

Application Note # CA-270359

Analysis of Free and Total Glycerine in B-100 Biodiesel Methyl Esters by Gas Chromatography

Introduction

ASTM D6584 is the standard test method commonly used for the quantitative determination of free and total glycerine in B-100 methyl esters by gas chromatography. The detection range for free glycerine is 0.005 to 0.05 mass %, and for total glycerine 0.05 to 0.5 mass %. This procedure is not applicable to the analysis of vegetable oil methyl esters obtained from lauric oils, such as coconut oil and palmkernel oil.

Instrumentation

Bruker 450 Gas Chromatograph

- Injector: Cold on-column (1093), full EFC control
- Detector: FID, full EFC control
- Automatic Liquid Sampler: CP-8410 GC control and data handling software
- Galaxie™ GC Workstation

Materials and Reagents

- Capillary Column: Select™ Biodiesel for Glycerides (Part No. CP-9079), 15 m x 0.32 mm (id) x 0.1 µm (film)
- Retention gap: 2.5 m x 0.53 (id)
- Connector: stainless steel ZDV (zero dead volume)
- Carrier gas (Helium or Hydrogen; 99.999 pure or better)
- N-methyl-N-trimethylsilyltrifluoroacetamide (MSTFA)
- N-Heptane
- Pyridine
- Volumetric flasks 50 and 100 mL
- Glass micro-syringes; 1, 100 and 250 µL capacity
- Precision pipette (1 mL)
- 10 mL glass vials and caps with PTFE faced sept

Sample Preparation

Standard mixtures and internal standard solutions were prepared according to the method and analyzed, via the conditions denoted below, to establish the various calibration curves for the target analytes. Approximately 100 mg of sample were weighed to the nearest 0.1 mg directly in a 10 mL glass vial with septa and cap. Using a micro syringe, exactly 100 µL of each internal standard and MSTFA were added. The vials were gently shaken and allowed to equilibrate for 15 to 20 minutes at room temperature. Then, approximately 8 mL of n-Heptane was added to each vial and shaken again. Finally, 1 µL of the mixture was injected into the GC and the analysis was started (see Table 2 for typical results).

Conditions

Inlet: Cool, on-column, 1 µL (note: immediately after injection, the inlet is programmed to follow the temperature program of the oven)

Detector: FID, 380 °C

Oven: 50 °C, (1 min) @ 15 °C/min to 180 °C

@ 7 °C/min to 230 °C

@ 30 °C/min to 380 °C (10 min)

Carrier Gas: Helium, 3 mL/min

Results and Discussion

As a result of the analysis of a B-100 Biodiesel sample, a chromatogram was obtained, shown in Figure 1. Calibration curves were obtained for glycerine, monoolein, diolein and triolein. Calibration curves for glycerine and monoolein, shown in Figures 2 and 3, are indicative of system performance for the application.

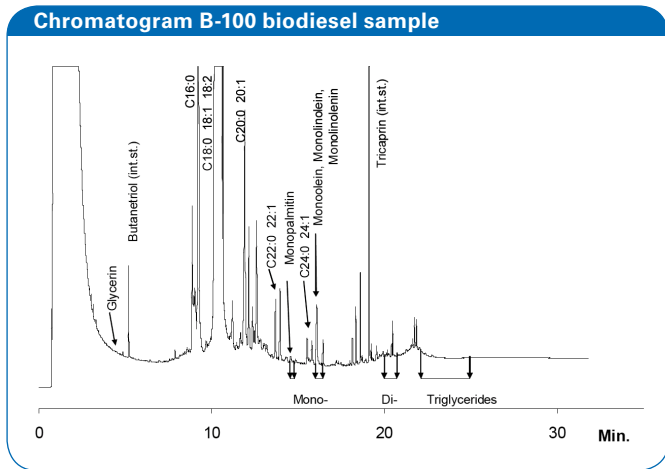


Figure 1: Biodiesel chromatogram.

