Determination of Free Glycerol Content in Fatty Acid Methyl Esters (FAME) and Biodiesel According to EN-14106

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Introduction

Biodiesel is produced by transesterification of the parent oil or fat with an alcohol, usually methanol, in the presence of a catalyst, usually potassium hydroxide or sodium hydroxide, or, increasingly, alkoxides.

The resulting product can contain not only the desired alkyl ester product but also unreacted starting material mono-, di- and triacylglycerides, residual alcohol and catalyst. Glycerol is formed as a by-product and separated from the biodiesel in the production process. However, traces of glycerol can be found in the final biodiesel product. In higher concentrations, glycerol has a negative effect on fuel behavior and performance.

For biodiesel to be used as a motor fuel or blended with petroleum diesel, it must conform to standard specifications (ASTM D6751 or EN-14214). There are GC methods in use today to determine whether biodiesel conforms to the standard specifications. One of these methods, EN-14106, is used to determine the glycerol content. This European Standard specifies a gas chromatographic method for the determination of free glycerol content in Fatty Acid Methyl Esters (FAME) in the range of 0.005 % to 0.070 %.

Index	Name	Area (µV / min)	Quantity (mass %)
1	Glycerol	175.3	0.04258
Total		175.3	0.04258

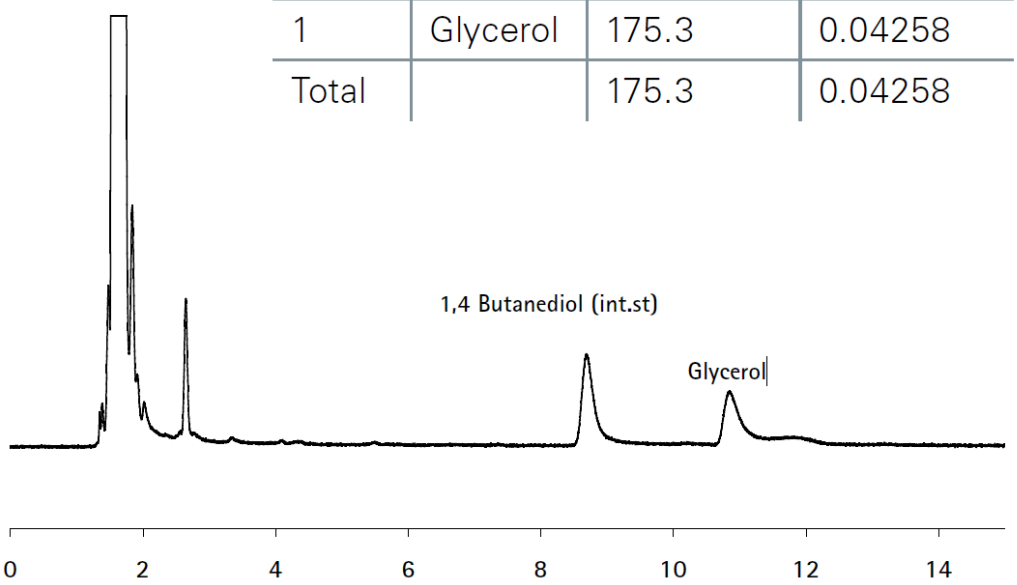

Fig. 1 Biodiesel Chromatogram

Experimental

The SCION Biodiesel analyser for EN 14106 is based on our 436-GC platform, a split/splitless injector, a custom PLOT Q column and an FID Detector.

Analytical conditions for the EN 14106 analysis can be found in table 1.

Injector	Split/Splitless @270°C
Column	10m x 0.32mm x 10µm PLOT Q (Custom column)
Oven Program	210°C Isothermal
Carrier	Helium @ 6,5 psi
Detector	FID @ 270°C
Inj. Volume	1µl
Software	Compass CDS

Table 1. Analytical conditions

Sample Preparation

Ethyl alcohol, water, hexane and a known amount of internal standard were added to a known quantity of sample.

Please note that when these solvents are added together, two phases are formed. The free glycerol 'transferred' into the lower of the two phases.

Approximately 3.5 g of sample was weighed into a 10 mL test tube. 1 mL of ethyl alcohol was added and gently shaken to ensure uniform mixing. Exactly 1 mL of internal standard solution and 4 mL of hexane were added. The tube was tightly plugged and shaken vigorously for ~ 5 minutes. After an ~15 minutes centrifuge, the lower phase was used for gas chromatographic analysis.

Calibration and calculation

A calibration mix containing known quantities of 1,4-Butanediol and Glycerol was used to determine the response factor of Glycerol.

Response Factor (Fr) = (A1/M1)/(A2/M2)

Where:

A1 is the peak area of internal standard

A2 is the peak area of Glycerol

M1 is the mass of 1,4-Butanediol in response factor solution, expressed in mg

M2 is the mass of glycerol in response factor solution, expressed in mg

The results were calculated using the following equation:

Free Glycerol, % (m/m) = (((A2/A1) * Fr * m1)/m)*100

A1, A2, Fr see formula 1

m1 mass of int std in sample (mg)

m mass of sample (mg)

Results

The sample of biodiesel used in this application was analyzed multiple times. A chromatogram of this analysis is shown in figure 1.

Table 2 shows the repeatability figures, average and standard deviation. Figure 2 shows

the individual numbers compared to repeatability and reproducibility limits described in the EN-14106 method.

File	Glycerol (% m/m)
1	0,04306
2	0,04275
3	0,04213
4	0,04267
5	0,04205
6	0,04258
7	0,04205
8	0,04268
9	0,04205
10	0,04299
Average	0,04250
STDEV	0,0003984
STDEV (%)	0,94

Table 2. Repeatability results for Glycerol in Biodiesel

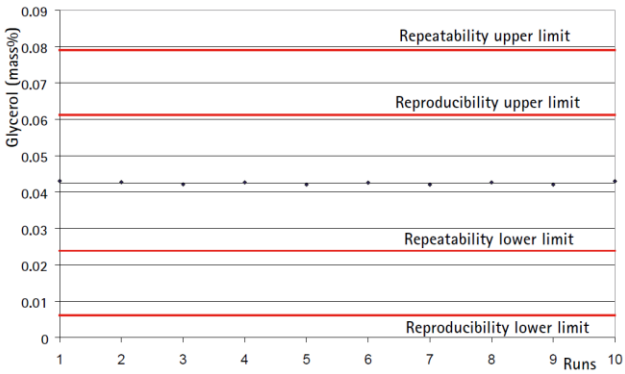

Fig. 2 - Repeatability based on 10 runs. Red lines indicate the maximum and minimum variation limits of the method.

Conclusion

This application note demonstrates the suitability of SCION Instruments Analyser for EN 14106, for the analysis of free glycerol in biodiesel.

The repeatability data demonstrates good system integrity.

Therefore, the system is well suited to the analysis of free in biodiesel in accordance with the standard method EN 14106

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