

Integra-Gap technology and Metal columns: Biodiesel Glycerides Analysis Made Easy and Reliable

Jaap de Zeeuw, Roy Lautamo, Barry Burger and Gary Stidsen
Restek Corporation, Bellefonte, PA, USA

One of the challenges in biodiesel fuel analysis is accurate determination of the residual triglyceride content: in biodiesel, triglycerides are present at low levels, and elute at high temperatures. For accurate analysis, on-column injection is required. Analytical methods ASTM D-6584 and EN-14105 describe the use of 0.32mm analytical columns coupled with a 0.53mm retention gap. The column must be operated at temperatures up to 380°C, which puts strong challenges on the mechanical stability of the capillary tubing, the stability of the phase, and the leak-tightness of the coupling. We developed a new line of 0.32mm ID and 0.53mm ID stainless steel capillary columns to address these concerns, using Siltek® deactivation technology to stabilize the stationary phase and assure reproducible retention times. Additionally, a new column connector makes a perfect leak-tight seal for either metal-to-metal or fused silica connections. In addition, we will discuss the performance of a column prepared with integra-gap technology. This solution eliminates the need for a column coupling and thus considerably simplifies the analysis, especially in the routine laboratory.

Introduction

There is a huge increase in the use of biodiesel fuels. Biodiesel oil is biodegradable, nontoxic, does not contain aromatics, and the absence of sulfur avoids sulfur emissions. Biodiesel basically is made by the trans esterification of vegetable- / animal- / waste cooking oils. The pure product, called B100, is added to normal diesel fuel in different amounts. The “B” number designates the percentage of biodiesel in a biodiesel/petroleum diesel blend (e.g., B20 is 20% biodiesel / 80% petroleum diesel).

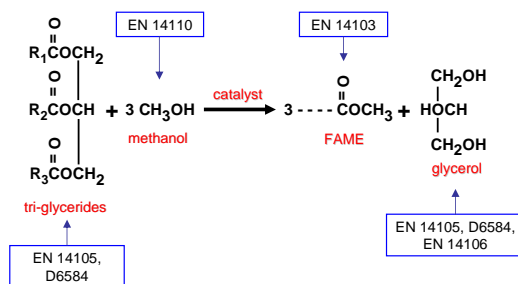


Figure 1: Reaction and standard methods

Glyceride residues in biodiesel and blends, can foul engine injectors and form deposits on essential parts in the diesel engine. Also, shelf-life time of fuels depend on the level of glycerine. It is essential that accurate, efficient methods for quantifying glycerin and glycerides are available to the biodiesel industry.

The American Society for Testing and Materials (ASTM) and the European method Deutsches Institut für Normung (DIN) describe the main physical and chemical testing

methods for biodiesel oil. Gas chromatography is ideal for measuring important parameters such as total glycerin, fatty acid methyl esters (FAMES) and methanol levels in biodiesel fuel. Methods like ASTM D-6584 and EN14105 are industry standards for testing total glycerin and glycerides in biodiesel oil. In these methods, the column recommendation is listed as a 10m x 0.32mm ID column with a 0.1µm film of 5% diphenyl/95% dimethyl polysiloxane. This column is connected with a retention gap to make the on-column injection feasible. The methods allow the use of fused silica as well as metal as tubing material. The 0.53mm MXT[®]-Biodiesel TG solution with the integrated Integra-Gap[™] retention gap, as introduced here, will hopefully trigger a review of these methods soon, to make the tryglycerides analysis more practical.

Unbreakable MXT[®] Column Solutions

Fused silica columns generally are very temperature stable and usually are the first choice for GC analysis. However, when operating at temperatures exceeding 350C, fused silica columns rapidly become black due to oxidation of the protective polyimide coating. This coating is in place to protect the fused silica column from mechanical damage. Any damage to the outside coating will make the lifetime of the column very unpredictable.

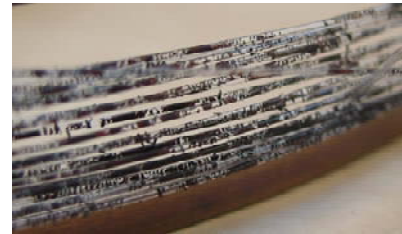


Fig. 2 Polyimide outside coating exposed at high temperatures, will make columns very fragile..

