Application Note: 10192

Determination of Free and Total Glycerin in B-100 Biodiesel via Method ASTM D6584

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Key Words

- TRACE GC Ultra
- ASTM 6584
- Biodiesel
- GC/FID
- Glycerin

Introduction

Biodiesel has gained recent popularity as a clean burning alternative fuel produced from domestic, renewable resources. Fuel-grade biodiesel is made from natural oils derived from soybean, canola, olive, or other plant oils or animal fats. These oils can be obtained from either natural oils crushed from plant seeds or from recycled, used oils (i.e., fryer oils). Biodiesel is made through a chemical process of transesterification whereby glycerin is separated from the fat or vegetable oil. The process results in two major products: Fatty Acid Methyl Esters (or biodiesel) and glycerin. The latter can be further used to produce soaps and other products. Once separated from glycerin, biodiesel can be blended with petroleum diesel in various concentrations that can be used in diesel engines with little or no modifications. Biodiesel blends are denoted as "BXX" with "XX" representing the percentage of biodiesel contained in the blend (e.g., B20 is 20% biodiesel, 80% petroleum diesel).

Free and bonded glycerin content of the finished biodiesel product indicates the quality of the product. A high glycerin content may cause problems in a fuel system that can lead to injector clogging and formation of deposits in injector nozzles, pistons, and valves.[1] The American Society for Testing and Materials (ASTM) has designated certain standards for the amount of free and total glycerin content in a finished biodiesel B100 product. Through this method, the analyst can determine the amount of free and total glycerin in the range of 0.005 to 0.05 mass % and 0.05 to 0.5 mass %, respectively. Analyzing the amount of free and total glycerin in the form of mono-, di- or triglycerides during the esterification process is mandatory when manufacturing biodiesel. ASTM has determined a cutoff value of 0.240% by mass as the amount of total glycerin that can be present in B100.[2]

ASTM D 6584 specifies the use of a gas chromatograph (GC) equipped with a cold on-column injector and an FID detector. In this application, we demonstrate the use of the Thermo Scientific TRACE GC Ultra™ and a PTV injector in simulated on-column mode to obtain rapid and accurate results when using the ASTM specifications.

Experimental

Materials and Sample Preparation

Reagents consisting of *n*-heptane, and *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MSTFA) were obtained from Thermo Fisher Scientific. Calibration and internal standards were obtained as an ASTM D6584 Individual Standard Solution and Internal Standards Kit, # 44918-U from Supelco (Bellefonte, PA). Analytes in the standard solution kit were glycerol (CAS 56-81-5), triolein (CAS 122-32-7), 1-mono (cis-9-octadecenoyl)-rac-glycerol (CAS 111-03-5) and 1,3-diolein (CAS 2465-32-9). The internal standards were identified as butanetriol (internal standard #1) and tricaprin (internal standard #2). All standard solutions were diluted in pyridine. Standards and samples were treated in an identical manner by weighing out approximately 100 mg of sample or standard, adding the internal standards, adding 100 µL of MSTFA and allowing the mixture to stand at room temperature for at least 20 minutes. 8 mL of *n*-heptane were added to each sample and standard, mixed, and analyzed on the GC.

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Analysis

A Thermo Scientific TRACE GC Ultra equipped with a Programmable Temperature Vaporizing (PTV) inlet in simulated on-column configuration and a flame ionization detector (FID) was used. Injections were performed with a Thermo Scientific AS3000 liquid autosampler. A 5% phenyl fused silica capillary column (10 m x 0.32 mm ID x 0.1 µm film thickness) was connected to an uncoated, deactivated 5 m x 0.53 mm ID fused silica pre-column with a press-tight fitting. 1 µL of each derivatized sample and standard was injected into the TRACE GC Ultra. Instrument conditions are shown in Table 1. A detailed view of the PTV inlet method parameters is shown in Figure 1. Thermo Scientific ChromQuest™ 4.2 software was used for data acquisition and analysis. Calculation of total glycerin was performed based upon normalized relative retention times for glycerin, monoglycerides, diglycerides and triglycerides as specified in ASTM 6584.[2]

