Reliable Analysis of Glycerin in Biodiesel Using a High-Temperature Non-metal GC Column

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Introduction

In the past decade, biodiesel has emerged as a leading alternative fuel source because it is easily derived from common feedstocks and can be used in unmodified diesel engines. The relative ease of biodiesel production can mask the importance of maintaining high quality diesel fuel standards. To support the growth of the biodiesel industry, the United States' American Society for Testing and Materials (ASTM) and the European Deutsches Institut fur Normung (DIN) recently outlined physical and chemical tests and specified the minimum quality standard for biodiesel fuel used in modern diesel engines.[1]

Arguably the most critical test for biodiesel is the measure of glycerin content. Glycerin is the major byproduct of the biodiesel production process, called transesterification, where oils and fats are reacted with an alcohol to produce fatty acid methyl esters (FAMEs).[1] High glycerin content can lead to a number of fuel problems, such as clogged fuel filters and fuel pressure drops, and its presence must be minimized.

ASTM D 6584 outlines testing methods measuring total amount glycerol in a biodiesel.[2] Although GC is the standard analysis technique for this method, it has several inherent challenges. These tests run at very high temperatures and standard fused silica columns are not engineered to withstand temperatures above 380 °C. In fact, at temperatures above 380 °C, the polyimide coating of most fused silica columns starts to degrade, eventually becoming brittle and inflexible.

The alternative, metal columns, present other challenges. While metal columns can withstand higher oven temperatures, they are inflexible, difficult to use, and require special tubing cutters. In addition, they often develop leaks due to the expansion and contraction that occurs during oven heating cycles and are highly active to acids and bases. Thus, using metal columns might compromise the accuracy of the biodiesel analysis.

Phenomenex, Inc., has recently developed unique fused silica columns designed specifically for high-temperature analysis. These columns, called the Zebron™ ZB-1HT and ZB-5HT Inferno™, are specially processed to be thermally stable up to 430 °C. As a result, their stationary phases and a polyimide coating are more rugged and can withstand higher temperatures than other conventional columns. This article compares the lifetime and stability of the Zebron Inferno column with the leading fused-silica columns and presents analysis results on the Zebron column using ASTM Method D 6584.

Methods

Lifetime Comparison

For the high temperature lifetime comparison, three columns were compared: Agilent's (J&W) DB-5ht, Varian's VF-5ht, and Phenomenex's Zebron ZB-5HT. The columns were held at 400 °C for 2 hours. After lowering the oven temperature to 120 °C, 1.0 µL of pentadecane standard was injected and its retention time was measured. This process was repeated 50 times, totaling 100 hours at 400 °C for each column tested.

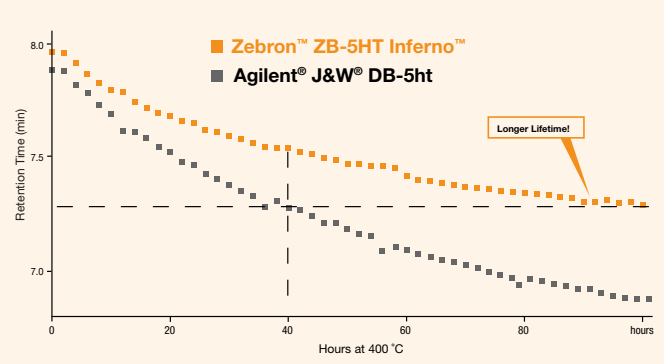

Figure 1. Lifetime comparison of the DB-5ht and ZB-5HT Inferno. The lifetime and bleed profile comparisons were performed on new, unused DB-5ht and ZB-5HT GC columns. Careful measures were taken to ensure that all conditions were similar for both columns.

Bleed Profile

Bleed (pA) was measured using a flame ionization detector (FID) as the GC oven program increased from 120 °C to 400 °C. The GC oven was held at 120 °C for 3 minutes then increased to 320 °C at 30 °C/minute. A null injection was made at 250 °C.

Biodiesel Analysis

Calibration standards, sample preparation, and GC analysis were performed as per ASTM Method D 6584 (Reference ASTM Method). In brief, the samples were derivatized with N-Methyl-N-trimethylsilyltrifluoroacetamide (MSTFA).

Results and Discussion

A good indicator of a column's stability is its consistency in retention time for hydrocarbons, such as pentadecane. The pentadecane retention time comparison revealed that the Zebron ZB-5HT has higher thermal stability than the DB-5ht and VF-5ht. After 40 hours at 400 °C, the VF-5ht column broke (data not shown). Pentadecane has the same retention time on the DB-5ht after 40 hours at 400 °C as on the Zebron ZB-5HT after 80 hours at that temperature. This suggests that the ZB-5HT is two times more stable and has twice the column lifetime as the DB-5ht.

Bleed can also be an indicator of the stability and lifetime of a GC column. In the bleed comparison test, the DB-5ht showed significantly higher bleed than ZB-5HT at 380 °C (Figure 2). This difference is amplified at 400 °C.

