A Fast, Unified Analysis of Key Components in Bio-Ethanol Fuels Using Heart-Cutting Multi-Dimensional Gas Chromatography (K.19)

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Introduction

Ethanol fuels made from renewable biomass are finding markets throughout the world as producers scale up production and automobile manufacturers develop ethanol capable vehicles. The key bottleneck for these fuels is denatured fuel ethanol, composed of 90 to 98 percent ethanol denatured with hydrocarbons. Final commercial fuels contain 20 to 85 percent ethanol with the balance of natural gasolines. To meet fuel requirements and environmental regulations, both the denatured ethanol and the various ethylene/gasoline blends must meet key specifications in regards to the content of ethanol, methanol, benzene and toluene. Industry consensus organizations such as ASTM have specified two GC methods to measure these components, D5501 and D5505. These methods require two instruments with specific column and valve configurations in long analysis times. Multi-dimensional capillary GC (MDGC) offers the possibility of combining several individual measurements into a single run. Additionally, using short, orthogonal columns a MDGC separation is often faster than with a single long capillary column. As applied to a simple analysis of denatured ethanol, this concept was demonstrated by the author using a Deans switch system in 2003 [1]. This poster presents a MDGC system for the analysis of key components in several fuel ethanol blends as an alternative to different ASTM methods. Analysis times were reduced from several hours to less than 15 minutes. The use of back flush techniques was combined with a MDGC analysis to further reduce run times as well as extend column life. Results were consistent with those found using the standard ASTM methods.

In 2003, the author published a poster [1] entitled "Fast Determination of Fuel Ethanol Purity by Two Dimensional Gas Chromatography". The method used a Deans switch to combine and analyze up to 12 individual fuel ethanol samples in a single run. This system with several improvements has been turned into an automated system using a Deans switch to combine analyses and a splitter to reduce the individual run times. This results in a total analysis time of less than 15 minutes compared to the standard ASTM methods.

The method uses two short, orthogonal columns. The first column is de-ethylated and the second column is de-methylated. The ethanol fuel is run in the first column, which uses the de-ethylated conditions, and the methanol is run in the second column, which uses the de-methylated conditions. The columns are connected by a splitter and a Deans Switch System. The system is designed to reduce the analysis time to a minimum by using a short column and by taking advantage of the MDGC technique.

Heart-Cutting MDGC Analysis of Ethanol and Methanol in Fuel Ethanol

Automated back flush was also used to reduce the analysis time. Ethanol eluted from the secondary column within 3 minutes with a 30 mL/min carrier gas flow. The heavy hydrocarbons are completely removed after 30 seconds of back flush. Using this technique, the overall analysis time for ethanol and methanol was reduced from 45 minutes to 3.5 minutes. This method uses a 12 port valve and a two columns to separate benzene from ethanol and hydrocarbons in the sample. This method works pretty well, it does require a lab to have another GC to completely measure key components in ethanol fuels.

Analysis of Other Commercial Ethanol Fuels Using Heart-Cutting MDGC

Commercial ethanol fuels are made by blending denatured ethanol fuel with various ratios of gasoline. The ethanol, methanol, benzene and toluene content must also be measured in these fuels. Two samples of commercial ethanol fuels, E25 and E85, were obtained and run along with the denatured fuel ethanol using the MDGC method. Three consecutive runs were made for each sample. The table below shows excellent precision for each sample.

Summary and Conclusion

- Improving Speed, Accuracy, and Productivity For Renewable Bio-Ethanol Fuel Analysis
- Analysis time reduced from 45 minutes to 3.5 minutes
- Heart-Cutting MDGC using two short, orthogonal columns
- Complete resolution of methanol from light hydrocarbons
- Back-flush capabilities to reduce run time to 3.5 minutes
- Isothermal conditions eliminates cycle time between runs
- Benzene and toluene analysis easily added to MDGC method eliminates the need for second GC