GC oven	50 °C for 1 min,15 °C/min to 180 °C, hold 0 min, 7 °C/min to 230 °C, hold 0 min, 30 °C/min to 380 °C, hold 8 min
Carrier gas	Helium at 3.0 mL/min, constant flow
Detector	FID at 400 °C, ignition threshold 0.5 mA, H_2 flow at 35 mL/min, air at 350 mL/min, N_2 (make-up) at 30 mL/min

Table 1: Instrument conditions

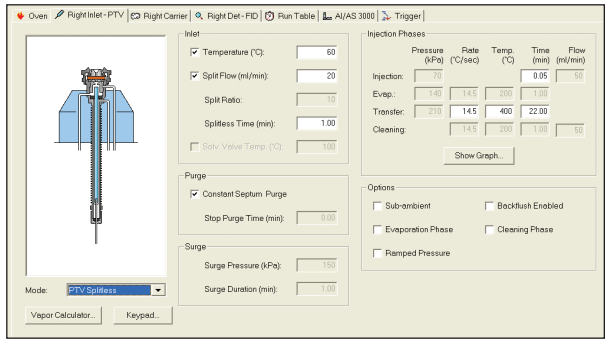


Figure 1: PTV conditions for simulated on-column injections

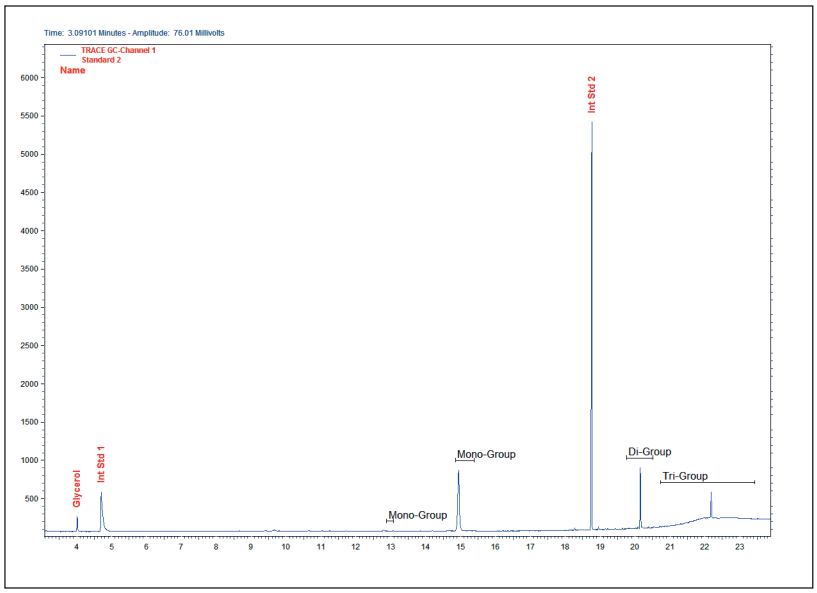
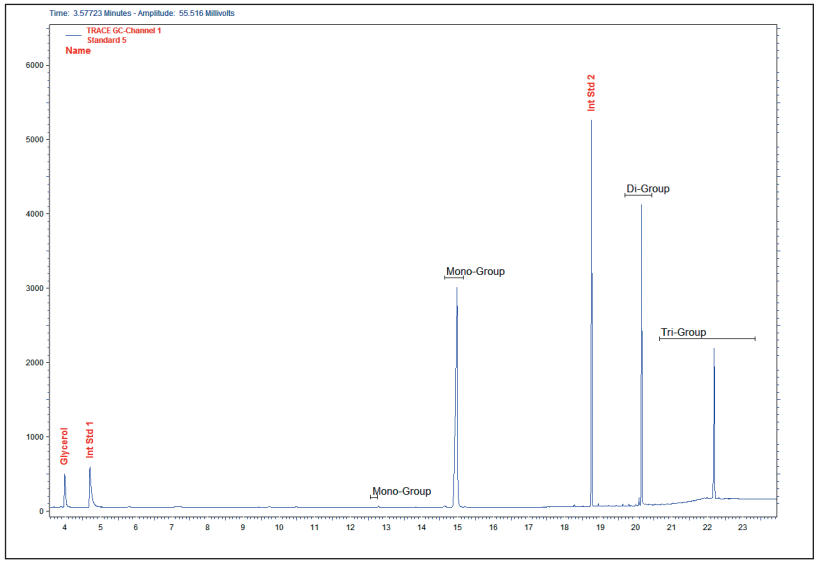


