



High Temperature Stability Problem Solved with New Metal Columns - Analysis of Total Glycerides in Biodiesel Oils by ASTM D-6584

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One of the biggest challenges in biodiesel fuel analysis is the accurate determination of residual triglyceride content. Triglycerides are present at low levels and elute at high chromatographic temperatures. Any suitable column must be operated at temperatures up to 380°C, which considerably strains conventional capillary tubing and stationary phases. Restek has developed new 0.32mm ID and 0.53mm ID MXT® stainless steel capillary columns—the MXT®-Biodiesel TG line—specifically for high temperature biodiesel analysis. Here we demonstrate the analytical advantages of full metal columns: unsurpassed stability at high temperatures, excellent peak symmetry for triglycerides, highly reproducible retention times, and unsurpassed column lifetimes.

Introduction

“Biodiesel”, “B100”, “B20”, “B10”, and “transesterification” are fast becoming everyday terminology. Biodiesel oil is biodegradable, nontoxic, does not contain aromatics, and the absence of sulfur from B100 precludes sulfur dioxide emissions. The “B” number designates the percentage of biodiesel in a biodiesel/petroleum diesel blend (e.g., B20 is 20% biodiesel / 80% petroleum diesel). Biodiesel is recognized as a desirable alternative energy source to petroleum-based products. However, excessive amounts of glycerides in biodiesel oil products can foul engine injectors and form deposits on valves, pistons, and injector nozzles. Also, separation of the glycerin during storage or in vehicle fuel tanks can reduce the shelf-life of the product. Clearly, accurate, efficient methods for quantifying glycerin and glycerides are critical to the biodiesel industry.

The American Society for Testing and Materials (ASTM) and the European method Deutsches Institut für Normung (DIN) describe several physical and chemical testing methods for biodiesel oil. Gas chromatography (GC) 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 set the industry standards for testing total glycerin and glycerides in biodiesel oil. The gas chromatographic column recommended for the analysis is a 10m x 0.32mm ID column with a 0.1µm film of 5% diphenyl/95% dimethyl polysiloxane, connected to a 0.53mm retention gap. The high temperatures required by these methods to elute triglycerides are a significant challenge to column stability and restrict column material choice to fused silica or metal.

Full Metal Advantage

Typically the fused silica column is the first choice for GC analysis, however at higher oven temperatures (>380°C) the polyamide coating on the fused silica tubing deteriorates, reducing column lifetimes (Figure 1). Even fused silica columns designed for high temperature applications (HT equivalents) become unpredictable and breakdown relatively quickly. In response, Restek has developed the MXT®-Biodiesel TG column line, a line of metal columns designed with stainless steel tubing and our patented Siltek® deactivation technology, ensuring maximum heat tolerance. The metal MXT® tubing does not degrade, even under temperatures up to 430°C, which allows analysts to “bake out” any residue eluting out after the triglycerides without damaging the column. This “bake out” process keeps the analytical system clean so subsequent injections do not have carry over from previous samples.

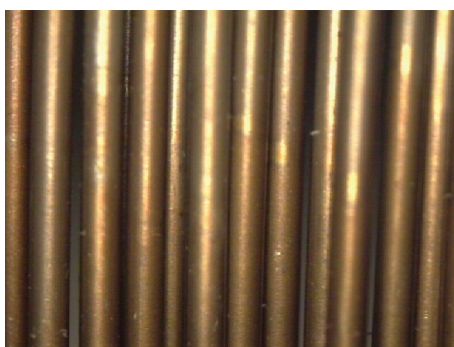


Figure 1a: MXT®-Biodiesel TG columns

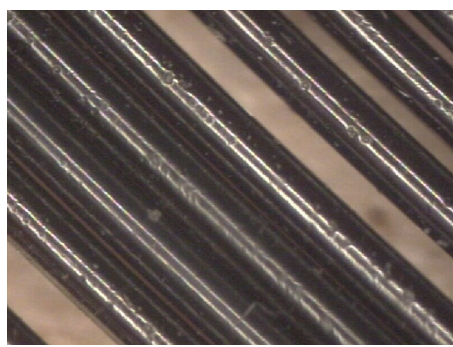


Figure 1b: HT fused silica columns

Figure 1a & 1b: MXT®-Biodiesel TG columns (Figure 1a) are undamaged by high temperature heat cycles compared to HT fused silica columns (Figure 1b) which breakdown under the same conditions (100 temperature cycles to 430°C totaling 500 minutes at maximum temperature.) Note extensive pitting on the fused silica column.

Stability Solutions

The MXT® Biodiesel TG columns 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 inertness is demonstrated by evaluating peak shape and retention time stability.