Conclusion

This application note demonstrates the suitability of Bruker's 450-GC equipped with a cold on-column injector and the Select™ Biodiesel for Glycerides column, for the analysis of biodiesel. The calibration curves and repeatability data demonstrate good system integrity. Therefore, the system is well suited to the analysis of free and total glycerol and mono, di and triglyceride content in biodiesel in accordance with the standard method ASTM D6584.

Table 1: Repeatability figures for a biodiesel sample.

File	Glycerine (mass %)	Monoglycerides (mass %)	Diglycerides (mass %)	Triglycerides (mass %)	Totals
1_2	0.00162	0.11441	0.00523	0.00358	0.12484
1_3	0.00164	0.11167	0.00530	0.00392	0.12274
1_4	0.00159	0.10894	0.00519	0.00374	0.11946
1_5	0.00147	0.10696	0.00519	0.00359	0.11721
1_6	0.00161	0.11115	0.00518	0.00398	0.12192
3_1	0.00168	0.10720	0.00531	0.00419	0.11838
3_2	0.00158	0.10835	0.00524	0.00383	0.11901
3_3	0.00160	0.10483	0.00527	0.00388	0.11558
3_4	0.00156	0.10721	0.00524	0.00376	0.11777
3_5	0.00160	0.10731	0.00526	0.00386	0.11802
Average	0.001595	0.108803	0.005241	0.003833	0.11949
St.Dev.	5.5E-05	2.8E-03	4.5E-05	1.8E-04	2.8E-03
St.Dev. (%)	3.4	2.6	0.9	4.7	2.4

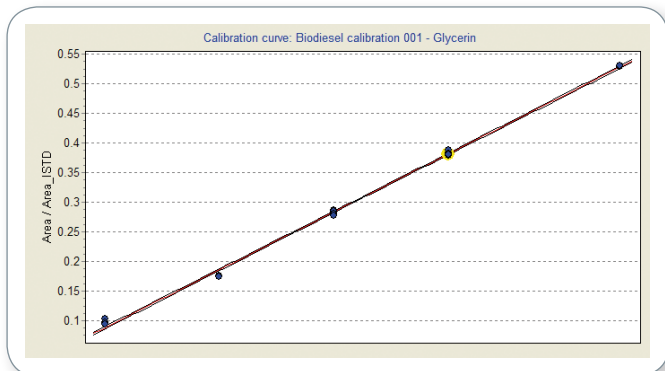


Figure 2: Calibration curve: Biodiesel calibration 001 – Glycerine.

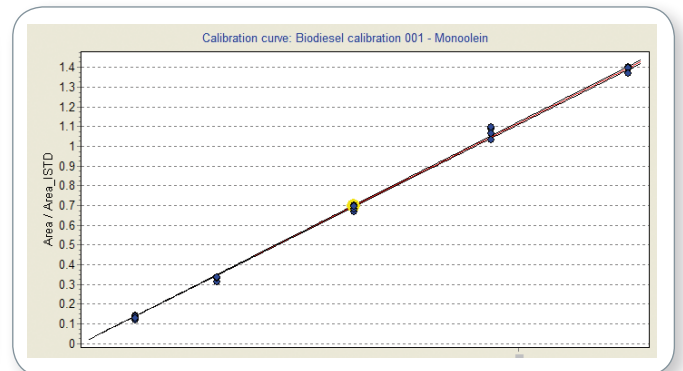


Figure 3: Calibration curve: Biodiesel calibration 001 – Monoolein.

Table 2: Typical analysis results of a biodiesel sample.

Index	Name	Area ($\mu\text{V}\cdot\text{Min}$)	Quantity (mass %)
1	Monoglycerides	14279.8	0.11441
2	Diglycerides	1468.4	0.00523
3	Triglycerides	188.6	0.00358
4	Glycerine	30.8	0.00162
Total		15967.6	0.12484

Keywords	Instrumentation & Software
Analysis of Biodiesel	Bruker 450
Free and total glycerine	Gas Chromatograph
ASTM D6584	Galaxie™ GC Workstation

For research use only. Not for use in diagnostic procedures.

References

- [1] Test Method for the Determination of Free and Total Glycerine in B-100 Biodiesel Methyl Esters by Gas Chromatography; ASTM D6584.