Figure 2a: Typical chromatogram for lowest level calibration standard

Figure 2b: Typical chromatogram for highest level calibration standard



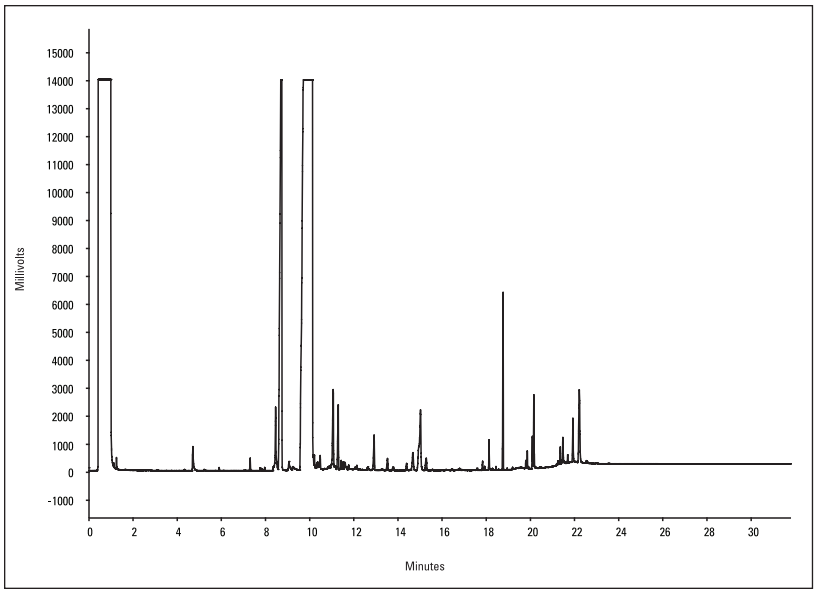


Figure 3: Typical chromatogram obtained from biodiesel derived from olive oil

Results and Discussion

Typical chromatograms for the low and high level standards are shown in Figure 2. A sample of biodiesel obtained from olive oil is shown in Figure 3. Calibration curves obtained from the 5-level standard set are shown in Figure 4 for each of the calibrant peaks, demonstrating good linearity for single replicate injections.

