Biodiesel Analysis by European Methodology

Exceptional Peak Symmetry, Using an Rtx®-Biodiesel GC Column

By Barry L. Burger, Petroleum Chemist

- Excellent peak shape, even for free glycerin.
- Low column bleed at >350°C.
- Quantify oil components more easily and more reliably.

In less than a decade biodiesel oil has become a significant fuel source, especially in European countries, where current usage has soared to 1,800,000 tons annually.[1] Transesterification of the rapeseed oil or other fats from which biodiesel oil is prepared yields two products: methyl esters – biodiesel oil – and glycerin. Glycerin is extremely challenging to analyze by GC, but because excessive amounts in biodiesel products can cause problems during storage or in the engine it is necessary to monitor glycerin levels. In the US, American Society for Testing and Materials (ASTM) Method D6584-00e1 is an accepted GC procedure for biodiesel oil analysis; the standard European method is Deutsches Institut fur Normung (DIN) EN14105. Both methods set limits on free glycerin and glycerides in biodiesel oil product. While these methods differ in GC column specifications and chromatographic conditions, both require a column that can perform reliably at elevated temperatures, with minimal bleed.

Figure 1 shows the chromatography for the DIN analysis, using an Rtx®-Biodiesel column. Peaks for glycerin and the glycerides exhibit minimal tailing, and bleed is low, even at 370° C. Thus, components of the oil can be more easily and more reliably quantified. These results confirm the Rtx®-Biodiesel column is a wise choice for biodiesel oil analysis according to DIN EN14105 conditions. The Rtx®-Biodiesel column also has proven well suited for analyzing biodiesel oil according to the ASTM method.[2]

To obtain Figure 1, we spiked a soybean oil-based sample of B100 biodiesel oil with internal standards butanetriol and tricaprin, silylated the mixture with MSTFA and, using simple on-column injection mode, injected a 1µL aliquot into a low dead volume direct injection liner in a Shimadzu 2010 GC equipped with an on-column injector (OCI). The liner has a 1mm internal diameter and a Press-Tight® constriction one-third of its length from the outlet end. The Rtx®-Biodiesel column forms a seal with the liner at the Press-Tight® constriction; the sample is injected into, and vaporizes in, the top two-thirds of the liner.

Glycerin is a notoriously difficult challenge in GC, particularly at the levels involved in biodiesel oil analysis, yet an Rtx®-Biodiesel column provides a symmetric peak that makes quantification easier and more reliable. Restek chromatographers always are happy to help you with your toughest analytical problems. If you have questions regarding biodiesel oil analysis, please call our technical service team, or contact your Restek distributor, for fast and reliable assistance.

Figure 1 Biodiesel oil analysis using an Rtx®-Biodiesel column and DIN EN14105 conditions: peaks for glycerin and glycerides are symmetric, and bleed is low, even at 370°C.

RESTEK PRODUCTS

- **GC Columns**
  Rtx®-Biodiesel Column (fused silica)
- **Analytical Reference Materials**
  Biodiesel Calibration Standards

