APPLICATION NOTE

Gas Chromatography

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Determination of Methanol and Ethanol in Denatured Fuel Ethanol Using GC/FID

Introduction

Ethanol is often used as an additive or supplement to improve product performance in commercial fuel products, and serves as a more environmentally friendly substitute for tetraethyl lead (TEL) and methyl tert-butyl ether (MTBE). Ethanol is produced by fermenting food sugars or processing cellulose, which leads to the existence of water and methanol in small quantities. Denaturants are added to ethanol to create the feedstock used for commercial fuels, also referred to as denatured fuel ethanol. As part of a rigorous quality control program, manufacturers regularly monitor the levels of methanol, water and ethanol in denatured fuel ethanol to ensure that their products are safe and fit-for-purpose.

Ethanol is the primary ingredient of denatured fuel ethanol, accounting for nearly 100% of the weight (% wt) of the product, with methanol representing only approximately 0.1 to 0.6 wt%. One of the primary analytical challenges faced by manufacturers in the simultaneous determination of ethanol and methanol is the drastic content difference between the two components in denatured fuel samples. To mitigate this challenge, PerkinElmer's Clarus® GC systems' wide-range flame ionization detector (FID) measures hydrocarbon compounds at very low and very high levels. With a linear response range of 107, the Clarus GC/FID allows users to accurately quantitate the largest and smallest peaks on a chromatogram, without changes to range or attenuation, offering a perfect solution for the determination of methanol and ethanol in denatured fuel ethanol.

In the study described herein, a method for the determination of methanol and ethanol in denatured fuel ethanol is performed using the PerkinElmer Clarus 690 GC/FID.

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Experimental Details

A PerkinElmer Clarus 690 GC/FID, operating in linear column velocity (LCV) mode, was used to perform the experiments described in this study, with the conditions presented in Table 1. The new narrow jet uses less hydrogen than previous designs, and the increased maximum attenuation (up to 64) enables the wider analytical range of the Clarus 590 and 690 series of instruments.

Table 1. Analytical parameters.

GC Parameters	
Injector Type	Capillary injector with capillary split deactivated glass liner with deactivated wool and tapered end
Inlet Temp	300 °C
Carrier Gas Linear Velocity	21 cm/s
Split Ratio	200:1
Injection Volume	0.1 µL
Injection Mode	Fast
Initial Oven Temp	60 °C
Oven Hold	15 min
Ramp	30 °C/min
2nd Oven Temp	250 °C
Oven Hold	23 min
FID Temp	300 °C
Air Flow	400 mL/min
H_2 Flow	40 mL/min

TotalChrom® software was used to control the GC system, which offers three choices for carrier pneumatics, including programed flow, programed velocity and pressure. The configuration of the LCV mode allows for easy operation by selecting the programmed velocity option in the instrument control page, as shown in Figure 1. The value of LCV was set using either constant or programed LCV mode by changing the hold time and velocity programming rate of each set point.

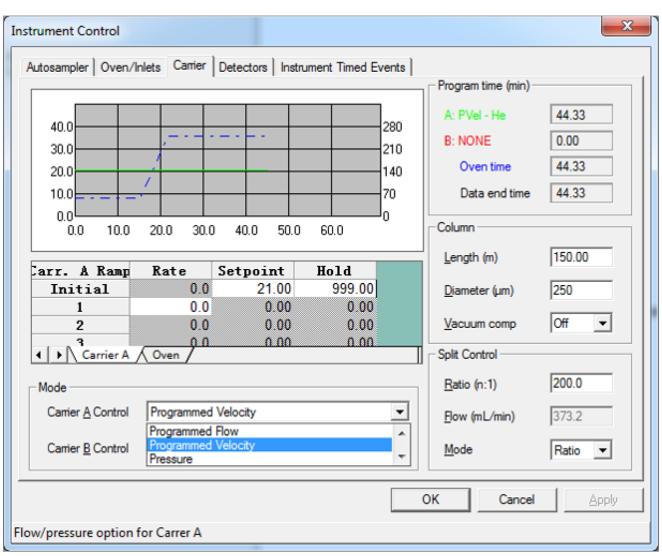

Figure 1. The instrument control page for the constant LCV mode.

