Analyze Biodiesel Oil for Glycerin

Using Restek's Robust Rtx®-Biodiesel Capillary GC Column

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- Linearity for all reference compounds exceeds method requirements on an Rtx®-Biodiesel Column.
- Alumaseal™ connector provides leak-free connection, guard column extends column life.
- Low column bleed at high temperatures.

"Biodiesel", "B100", "B20", "B10", and "transesterification" are becoming everyday terminology as of late. Biodiesel oil is biodegradable, nontoxic, and contains no 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). In the United States, biodiesel is recognized as an alternative energy source by the Environmental Protection Agency and the Department of Energy, which qualifies the fuel for mandated programs under the Clean Air Act of 1992.

Transesterification of the animal fat or used vegetable oil from which biodiesel oil is prepared yields two products: methyl esters (biodiesel oil) and glycerin. Excessive amounts of free or bound glycerin in biodiesel oil product can foul injectors and form deposits on valves, pistons, and injector nozzles. Separation of the glycerin during storage or in vehicles' fuel tanks can reduce the shelf life of the product. The American Society for Testing and Materials, ASTM, describes several physical and chemical testing methods for biodiesel oil. In this article we focus on gas chromatographic method ASTM D-6584-00, which sets the industry standards for testing B100 biodiesel oil. Through this method, the analyst can quantify free glycerin in the range of 0.005 to 0.05 mass % and total glycerin from 0.05 to 0.5 mass %. The column recommended for the analysis is a 10m x 0.32mm ID fused silica column with a 0.1µm film of 5% diphenyl/95% dimethyl polysiloxane. The stationary phase and the polyimide coating on the tubing must be sufficiently robust to withstand high temperatures, and the column must exhibit low bleed.

We initiated this project to demonstrate the performance of our Rtx®-Biodiesel fused silica column for conformance to the ASTM method. In addition, we used a 5m x 0.53mm intermediate polarity (IP) deactivated fused silica guard column, coupled to the analytical column through an Alumaseal™ connector, to trap high molecular weight sample components and thereby increase the longevity of the analytical column. An Agilent 6890 GC, equipped with a cool on-column injector and FID, was used for analysis. Hydrogen, supplied from a Parker/Balston hydrogen generator, was both the FID fuel gas and, for optimum performance, the carrier gas. ChemStation® software was used as the data collection system.

The column was conditioned at 380°C for an hour prior to analysis. Calibration standards were prepared and silylated per ASTM method D-6584-00. To achieve the highest degree of accuracy we chose, and recommend the use of, a 250µL glass syringe, as opposed to automatic pipette-type dispensers. After adding the N-methyl-N-trimethyltrifluoracetamide (MSTFA) silyating agent, we gently agitated the vial for approximately two minutes, and then allowed it to stand at room temperature for 20 minutes.

GC parameters were as recommended in the method. Figure 1 illustrates the calibration curves for each reference compound. Each plot from the Rtx®-Biodiesel column, including triolein, complies with the established method linearity criteria ($r^2 \geq 0.99$). Triolein, used for triglyceride quantification, historically has been difficult to calibrate. During this study we also evaluated a competitor's column and, while the linearity for other compounds was acceptable, the result for triolein ($r^2 = 0.9698$) on the competitor's column did not conform to the method specification. This low r^2 value could not be corrected by reinstalling the column or optimizing the GC conditions.

RESTEK PRODUCTS

- **GC Columns** Rtx®-Biodiesel Column
- **Analytical Reference Materials** Biodiesel Calibration Standards
- **Column Ferrules** Alumaseal™ Ferrules
- **Purus Gas Systems** Parker ChromGas° Hydrogen Generators
- **Reference Book** Chromatographic Detectors. Design, Function, and Operation

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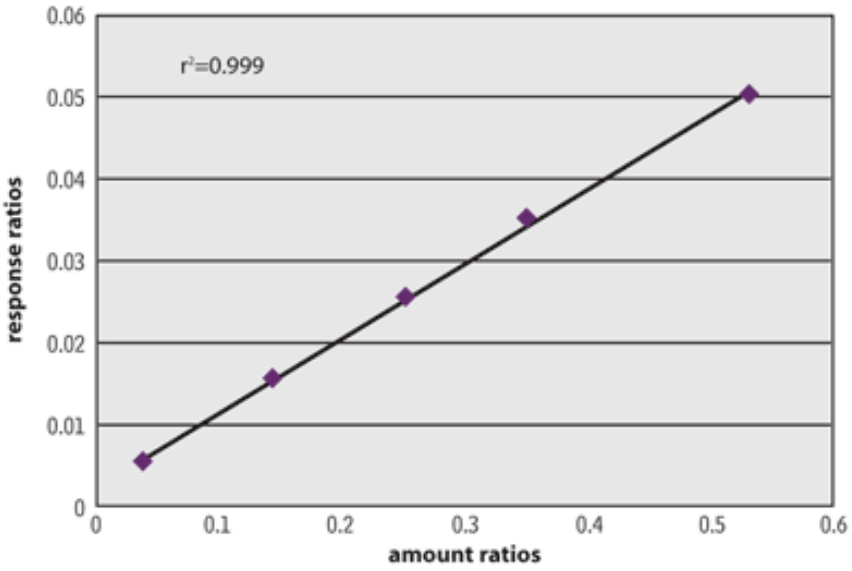
After developing the calibration curves, we spiked a sample of B100 biodiesel oil with the two internal standards, butanetriol and tricaprin, then silylated the mixture with MSTFA. Data from the subsequent analysis are illustrated in Figure 2. Results using the Rtx®-Biodiesel column were 0.05 mass % free glycerin, 0.44 mass % bound glycerin, and 0.49 mass % total glycerin, which are within the target range of the method. Column performance at high temperatures also was strong – bleed was low even at 380°C.