ALSO OF INTEREST

- Analyze Biodiesel Oil for Glycerin

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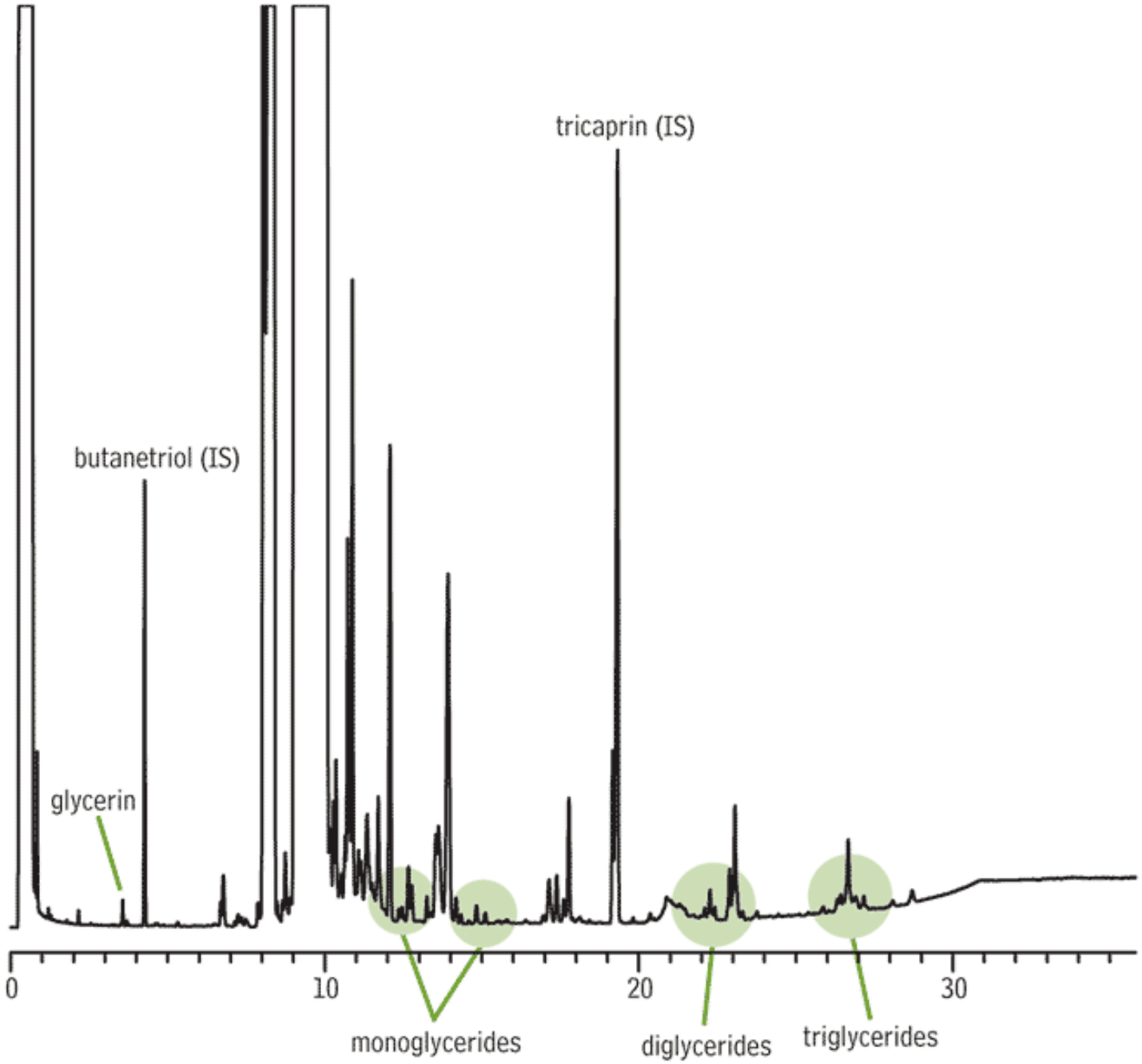

GC_PC00901

Column:	Rtx®-Biodiesel, 10m, 0.32mm ID, 0.10µm (cat.# 10292)
Sample:	B100 biodiesel oil plus butanetriol and tricaprin, in heptane, derivatized with MSTFA
Inj.:	1µL onto Shimadzu on-column injector (OCI) equipped with low dead volume Shimadzu direct injection liner
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., to 230°C @ 7°C/min., to 370°C @ 10°C/min. (hold 5 min.)
Det.:	FID
Det. temp.:	390°C

Analyze Biodiesel Oil for Glycerin

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

By Barry L. Burger, Petroleum Chemist

- 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

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

ALSO OF INTEREST

- Parker ChromGas® Hydrogen Generators
- GC Analysis of Total Reduced Sulfurs at ppbv Levels Using an Rxi -1ms Column and Sulfur Chemiluminescence Detection
- Sulfinert®-Treated Sample Cylinders Store Active Sulfur Compounds at ppb Levels