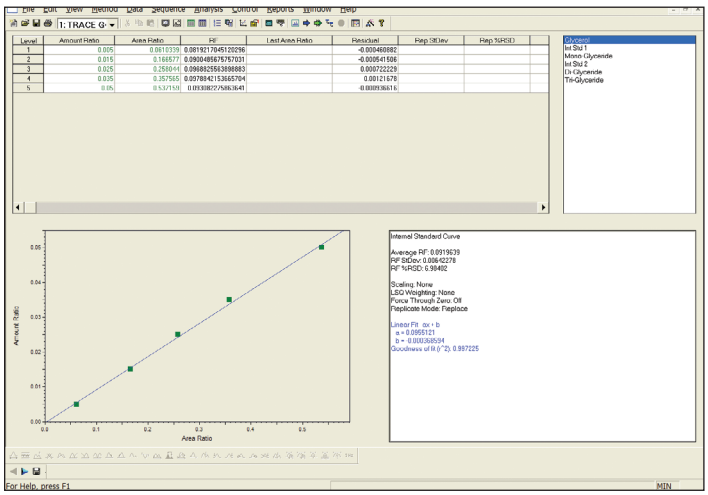


Figure 4a: Calibration curve for glycerol

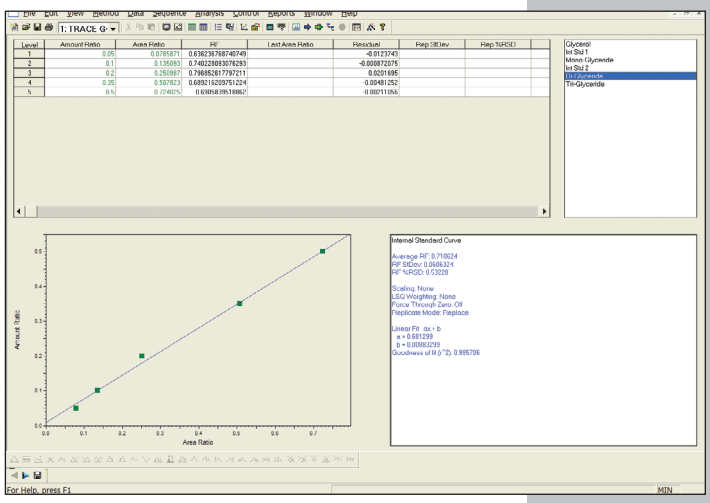


Figure 4c: Calibration curve for diglyceride

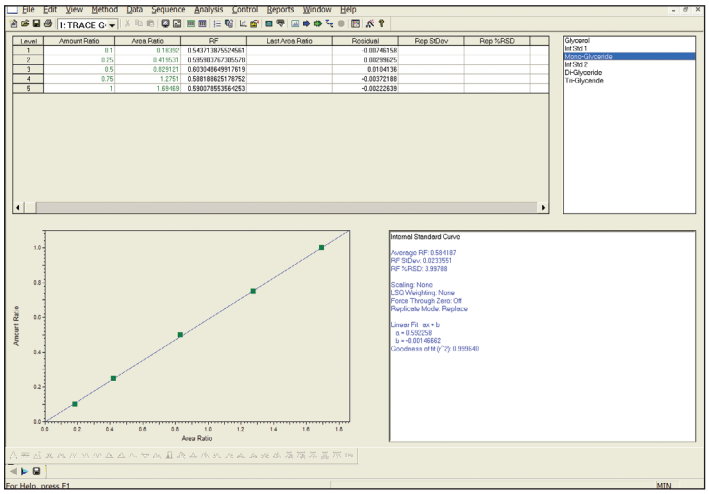


Figure 4b: Calibration curve for monoglyceride

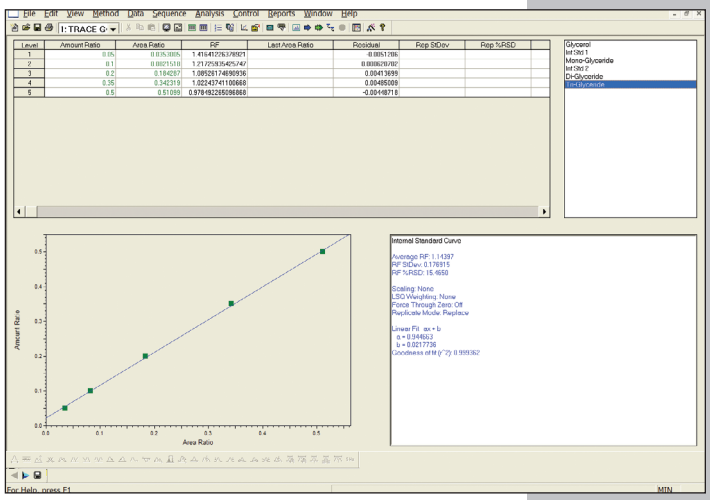


Figure 4d: Calibration curve for triglyceride

Glycerin along with each group of glyceride (mono-, di- and triglyceride) was calculated according to the ASTM method. Each group of glyceride was multiplied by its specific multiplier as specified in ASTM 6584. All groups were summed to obtain the total glycerin in the biodiesel sample. The free and total adjusted glycerin mass percent was reported as shown in Figure 5.