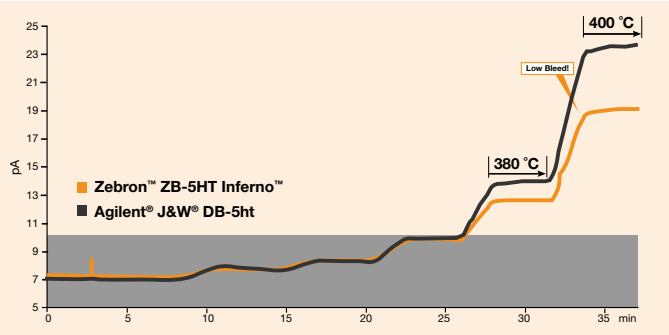

Figure 2. Bleed comparison of the DB-5ht and ZB-5HT Inferno. The shaded area depicts the bleed criteria for MS certified columns on a MS detector. MS bleed certification values are typically read at 320 °C. The ZB-5HT demonstrated lower bleed than the DB-5ht. It meets MS certification limits, even at 360 °C.

After these initial comparative tests, we conducted the ASTM D 6584's free and total glycercin analysis on the Zebron ZB-5HT column. The calibration curve for each reference components had a correlation coefficient (r^2) greater than 0.99 (data not shown).

Good peak shape is also indicative of a column's suitability for a designated method. ASTM D 6584 specifies that Butanetriol and Tricarpin be used as internal standards because they have similar properties as many components in a biodiesel sample. Because we observed good peak shape in the biodiesel GC run, it indicates that the Zebron ZB-5HT is well suited for the analysis and exhibits very low activity for the analytes (Figure 3).

Technical Tip

Did you know that many GC problems are related to improper column installation? To ensure the best chromatography, use the Cool-Lock™ Nut to get the proper installation depth. This patent pending tool will also help you to avoid burning your fingers while installing your column accurately in record breaking time. For more information, call your local Phenomenex representative.

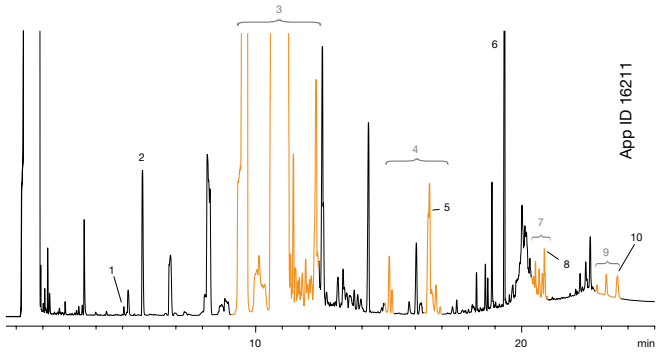

Figure 3. The standards and biodiesel sample were both run under the same conditions using a 15 m x 0.32 mm x 0.10 µm Zebron ZB-5HT Inferno column (7EM-G015-02) with a 2.0 m x 0.53 mm high-temperature guard column. 1 mL of the reaction mixture was injected onto a cool-on-column injector connected to a HP 6890 Gas Chromatograph (Agilent Technologies, Palo Alto, California, USA) and detected by Flame Ionization (FID). The GC oven is as follows: 50 °C for 1 min to 180 °C @ 15 °C/min to 230 °C @ 7 °C/min to 380 °C @ 30 °C/min for 10 min. Samples: 1. Glycerol, 2. Butanetriol (ISTD1), 3. Esters, 4. Monoglycerides, 5. 1-Monooleoyl-rac-glycerol, 6. Tricarpin (ISTD2), 7. Diglycerides, 8. 1,3-Diolein, 9. Triglycerides, and 10. Triolein.

Conclusion

To ensure the quality of the biodiesel product, the US ASTM D 6584 method specifies a high temperature analysis of free and total glycerin in biodiesel products. However at temperatures above 380 °C, most fused silica columns become brittle and spontaneously break. Our studies suggest that Phenomenex's Zebron ZB-5HT is well suited for high temperature analyses. When compared to Agilent's DB-5ht, the Zebron ZB-5HT has less bleed, more thermal stability, and longer lifetime.

Having a rugged and durable high temperature GC column will help manufactures to develop methods that will produce high quality, alternative fuel products. In addition, a column with longer lifetime will help lower the cost per sample of the analysis, thus driving down the cost of production.

References

1. Van Gerpen, J., Shanks, B., Pruszko, R., Clements, D., and Knothe, G. Biodiesel Analytical Methods, National Renewable Energy Laboratory, 2004
2. ASTM Standard D 6584 – 00, "Test Method for Determination of Free and Total Glycerin in B100 Biodiesel Methyl Esters by Gas Chromatography," ASTM International, West Conshohocken, PA, www.astm.org

ORDERING INFORMATION

Part No.	Description
7EM-G015-02-TN	ZB-5HT, 15 m x 0.32 mm x 0.10 µm