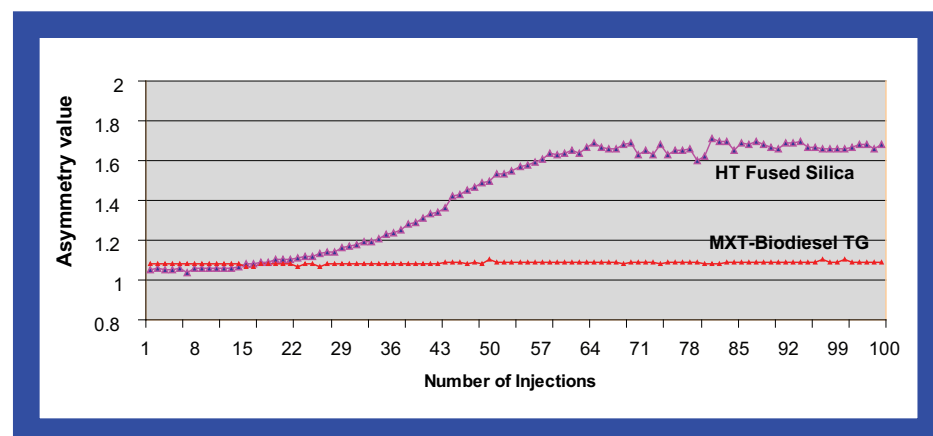


Figure 2: Metal MXT®-Biodiesel TG columns are more stable and inert than commercially available fused silica columns as evidenced by symmetric and consistent peak shape for the internal standard butanetriol.

Peak shape can be affected by active sites in the analytical column; higher asymmetry values indicate greater exposure to active sites, meaning the column is less inert. Peak symmetry of butanetriol on a commercial HT equivalent fused silica column deteriorates after just 20 injections, compared to the excellent symmetry that is maintained on the MXT®-Biodiesel column (Figure 2). While the HT column was specified to be stable up to 430°C the metal MXT®-Biodiesel TG column shows no sign of activity and is clearly more inert and stable than the fused silica column.

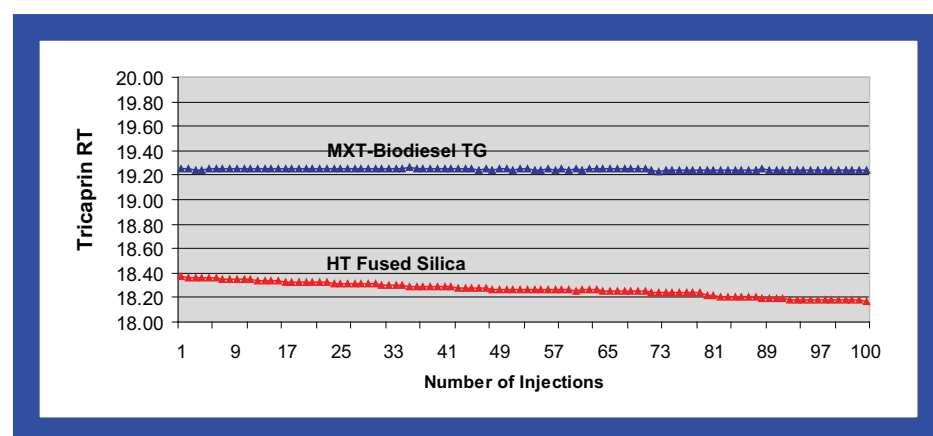


Figure 3: Retention time is stable on metal MXT®-Biodiesel TG column, even under high temperature cycling.

In addition to peak shape, consistent analyte retention times can be used to demonstrate column stability. The data in Figure 3 show the retention time of tricaprins over 100 injections for the fused silica column and the MXT®-Biodiesel TG column. The decrease in retention time of tricaprins on the fused silica column indicates liquid phase is being lost from the column. In contrast, the retention time for tricaprins on the MXT®-Biodiesel TG column stays consistent, indicating no phase loss due to cycling the column at high temperature. Practically, this translates into reliable performance and longer column lifetimes.

Unique Solutions that Simplify Practical Operation

Factory connected 0.32mm MXT®-Biodiesel TG columns & 0.53mm retention gaps

For accurate analysis of heavy triglycerides, on-column or PTV injection is required. Analytical methods ASTM D-6584 and EN-14105 describe the use of a 0.32mm analytical column coupled with a 0.53mm retention gap. The 0.53mm ID retention gap allows the on-column technique to be used, but care must

be taken to minimize dead volume and to establish a leak-tight connection. Restek's 0.32mm MXT®-Biodiesel TG columns are factory-coupled to a 0.53mm MXT® retention gap with an Alumaseal™ connector, ensuring a leak-tight connection. Target analytes resolve well and the solvent and triglyceride peaks show excellent symmetry (Figure 4).