Even fused silica columns with special high temperature polyimide coating (HT equivalents) become unpredictable and break down relatively quickly. Figure 2 shows the impact of long-term exposure at 430°C: the polyimide hardens, becomes black and eventually disappears completely. Even in an early stage of this process, the risk for column breakage increases. To overcome this problem, a stabilized metal column line was developed: MXT[®]-Biodiesel TG. These MXT[®] columns are deactivated using Siltek[®] deactivation technology. This technology not only deactivates, but also stabilizes the stationary phase, making the column extremely stable. The MXT[®]-Biodiesel TG

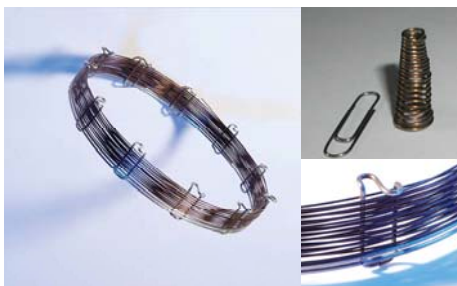


Fig 3: MXT Biodiesel TG columns in 0.32/0.53mm, stable up to 450C, wound on standard cage

columns virtually do not degrade, even under temperatures up to 430°C. Thus it is possible to “bake out” any residue eluting out after the triglycerides without damaging the column. This process keeps the analytical system clean so subsequent injections do not have carryover from previous samples. Metal columns are virtually unbreakable and can therefore be used for “tough” environments like high temperature GC, process applications, space missions and miniaturized solutions (Figure 3).

Injection Techniques for Biodiesel

To measure the high boiling triglycerides at low levels, it is essential to have a good injection set-up that allows quantitative measurement of triglycerides. The best technique is cold-on-column, where the sample is introduced as a liquid into the capillary column. Other techniques, like splitless and PTV, will show a significant degree of discrimination.

In order to obtain a good on-column injection, it is necessary to use a retention gap to make sure we have a band focusing mechanism in place. The retention gap usually is a 2-3 meters non polar deactivated capillary tubing with an inside diameter of 0.53mm to allow most on-column injections

The mechanism of the retention gap is described below and illustrated in Figure 4

1. When applying on-column injection, the solvent with analytes will be distributed over a section of the retention gap. The length of this section depends on the injection speed, the carrier gas flow, the type of solvent and the temperature. The solvent must be distributed evenly over the retention gap. This will only happen if the wettability of the surface of the retention gap allows this. Practically, for nonpolar solvents like heptane, cyclohexane, we use nonpolar (polydimethyl siloxane) deactivated retention gaps.

2. During and after injection the solvent will evaporate and the analytes will deposit on the retention gap surface. This is the initial band width which can be significant depending on the injection parameters.

3. Starting the temperature program will move the analytes toward the column where they will concentrate in the stationary phase, focusing the broad initial injection band.

4. The result is correct chromatographic peaks: No peak splitting or peak broadening.

Retention gaps are commercially available with different deactivations. If not offered as a "retention gap" one can also purchase 0.53mm ID deactivated fused silica or MXT[®] tubing and use that as retention gap.

Connection of the Metal Retention Gap: Alumaseal™

A new seal was developed for coupling fused silica as well as metal capillary columns under high temperature conditions: the Alumaseal™ connector (Figure 5). This seal made of aluminium, makes a near perfect connection between columns of different ID,

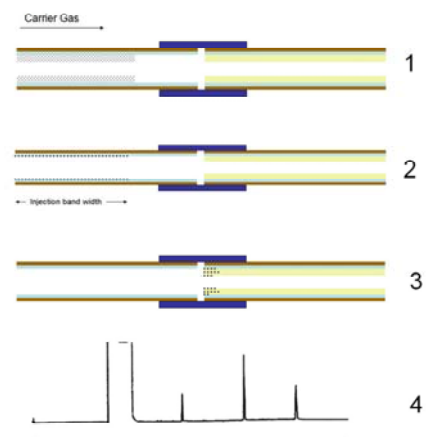


Figure 4: Principle of the retention gap

fused silica as well as MXT[®] tubing. It was tested using temperature ramping in MS applications and shows no sign of leaks. Alumaseal[™] connectors also do not have to be re-tightened after the first ramps and can be used to 430°C.

