BEYOND MEASURE

SCION INSTRUMENTS

Determination of Free Glycerol in Fatty Acid Methyl Esters and Biodiesel according to EN-14106

Application Note AN0017

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. Alkoxides are now becoming more increasingly popular. The resulting biodiesel product contains not only the desired alkyl ester product but also non or partly reacted starting material mono-, di-, and triacylglycerides, residual alcohol and catalysts. 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 behaviour and performance. In order for biodiesel to be used as a motor fuel or blended with petroleum diesel, it must conform to standard specifications, either ASTM D6751 or EN-14214. EN-14106 offers a specific standard method for the determination of free glycerol content in fatty acid methyl esters (FAMEs), in a range of 0.005% to 0.070%. This application demonstrates the capabilities of the SCION Biodiesel analyser for the determination of free glycerol in accordance with EN-14106, with reference to EN-14214 specifications.

EXPERIMENTAL

A SCION 456 GC was equipped with a split/splitless injector and flame ionisation detector (FID) and configured to meet EN-14106 specifications. Table 1 shows the analytical parameters implemented during this application note.

Table 1. Analytical conditions of the GC-FID

Conditions	
S/SL	270°C, Split 75mL/min
Column	SCION PLOT Q 10m x 0.32mm x 0.10µm
Oven Programme	60°C (hold 12 min), 20°C/min to 120°C (1 min)
Carrier Gas	Helium, 18psi (12 mins), 4psi/min to 30psi (1min)
FID	300°C

A pure biodiesel sample, conforming to EN-14214 specifications, was obtained and ran throughout this application. The sample was prepared using the following method. 3.5g of biodiesel was added to a 10mL test tube. 1mL of ethyl alcohol was added and gently shaken. 1mL of internal standard, 1,4-Butanediol, and 4mL of hexane was added to the test tube and centrifuged for 15 minutes. The lower phase of the mixture was transferred into GC vials for injection into the GC.

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

In order to calculate the response factor of glycerol there are two calculations that must be adhered too, detailed below in Figure 1.

Equation 1:

$$Fr = \frac{A1/M1}{A2/M2}$$

Fr = Response Factor
A1 = peak area of internal standard
A2 = peak area of Glycerol
M1 = mass of 1,4-Butanediol in solution (mg)
M2 = mass of Glycerol in solution (mg)

Equation 2:

$$\text{Free Glycerol \% (m/m)} = [(A2/A1) * Fr * m1/m] * 100$$

m1 = mass of internal standard (mg)
m = mass of sample (mg)

Fig 1. Calculations for response factor of glycerol

RESULTS

The biodiesel sample was analysed ten times, in sequence, to establish the repeatability of the SCION Biodiesel analyser, as stated in both the EN-14106 and EN-14214 methods. Figure 2 shows a chromatogram from a single biodiesel injection.

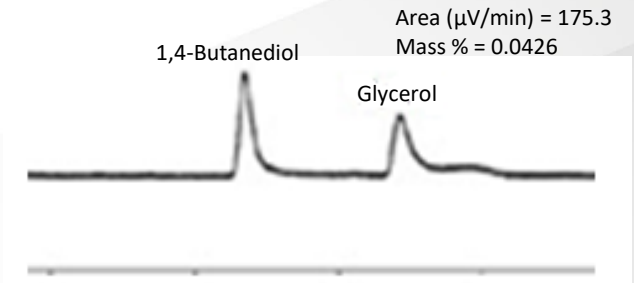

Fig 2. Biodiesel sample with area and mass %

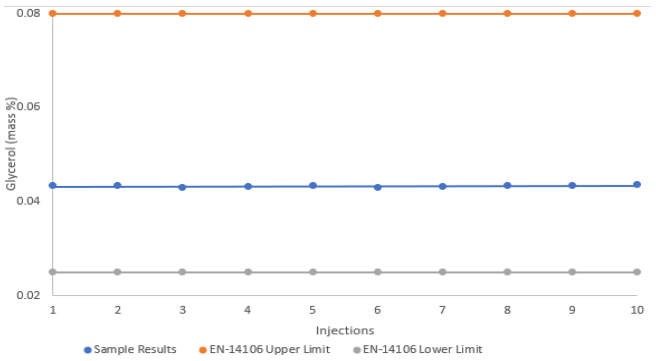

Fig 3. Repeatability of sample with EN-14106 repeatability limits (n=10)

Repeatability of the system was tested using ten consecutive injections of the biodiesel sample. Figure 3 shows the repeatability graph with the defined limits specified in EN-14106. Table 2 details the repeatability data, average, standard deviation and relative standard deviation (RSD %) of the ten injections.

Table 2. Analysis repeatability value

N	Conc (%m/m)
1	0.04306
2	0.04275
3	0.04213
4	0.04367
5	0.04205
6	0.04258
7	0.04205
8	0.04268
9	0.04205
10	0.04299
Average	0.04250
Std Dev	0.00039
RSD %	0.94

EN-14106 states that the repeatability values from the biodiesel sample (with ten injections) must be at a concentration of between 0.03 mass % and 0.08 mass %. The repeatability study from this analysis shows that the ten biodiesel sample injections gives a mass % of 0.0425 with an RSD% of 0.94, clearly within the limits specified.

CONCLUSION

This application note demonstrates the excellent capability of the SCION GC-FID analyser for the analysis of free glycerol according to the EN-14106 method. The response factor of the glycerol was accurately quantified with the system showing excellent repeatability of biodiesel samples containing free glycerol.

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