Recently 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. 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) outlined physical and chemical tests to specify 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). High glycerin content can lead to a number of fuel problems, such as clogged fuel filters and fuel pressure drops, so its presence must be minimized.

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. At temperatures above 380 °C, the polyimide coating of most fused silica columns starts to degrade, eventually becoming brittle and inflexible.

Metal columns, the alternative to fused silica, 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. Their stationary phases and polyimide coating are more rugged and can withstand higher temperatures than conventional columns. This article compares the lifetime and stability of the Zebron ZB-5HT with the leading fused silica columns and presents analysis results on the Zebron column, using the ASTM D6584 method (2).

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. The oven was lowered to 120 °C then 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.

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 D6584.2

Results and Discussions
A good indicator of a column’s stability is its consistency of hydrocarbon retention time. 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). In addition, 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 400 °C. This suggests that the ZB-5HT is two times more stable and has twice the column lifetime as the DB-5ht (Figure 1).

Bleed is also 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.

After the initial comparative tests, we conducted the ASTM D6584’s free and total glycerin analysis on the Zebron
The ZB-5HT column (Figure 3). The calibration curve for each reference component had a correlation coefficient ($r^2$) greater than 0.99 (data not shown).

Conclusions
To ensure the quality of the biodiesel product, the ASTM Method D6584 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 (J&W) DB-5ht and Varian's VF-5ht, the Zebron ZB-5HT Inferno has less bleed, more thermal stability, and longer lifetime.

Having a rugged and durable high temperature GC column will help manufacturers 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