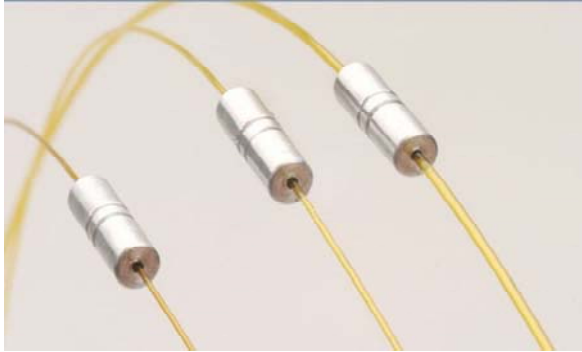


Figure 5: The alumaseal connector: Used for coupling fused silica and MXT, providing a universal leak tight connection

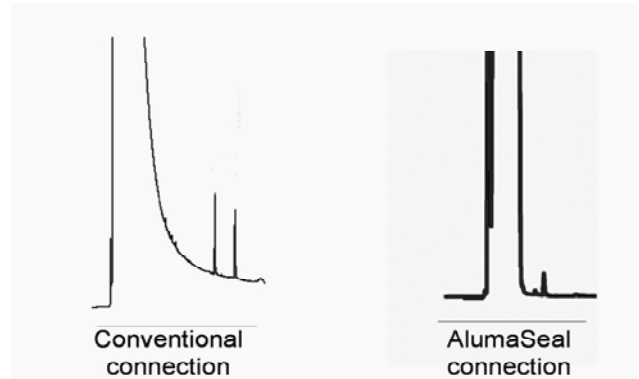


Figure 6: comparison conventional, (metal body & fitting) and alumaseal

Figure 6 shows a comparison between a typical conventional connector and the Alumaseal[™] when making a connection between 0.53 and 0.32mm columns. A good indicator is the peak shape of the solvent peak. Any solvent tailing is caused by dead-volume in the connector. Figure 7 shows a biodiesel analysis following the ASTM D-6584 using the factory coupled 10m x 0.32mm MXT[®]-Biodiesel TG, coupled with a 2m x 0.53mm retention gap using the Alumaseal[™] technology. Note the excellent solvent peak shape.

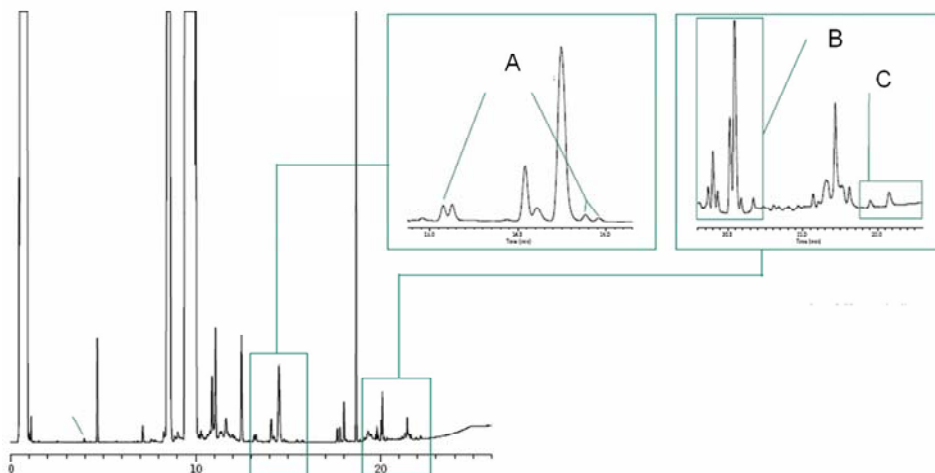


Figure 7: analysis of Biodiesel acc to ASTM D 6584, using a full MXT solution (10m/0.32mm MXT-Biodiesel TG coupled with 2m x 0.53mm retention gap using Alumaseal)

Integra-Gap™ Solutions

Restek was the first company to introduce Integra-Guard™ column technology. By using a segment coating technique, it was possible to deposit stationary phase only in the part of the capillary where it is needed. The same technique also is used to make Integra-Gap™ integrated retention gaps (Figure 8). As retention gaps ideally need to be 0.53mm ID to make on-column liquid injections possible, the Integra-Gap™ technology was applied to 0.53mm tubing, eliminating the need for column coupling.