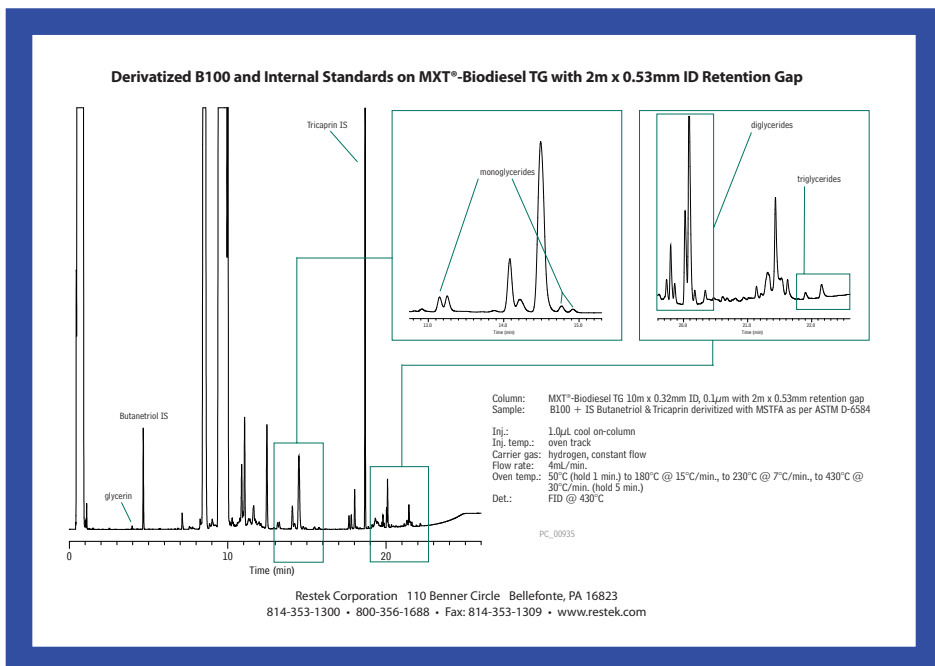


Figure 4: Glycerin and glycerides in derivitized B100 samples resolve well and show excellent peak symmetry on the 0.32mm MXT®-Biodiesel TG column, which is factory-coupled to a 0.53mm MXT® retention gap.

0.53mm MXT®-Biodiesel TG columns

The 0.53mm MXT®-Biodiesel TG columns are a simpler alternative to using a 0.32mm column coupled to a 0.53mm retention gap. Restek applied the Integra Gap™ technology to the 0.53mm MXT® Biodiesel TG columns, eliminating the column coupling. These 100% leak-proof columns feature a built-in retention gap, reducing the risk of peak broadening and tailing, and guaranteeing the user many analyses without downtime. Chromatography from the 0.53mm MXT®-Biodiesel TG with Integra Gap™ technology (Figure 5) is excellent and comparable to that obtained on the 0.32mm ID column in (Figure 4).