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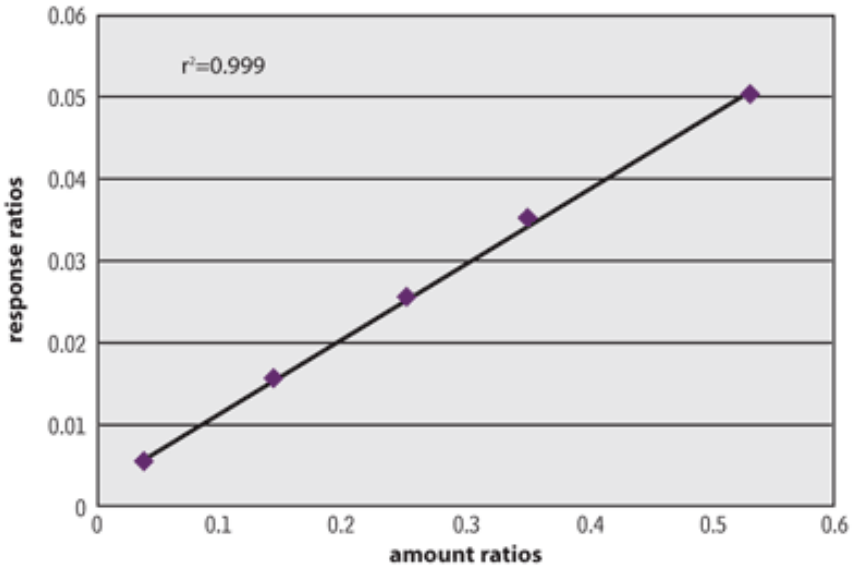
GC conditions.

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.

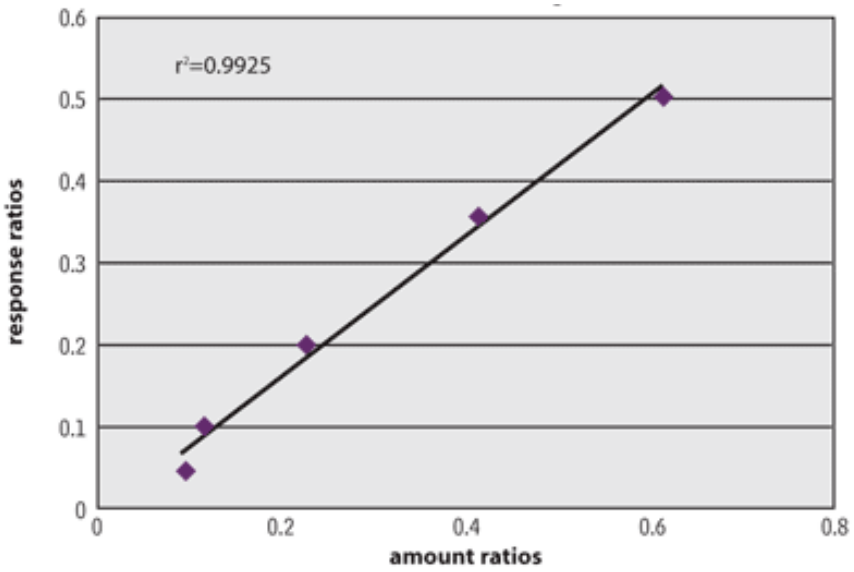
The Rtx®-Biodiesel column, coupled to a guard column through an Alumaseal™ connector, guarantees the performance required to meet the stringent standards for biodiesel analysis. Restek's technical experts are here to offer practical solutions to your toughest analytical problems. If you have questions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