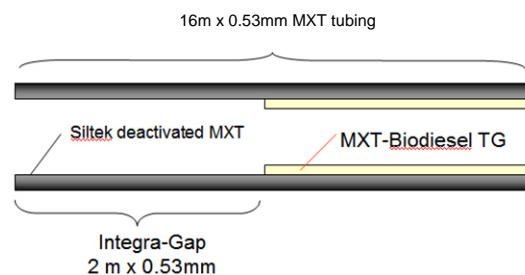


Figure 8: schematic of the Integra-Gap in a MXT-Biodiesel TG capillary

The result is a 100% leak-proof column feature. The built-in retention gap reducing the risk of leakage, peak broadening and tailing and is for the user a guarantee for many analysis without downtime. Especially when working at high temperatures the elimination of coupling will be appreciated as the coupling is a known source of leaks. The 0.53mm MXT®-Biodiesel TG columns with Integra-Gap™ are a simpler alternative to using a 0.32mm column coupled to a 0.53mm retention gap. Figure 9 shows the analysis of B100 biodiesel. Chromatography is excellent showing symmetrical peaks for glycerine up to the heavy triglycerides. To make sure that the resolution is not compromised, the 0.53mm column is made longer. Figure 10 and 11 shows the comparison of the actual separations obtained. Separations are better on the 0.53mm making the 0.53mm column directly applicable for biodiesel glyceride measurements. Note that the response of the triglyceride peaks is significantly higher using the integra-gap approach

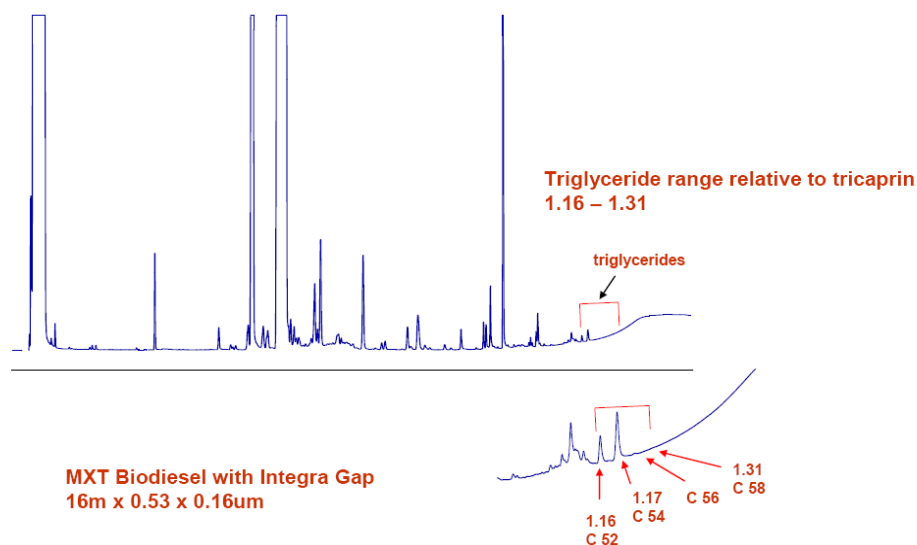
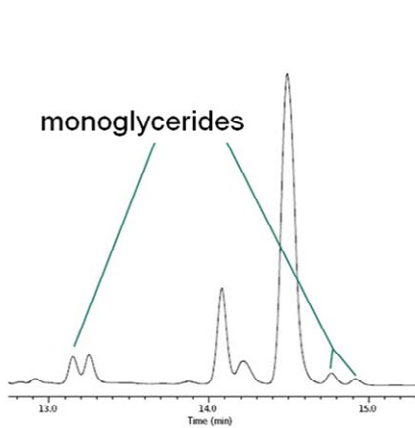
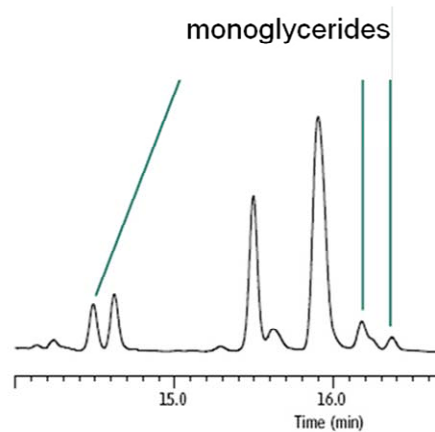


Figure 9: B-100 biodiesel on a 14(16)m x 0.53mm MXT-Biodiesel TG with a 2m integra-Gap