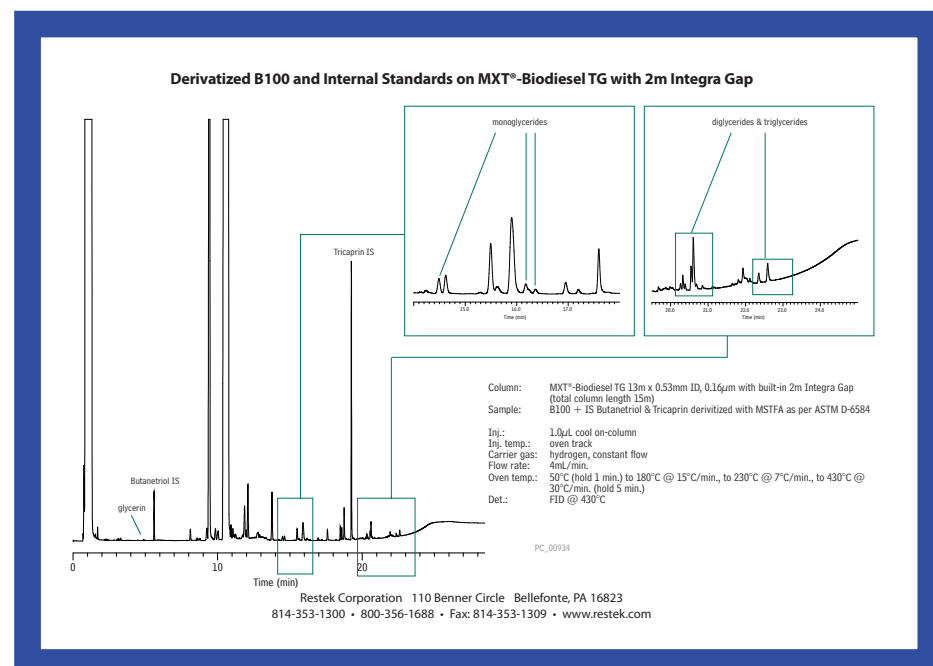


Figure 5: Equivalent chromatographic quality can be obtained on the 0.53mm MXT®-Biodiesel TG analytical column. The built-in retention gap eliminates the need for a connector, thus preventing peak tailing from dead volume.

Conclusion

As demonstrated, for high temperature GC analysis, the metal MXT-Biodiesel TG column is a rugged column that withstands the harsh temperatures required for total residual glycerin analysis. The column has the resolution needed for accurate, reliable results and is more stable at high temperatures than competitive fused silica columns. This high temperature stability leads to longer column lifetimes and less down time for maintenance and/or column change outs.

For additional information about the MXT®-Biodiesel TG capillary column or other analytical needs for biodiesel analysis contact your nearest Restek Sales Representative or Distributor.

New Biodiesel Analyser



Globally, public authorities promote the use of blends of biofuel and conventional fuel through directives and by setting ambitious goals. Standardization bodies, such as ASTM and CEN, have already published methods that outline specifications for biodiesel as blending component and test methods are available to determine the quality of the biodiesel.

AC Analytical Controls (The Netherlands) offers a new chromatographic solution that complies with all ASTM & EN test methods for biodiesel analysis.

The AC Biodiesel Systems use an Agilent Technologies high performance 7890 or the more compact, easy to use 6850 gas chromatograph equipped with: a Electronic Pneumatics Control (EPC) for setting flow and pressure parameters, a Flame Ionization Detector (FID) for signal generation, an Automatic Liquid Sampler and an a Capillary Column.

Companies Warned Ignoring the Environment on Biofuels Could Cost Future Profits

Companies are jeopardising future performance by ploughing headlong into biofuels without considering the long-term issues according to a new report launched on 14 May by **Co-operative Insurance**.

Investment in biofuels has surged in recent years because of its attraction as a supposedly eco-friendly alternative to fossil fuels. While Co-operative Insurance supports the use of biofuels it is concerned about the potential environmental and social dangers if growth continues at its current rate. It is therefore warning companies that investing in biofuels could backfire unless sustainability criteria are built into the supply chains.

Biofuel production is heavily supported worldwide by governments keen to reduce their reliance on oil as well as provide additional income to farmers. However, the area of land required to grow biofuels is so great that it could cause serious environmental problems if not managed correctly. For example, meeting increased demand could lead to deforestation, as has been the case with palm oil production in South East Asia (palm oil is a key ingredient for some biofuels). It may also push up global food prices and have disastrous effects on biodiversity. These concerns were echoed in a separate recent report issued by the UN.*

As a responsible shareholder, Co-operative Insurance wants companies in which it invests to develop effective approaches to address the challenges. It will now use the report's recommendations to engage with companies and seek reassurance that they will put strategies in place to mitigate the risks. As a shareholder Co-operative Insurance has an interest in protecting long term shareholder value by ensuring companies fully address their risks and opportunities.

Sam Lacey, Responsible Shareholding Analyst at Co-operative Insurance and author of the report, said: "Biofuels are not a panacea for climate change but can play their part if governments and companies start thoroughly managing the social and environmental impacts.

"The current growth of the industry is happening without paying attention to long-term impacts. It must be pushed in a more sustainable direction and complemented by fuel efficiency measures and reducing our use of fossil fuels."

The report makes a number of recommendations in three key areas: Examples include: Environmental and Social – Ensure that conversion of land to grow biofuels does not cause significant environmental damage. Conduct thorough stakeholder consultation prior to land conversion to avoid civil unrest. Strategic – Incorporate sustainability criteria into decision-making processes and contracts throughout the supply chain and consult with stakeholders affected. Sector Specific – Food Retailers: Prioritise sustainability in biofuels approved and seek to mitigate risks of increasing commodity prices.

Co-operative Insurance has already encouraged investee companies involved in the palm oil supply chain to join the Roundtable for Sustainable Palm Oil (RSPO). Palm oil is a key ingredient in a huge number of everyday products, such as margarine, crisps, lipstick and soap, as well as biodiesel. Many major UK businesses joined up and are working towards sustainable supply chains following engagement with CIS.