APPLICATION NOTE

AN075

Analysis of Free and Total Glycerin in B-100 Biodiesel Methyl Esters (ASTM D6584)

Advanced Projects & Custom Solutions Department

Introduction

The American Standard, ASTM D 6584, is the standard test method commonly used for the quantitative determination of free and total glycerin content in Fatty Acid Methyl Esters (FAME), typically intended for pure biodiesel or as a blending component for domestic and diesel fuels.

Total glycerol content is calculated from the results obtained.

The method is suitable for FAME from rapeseed, sunflower and soybean oils*.

A metal capillary GC column was specifically used for this high temperature method.

This column will not break during the extreme oven conditions and is used with a retention gap which provides both the performance and robustness required to run this application for an extended period.

*not suitable for FAME produced from or containing lauric oils, such as coconut and palm kernel oils, due to the problem of peak overlapping.

A typical chromatogram is shown in Figure 1.

Biodiesel is produced by trans-esterifying the parent oil or fat with an alcohol, usually methanol, in the presence of a catalyst, usually a strong base such as sodium or potassium hydroxide, or preferably and increasingly more commonly, alkoxides.

The resulting product therefore can contain not only the desired alkyl ester product but also unreacted starting material, namely TAG's (triacylglycerides), residual alcohol, and residual catalysts.

Glycerol is formed as a by-product and separated from biodiesel in the production process, however, traces thereof can be found in the final biodiesel product.

Since trans-esterification is a stepwise process, MAG (monoacylglycerides) and DAG (diacylglycerides) formed as intermediates can also be found in biodiesel [Knothe, 2006].

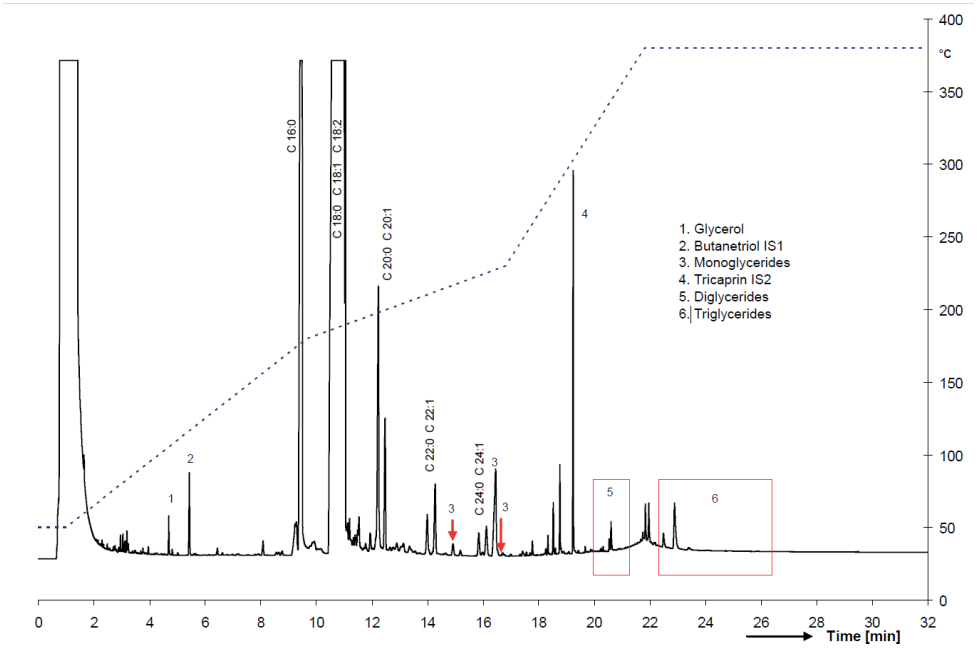

Fig. 1 - Example chromatogram of a typical B-100 biodiesel sample made from rapeseed oil (with extra glycerol and triglycerides added) after a derivatizing reaction with MSTFA. Peaks of interest are separated from the complex matrix which consists mainly of the C18 and C16 FAMEs and other minor compounds, like sterols.

Experimental

The SCION Biodiesel analyser for ASTM D6584 is based on our 436-GC platform, a cold-on-column injector, a SCION-Glycerides Inert Steel analytical column with a 2m retention gap and a High-Temp FID Detector.

The customer has a choice between what type of cryogenic oven cooling they would like to use, either configured for liquid Carbon Dioxide or liquid Nitrogen.

