methanol and ethanol using Zebron ZB-1 and ZB-Bioethanol GC columns. Each area percent (Area %) data point is an average of 3 replicate injections. Results show that both the 15 and 30 meter Zebron ZB-Bioethanol GC columns produce virtually the same results as the Zebron ZB-1 GC column.

	Methanol Area %	Ethanol Area %
Zebron ZB-1 (100 meter)	0.057	92.52
Zebron ZB-Bioethanol (30 meter)	0.058	92.60
Zebron ZB-Bioethanol (15 meter)	0.057	93.11
Average	0.057	92.74
Relative Standard Deviation	0.89 %	0.35 %

Table 2.
Reproducibility of bioethanol field samples using Zebron GC columns. The average and standard deviation of three denatured bioethanol injections were calculated to show that Zebron GC columns produce amazing results with virtually no difference from sample to sample.

	Zebron ZB-1 (100 meter)		**Zebron ZB-Bioethanol (30 meter)**		**Zebron ZB-Bioethanol (15 meter)**	
	Methanol Area %	Ethanol Area %	Methanol Area %	Ethanol Area %	Methanol Area %	Ethanol Area %
Injection #1	0.057	92.50	0.058	92.57	0.058	93.09
Injection #2	0.057	92.54	0.056	92.69	0.057	93.10
Injection #3	0.057	92.51	0.060	92.54	0.057	93.14
Average	**0.057**	**92.52**	**0.058**	**92.60**	**0.057**	**93.11**
Relative Standard Deviation	**0.00 %**	**0.02 %**	**3.45 %**	**0.08 %**	**1.01 %**	**0.03 %**

Conclusions

Determining the accurate amount of methanol and ethanol is critical to ensure the quality of the bioethanol fuel produced. Using the Zebron ZB-Bioethanol GC column, a new phase specially designed for fuel ethanol analysis, resolution of methanol and ethanol from a sample denatured with gasoline can be achieved in less than 5 minutes.

The results obtained by the Zebron ZB-Bioethanol GC columns were found to be equivalent to those obtained using the 100 meter column specified by the ASTM Method D 5501 and prEN 15376. The intra-column variability test performed shows virtually no day-to-day or run-to-run variability on either the Zebron ZB-1 or ZB-Bioethanol GC columns.

As a result, the ZB-Bioethanol GC column is perfectly suited for the fuel ethanol analysis following ASTM Method D 5501 and Europe prEN 15376. It also provides dramatic time savings that allows producers the ability to test the fuel trucks before they leave the facility, thereby reducing potential problems.

References

1. World's Ethanol Production Forecast 2008 – 2012, January 26, 2008. http://www.marketresearchanalyst.com/2008/01/26/world-ethanol-production-forecast-2008-2012/

Ordering Information

Part No.	Description	Unit
7HG-G020-22	Zebron ZB-Bioethanol, 30 meter x 0.25 mm x 1.00 µm	ea
7EG-G020-22	Zebron ZB-Bioethanol, 15 meter x 0.25 mm x 1.00 µm	ea
7MG-G001-17	Zebron ZB-1, 100 meter x 0.25 mm x 0.50 µm	ea
AG0-5155	Zebron ZB-1 Test Mix	ea