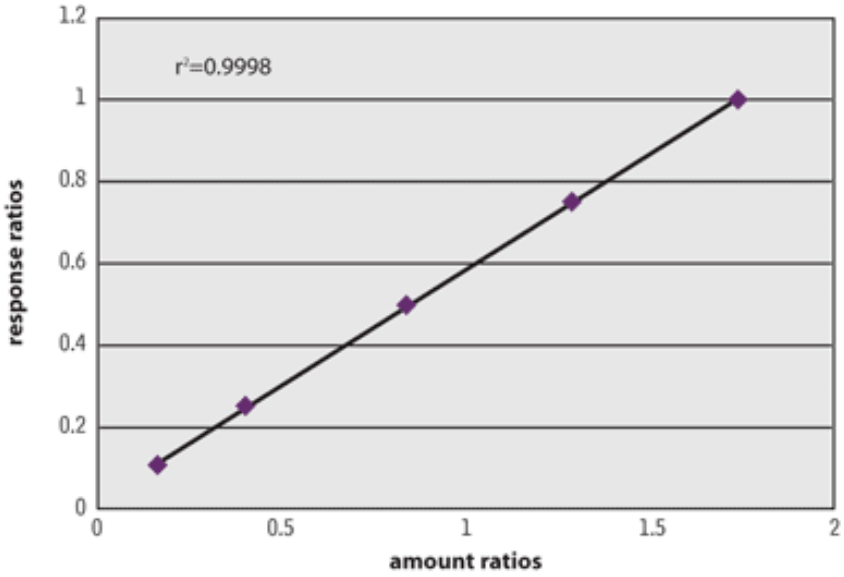
Glycerin (5-50mg)



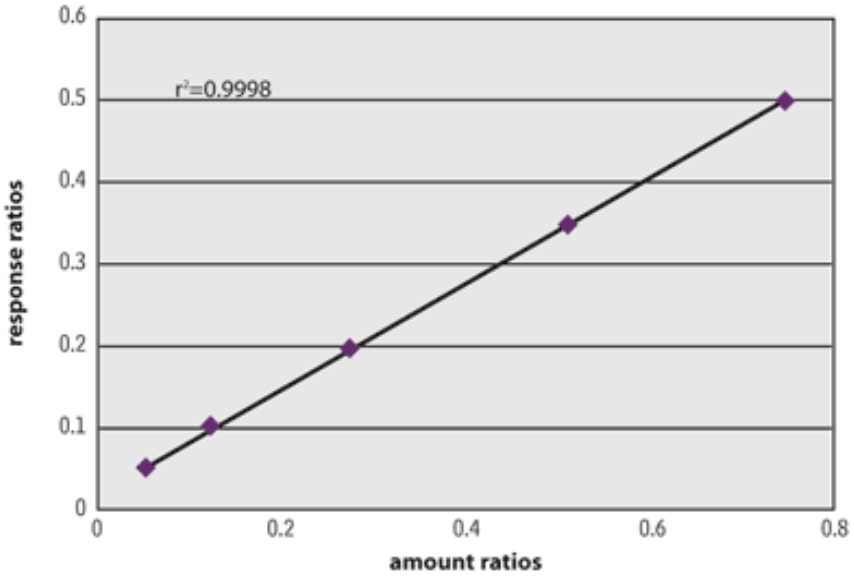
Triolein (50-500mg)



Monolein (100-1000mg)