Analytical conditions for the ASTM D6584 analysis can be found in table 1.

Injector	Cold-on-Column Start @ 100°C (1 min) 15°C/min to 370°C
Column	10m x 0.32mm x 0.10µm SCION-Glycerides Inert Steel (SC38613) w/ Ret. Gap
Oven Program	Start @ 50°C (1 min) 15°C/min to 180°C 7°C/min to 230°C 30°C/min to 380°C End @ 380°C hold 10 min.
Carrier	Helium @ 3ml/min
Detector	FID @ 380°C
Inj. Volume	1µl
Software	Compass CDS

Table 1. Analytical conditions

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 septum 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).

Index	Name	Area (µV.min)	Quantity (% m/m)
1	Monoglycerides	14279,8	0,11441
2	Diglycerides	1468,4	0,00523
3	Triglycerides	188,6	0,00358
4	Glycerin	30,8	0,00162
TOTAL		15967,6	0,12484

Table 2. Typical results for B-100 Biodiesel

Results

Calibration curves were obtained for glycerin, monoolein, diolein and triolein. Calibration curves for glycerin and monoolein, shown in Figures 2 and 3, are indicative of system performance for the application.

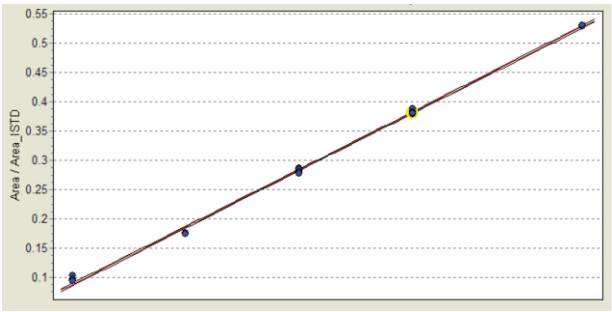

Fig. 2 - Biodiesel calibration 001 - Glycerin

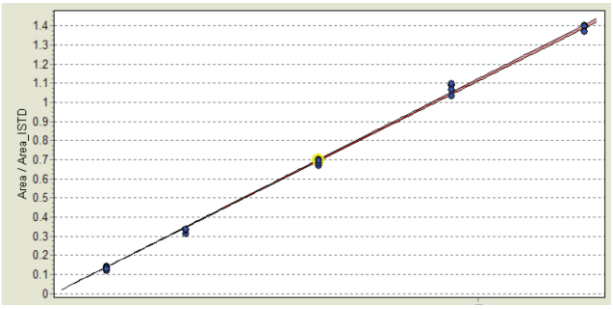

Fig. 3 - Biodiesel calibration 001 - Monoolein

File	Glycerin (% m/m)	Monoglycerides (% m/m)	Diglycerides (% m/m)	Triglycerides (% m/m)	Totals
1	0,00162	0,11441	0,00523	0,00358	0,12484
2	0,00164	0,11167	0,00530	0,00392	0,12274
3	0,00159	0,10894	0,00519	0,00374	0,11946
4	0,00147	0,10696	0,00519	0,00359	0,11721
5	0,00161	0,11115	0,00518	0,00398	0,12192
6	0,00168	0,10720	0,00531	0,00419	0,11838
7	0,00158	0,10835	0,00524	0,00383	0,11901
8	0,00160	0,10483	0,00527	0,00388	0,11558
9	0,00156	0,10721	0,00524	0,00376	0,11777
10	0,00160	0,10731	0,00526	0,00386	0,11802
Average	0,001595	0,108803	0,00524	0,00383	0,11949
STDEV	5,5E-05	2,8E-03	4,5E-05	1,8E-04	2,8E-03
STDEV (%)	3,4	2,6	0,9	4,7	2,4

Table 3. Repeatability results for B-100 Biodiesel

Conclusion

This application note demonstrates the suitability of SCION Instruments Analyser for ASTM D6584, 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.

SCION Instruments

UK
Livingston Business Centre
Kirkton South Road, Livingston
West Lothian EH54 7FA
Scotland, UK
Phone +44 1506 300 200
sales-eu@scioninstruments.com

The Netherlands
Amundsenweg 22-24
4462 GP Goes,
The Netherlands
Phone +31 (0) 113 287 600
sales-eu@scioninstruments.com