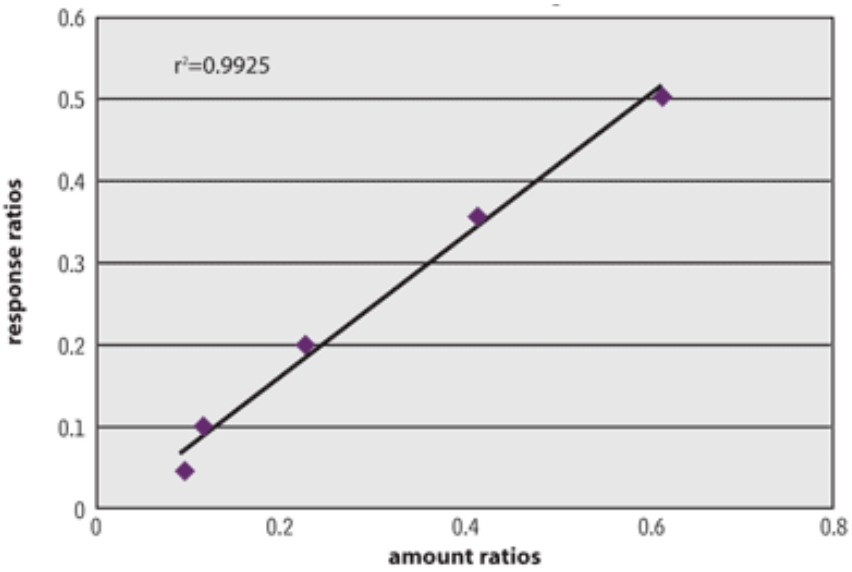
The Rtx®-Biodiesel column, coupled to a guard column through an Alumaseal™ connector, guarantees the performance required to meet the stringent standards for biodiesel analysis. Restek's technical experts are here to offer practical solutions to your toughest analytical problems. If you have questions regarding biodiesel analysis, or other challenging applications, please call our technical service team for assistance.

Figure 1 An Rtx®-Biodiesel column meets correlation coefficient specifications for determining glycerin in biodiesel oil.

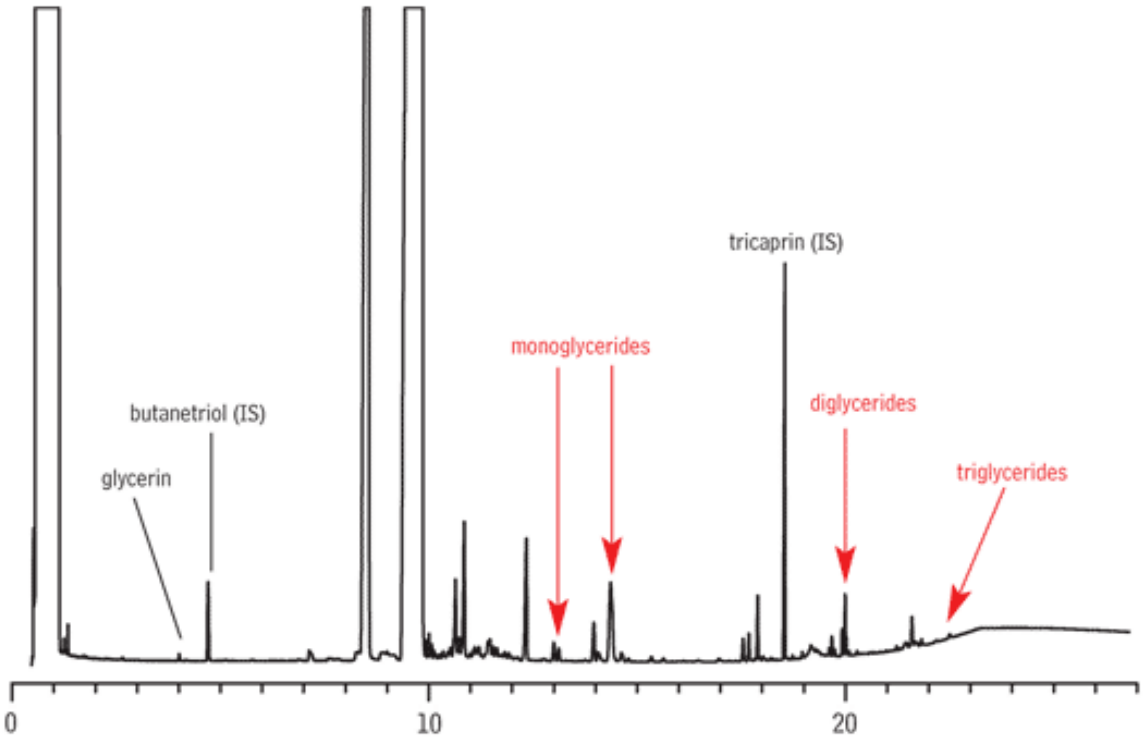
Glycerin (5-50mg)



Triolein (50-500mg)



Monolein (100-1000mg)



GC_PC00908

Column:	Rtx®-Biodiesel, 10m, 0.32mm ID, 0.10µm (cat.# 10291) 2m, 0.53mm ID Hydroguard connected via Alumaseal™ connector
Sample:	biodiesel oil (B100) plus internal standards butanetriol and tricaprin, and derivatized per ASTM Method D 6584
Inj.:	1µL, cool on-column
Inj. temp.:	oven track
Carrier gas:	hydrogen, constant flow
Flow rate:	4mL/min.
Oven temp.:	50°C (hold 1 min.) to 180°C @ 15°C/min. (hold 7 min.) to 230°C @ 30°C/min. to 380°C @ 30°C/min. (hold 5 min.)
Det.:	FID
Det. temp.:	380°C