Conclusion

ASTM 6584 specifies the use of a Cold On-column injector. The TRACE GC Ultra gas chromatograph can be fitted with either a dedicated cold on-column inlet or a PTV injector that can be set up for use as a simulated on-column inlet, delivering equivalent results in compliance with the ASTM method specifications. All peaks of the calibrators were detected with either injector. The PTV was heated to 400 °C after injection and was held at this temperature for the duration of the GC run time, which resulted in excellent shapes for the peaks eluting at the end of the run (i.e., triglycerides).

The PTV inlet can be used in a conventional split/splitless application as well as in applications that call for a cold on-column configuration. The versatility of this inlet makes it an attractive option for labs that run ASTM 6584, but also need to run other GC applications on the same system.

With increased interest in biodiesel production, the issue of product quality will be an ongoing concern. We have demonstrated that the TRACE GC Ultra for determination of free and total glycerin provides excellent chromatographic data in an easy-to-use format for compliance with ASTM specifications.

References

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2. ASTM International. 2000. Test method for determination of free and total glycerin in B-100 biodiesel methyl esters by gas chromatography, Designation D 6584-00. ASTM International, West Conshohacken, PA, USA.

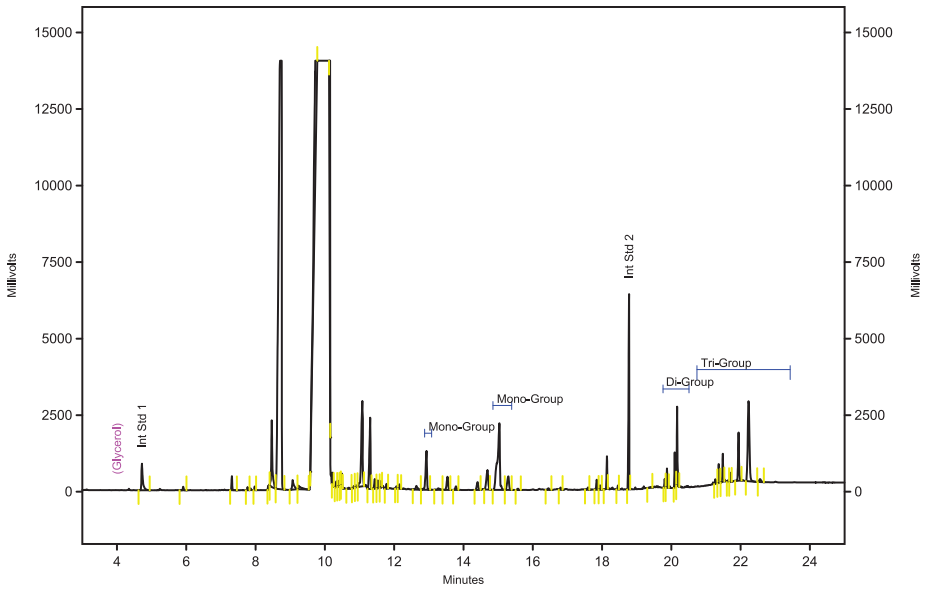

Figure 5: Typical report for an "unknown" biodiesel sample

TRACE GC-Channel 1
Results (System
(4/5/2007 11:36:20 AM)
(Reprocessed))

Name	Retention Time	Area	Concentration (%)
Int Std 1	4.720	24031016	0.000
Int Std 2	18.780	90666822	0.000
Totals		114697838	0.000
Mono-Group		160474656	0.270
Di-Group		61654488	0.067
Tri-Group		157237120	0.189
Totals		379366264	0.527

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