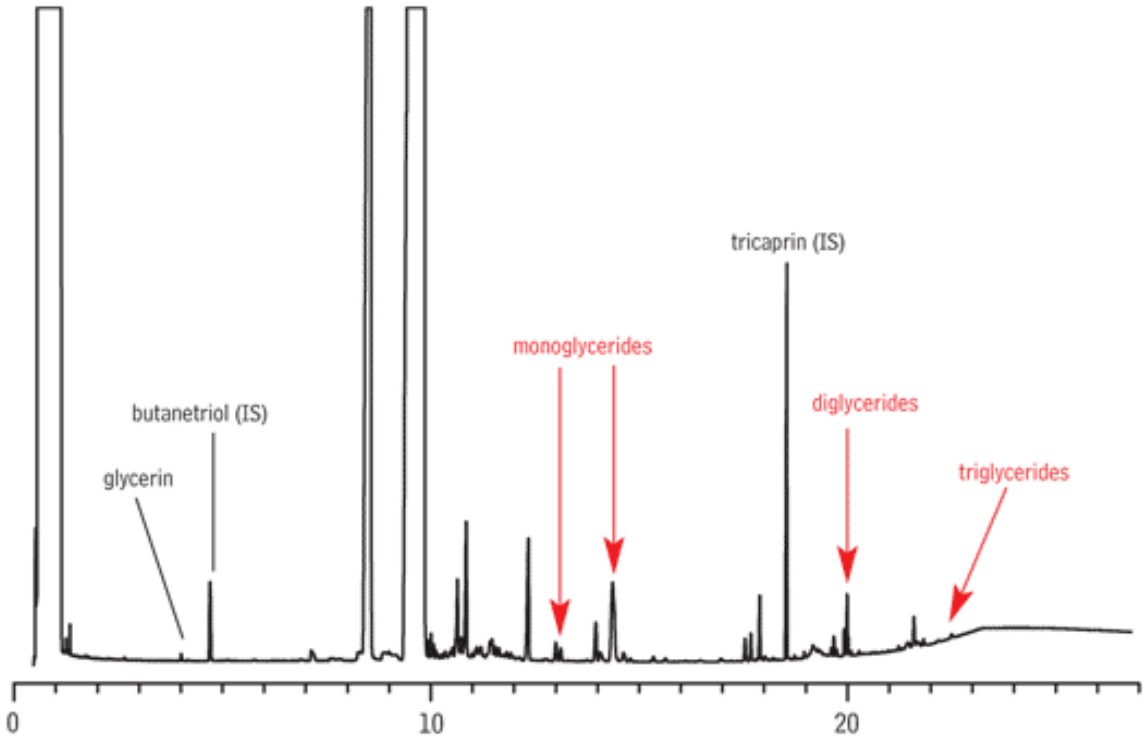


Diolein (50-500mg)



For conditions, see Figure 2.

Figure 2 Resolution of biodiesel oil (B100) and internal standards: the Rtx®-Biodiesel column provides reliable data for mono-, di- & triglycerides.



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

Biodiesel Calibration Standards

Determining Free and Total Glycerin in B-100 Biodiesel Methyl Esters by GC
In the manufacture of biodiesel fuel, triglycerides are split into their monoalkyl ester components via transesterification. The fatty acid monoalkyl esters can be used as fuel in diesel engines. Amounts of free glycerin and total glycerin indicate the quality of the conversion of the oil or fat to monoalkyl esters. D6584-00 and DIN EN14105 are test methods for quantitative determination of free glycerin, total glycerin, and mono-, di-, and triglycerides in biodiesel fuel methyl esters by GC, after silylation of the sample with N-methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA).

Concentration is µg/mL, unless otherwise noted. Volume is 1mL/ampul unless otherwise noted.

Description	Volume	CAS #	Solv. Code	Conc.	qty.	Cat.#
(s)-(-)-1,2,4-butanetriol		42890-76-6	pyridine	1,000	ea.	33024
(s)-(-)-1,2,4-butanetriol	5mL	42890-76-6	pyridine	1,000	ea.	33032
diolein (1,3-di[*cis*-octadecenoyl]glycerol)		2465-32-9	pyridine	5,000	ea.	33022
glycerin		56-81-5	pyridine	500	ea.	33020
monolein (1-mono[*cis*-9-octadecenoyl]-rac-glycerol)		111-03-5	pyridine	5,000	ea.	33021
monopalmitin		524-44-9	pyridine	5,000	ea.	33026
tricaprin (1,2,3-tricaprinoylglycerol)		621-71-6	pyridine	8,000	ea.	33025
tricaprin (1,2,3-tricaprinoylglycerol)	5mL	621-71-6	pyridine	8,000	ea.	33033
triolein (1,2,3-Tri[*cis*-octadecenoyl]glycerol)		122-32-7	pyridine	5,000	ea.	33023