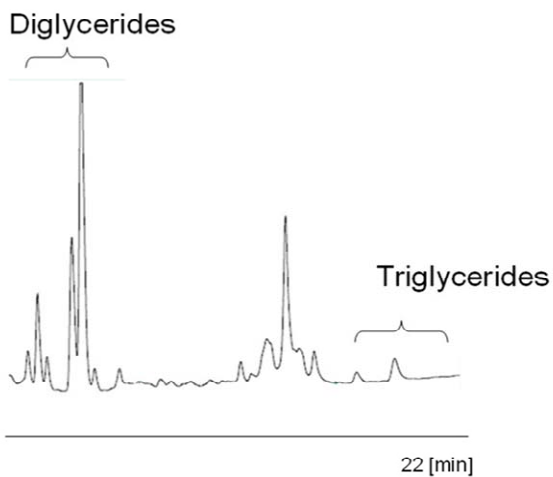


10m x 0.32 mm MXT-Biodiesel TG, coupled with 2 m x 0.53mm retention gap

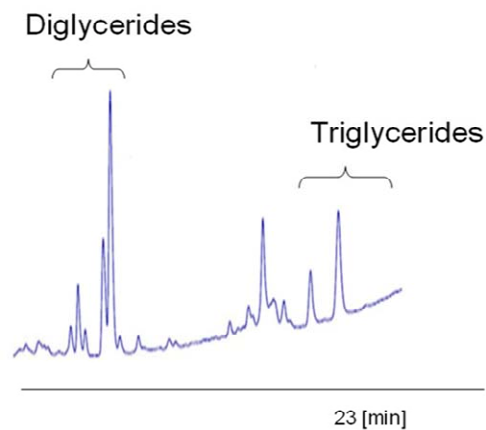


16m x 0.53mm MXT-Biodiesel TG, with 2m x 0.53mm integra-gap

Figure 10: Separation of monoglycerides on 0.32mm and 0.53mm MXT capillaries, both with retention gaps



10m x 0.32 mm MXT-Biodiesel TG, coupled with 2 m x 0.53mm retention gap



16m x 0.53mm MXT-Biodiesel TG, with 2m x 0.53mm integra-gap

Figure 11: Separation of di-and triglycerides on 0.32mm and 0.53mm MXT capillaries, both with retention gaps. Note the high triglyceride response for the Integra-gap solution..

Stability of new MXT[®] Biodiesel TG phase

The MXT[®]-Biodiesel TG columns as well as the retention gaps are deactivated using Siltek[®] technology, which creates a unique intermediate layer that stabilizes the stationary phase and provides unsurpassed inertness. Due to Siltek[®] deactivation, the stationary phase is extremely stable, exhibiting virtually no bleed even at temperatures as high as 430°C. Column stability is demonstrated by evaluating retention time stability. Figure 12 shows the first and last analysis after 100 biodiesel runs up to 430°C. The retention times remain virtually unchanged showing the excellent stability of the MXT[®]-Biodiesel TG columns. When running a similar series of samples using a commercial “HT” fused silica column, triglycerides can hardly be recognized chromatographically (Figure 13).