An Rtx-150-DHA column (150 m x 0.25 mm x 1.0 µm) was used to separate the eluting compounds, owing to the complexity of the hydrocarbon denaturant in the denatured fuel ethanol.

n-Heptane was used in place of the denaturant to prepare calibration standards in this study. Calibration standards of methanol, ethanol and n-heptane were purchased from ANPEL Laboratory Technologies (Shanghai) Inc. The average response factors (R) and relative standard deviation of R were calculated by running nine calibration standards. The calibration range was 0.05-0.6 wt% for methanol, and 93-98 wt% for ethanol.

Commercial denatured fuel ethanol samples were obtained from a producer. Precision was investigated with six injections of the sample.

Results and Discussion

A single point calibration was adopted to save time and resources. The response factors for methanol and ethanol on a weight basis are calculated using the formula described in ASTM practice D4626[1]:

$$R = \frac{M}{A}$$

where:

R = mass (weight) responds factor for a compound

M = mass (weight) of a compound

A = peak area of a compound

The fast injection mode was used in this study to reduce the effect of error on method precision owing to the low boiling points of methanol, ethanol and other components. The response factors (R), as well as the average value and relative standard deviation of R for methanol and ethanol, are summarized at each calibration level in Table 2. The relative standard deviation (RSD%) of R for methanol and ethanol are 1.69% and 0.49% respectively, which is better than the requirements of most common validation standards.

Table 2. The response factors (R), average value and RSD% of R for methanol and ethanol.

	Methanol		Ethanol	
	wt%	R	wt%	R
1	0.05%	0.000121	98%	8.02E-05
2	0.10%	0.000123	98%	8.05E-05
3	0.05%	0.000118	97%	8.08E-05
4	0.10%	0.000118	97%	8.07E-05
5	0.20%	0.000117	96%	8.09E-05
6	0.30%	0.000120	95%	8.09E-05
7	0.40%	0.000121	94%	8.04E-05
8	0.50%	0.000122	93%	7.99E-05
9	0.60%	0.000119	93%	7.99E-05
Average	-	0.000120	-	8.05E-05
RSD%	-	1.69	-	0.49

Figure 2 diplays the chromatogram of a commercial denatured fuel ethanol sample, with a good peak profile for methanol. The weight percentage of methanol and ethanol were calculated using the average response factors. The average weight percentage is 0.0475% for methanol and 98.084% for ethanol, with six injections of the sample. The area repeatability data (RSD%) are 0.29 and 1.16% for ethanol and methanol respectively, which shows the excellent precision for the low level methanol and the large level ethanol (Table 3).

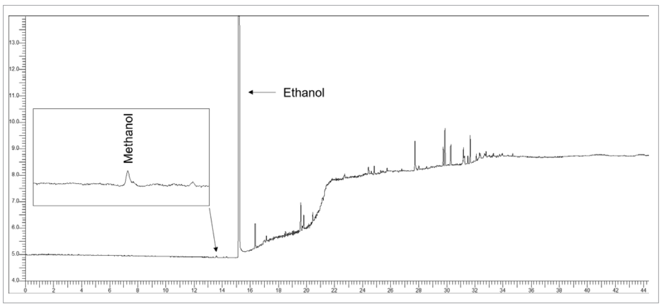

Figure 2. The chromatogram of a commercial denatured fuel ethanol sample.

Table 3. The area repeatability for methanol and ethanol in denatured fuel ethanol.

No.	Methanol	Ethanol
1	319	1001100
2	330	1002204
3	325	1004957
4	327	999968
5	325	1007766
6	328	1004701
RSD %	1.16	0.29

Summary

In this study, the analysis of methanol and ethanol in denatured fuel ethanol was performed using a PerkinElmer Clarus 690 GC/FID. The excellent precision demonstrates the superior performance of the inlet without sample carryover and reactivity, and the wide detection range for the FID. The PerkinElmer Clarus 690 GC/FID satisfies the needs of the commercial denatured fuel ethanol industry.

Reference

1. 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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