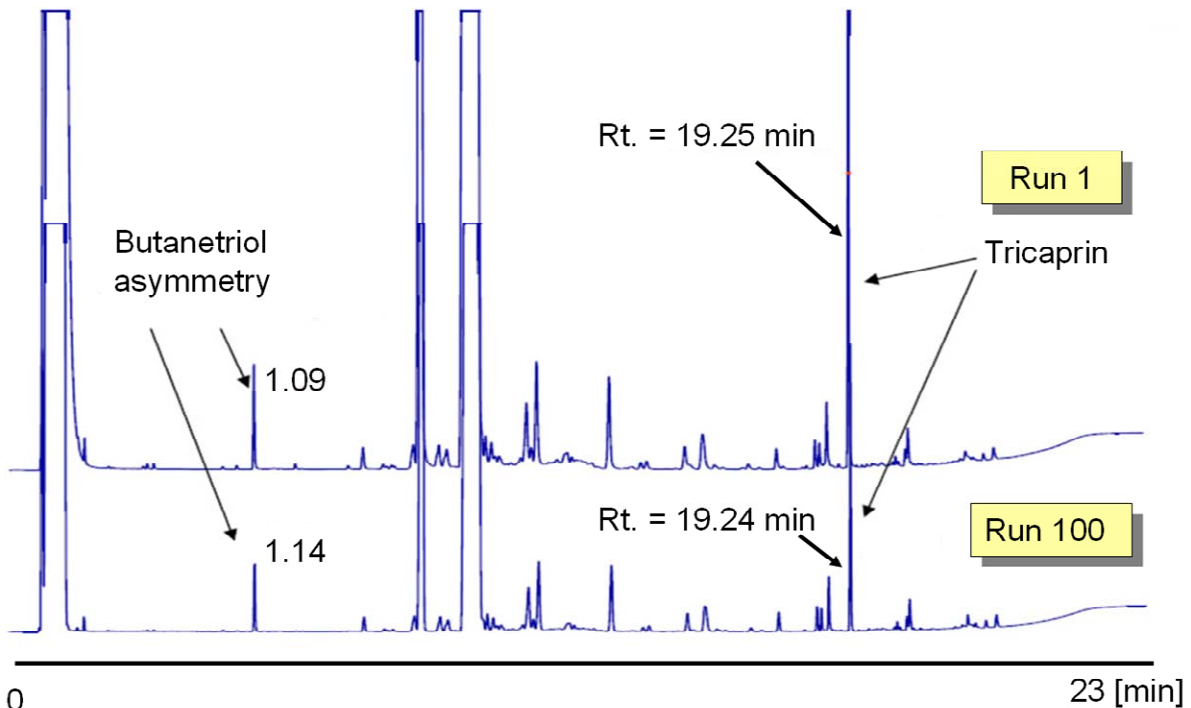


Figure 12: stability test. After 100 analysis up to 430 C, virtually no change in retention: MXT Biodiesel TG stationary phase is stabilized by Siltek deactivation

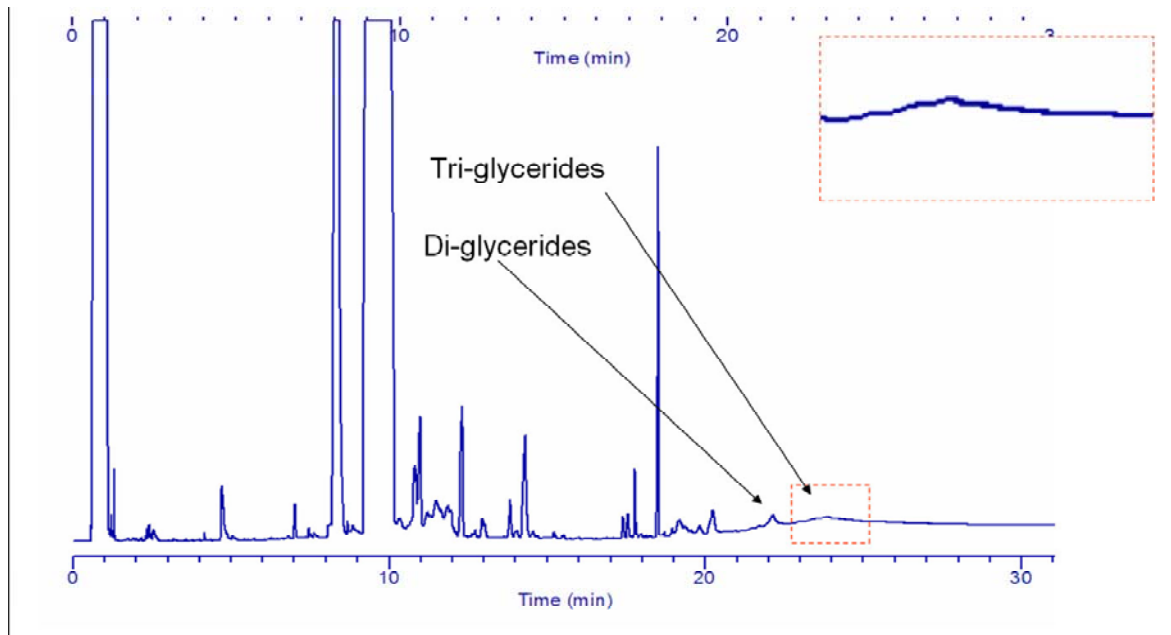


Figure 13: Stability test of a high temperature column with polymite"HT". FAME elution is OK, but di-and triglycerides are highly broadened

Conclusion

For high-temperature GC analysis, the metal MXT[®]-Biodiesel TG column is a rugged column that withstands the harsh temperatures required for total residual glyceride analysis. The column has the resolution needed for accurate, reliable results and is more stable at high temperatures than state of the art competitive fused silica columns. This high temperature stability leads to longer column lifetimes and less down time for maintenance and/or column change outs. The use of the Alumaseal[™] connection ensures a leak-tight connection between MXT[®] 0.53mm retention gaps and MXT[®] 0.32mm separation columns.

The use of Integra-Gap[™] technology as applied with the 0.53mm MXT[®]-Biodiesel TG columns will further greatly simplify practical operation for biodiesel TG analysis. It will significantly add to column lifetime and sensitivity as the column-coupling is eliminated.