APPLICATION NOTE

Analysis of Methanol in Biodiesel by HT3 and Versa Headspace Sampling

AN096v2; Nov 2023, SCION Instruments

Introduction

With the rising prices of fossil fuels, more emphasis is being put on renewable resources and green technologies. Alternative fuel sources, such as biodiesel, are becoming increasingly viable. B-100 biodiesel, an alternative fuel source, is manufactured through the transesterification of renewable oils with methanol, and must meet quality specifications specified in ASTM D6751-12 and EN 14214. Specifically, EN 14110 is the standardized test method for methanol content in Fat and Oil derivatives, specifically Fatty Acid Methyl Esters (FAMEs). FAMEs can be used as a source of pure biodiesel or as a blending component for domestic heating fuels and diesel based fuels.

This application note will demonstrate the versatility of the HT3 and Versa automated headspace vial samplers for determining methanol in biodiesel samples following the European Standard, EN 14110, Fat and oil derivatives – Fatty Acid Methyl Esters (FAME) – Determination of Methanol Content.

Experimental

The HT3 and Versa headspace samplers were coupled with a GC/FID for the analysis of methanol in biodiesel. A sample of biodiesel was used as a reference FAME. Sample preparation on the biodiesel was performed to ensure that the concentration of methanol was 0.0005%, significantly low enough to not interfere with the calibration. This preparation is the FAME Reference Standard (FAME RS).

Three methanol calibration solutions were prepared at 0.01% (m/m), 0.1% (m/m) and 0.5% (m/m) using the FAME RS solution. Procedure B of the EN 14110 method was used. A sample containing methanol and 2-propanol was prepared. 20 sample headspace vials of unwashed biodiesel were analyzed to demonstrate repeatability and reproducibility, using both helium and nitrogen as carrier gas. Table 1 details the GC-FID method parameters. Tables 2 details the HT3 and Versa headspace sampler parameters.

Figure 1. SCION Instruments HT3 Headspace Sampler (left) and SCION Instruments Versa Headspace Sampler (right)

Table 1. GC Method Parameters

Parameter	Settings
Injector	150°C, 20:1
Column	624-type, 30m, 0.32mm ID, 1.8µm dF
Carrier Gas	Helium and Nitrogen
Oven Program	40°C (5 min), 35°C/min to 280°C (2min)
Detector	280°C, Hydrogen: 40 mL/min, Air: 400 mL/min, Makeup: 30 mL/min

Table 2. HT3 and Versa method parameters

Variable	HT3 Values	Versa Values
Constant Heat Time	On	
GC Cycle Time	23 min	23 min
Valve Oven Temp	105°C	105°C
Transfer Line Temp	110°C	110°C
Standby Flow Rate	50 mL/min	18 psi (equivalent to 50mL)
Sample Temp	80°C	80°C
Platen Temp Equil Time	1 min	0.1 min
Sample Equil Time	45 min	45 min
Pressurize	10 psig	10 psig
Pressurize Time	2 min	2 min
Pressurize Equil Time	0.20 min	0.2 min
Loop Fill Pressure	7 psig	7 psig
Loop Fill Time	2 min	2 min
Inject Time	1 min	1min

Results

The resolution between methanol and 2-propanol was also calculated. Figure 2 shows a chromatogram of a resolution solution.

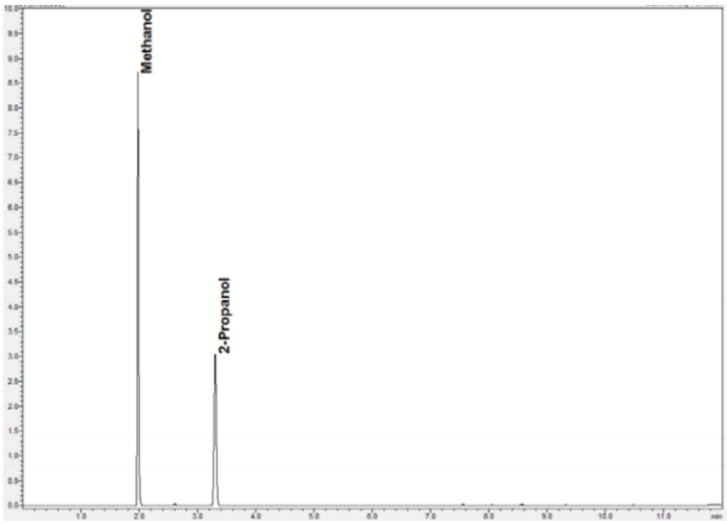

Figure 1. Chromatogram of Methanol/ 2-Propanol reference standard

The correlation coefficient (r^2) and the coefficient of the variation of the three calibration standards were calculated for the HT3 and Versa, using both helium and nitrogen as carrier gas. The coefficient of variance of the calibration factor for methanol was evaluated to demonstrate the accuracy of the instruments without an internal standard. These values are listed in Table 3.

Table 3. Resolution and Calibration Data for Methanol in Biodiesel

Instrument	Carrier Gas	Resolution	Correlation Coeffecielnt r^2	Coefficient of Variation
HT3	Helium	24.7	1.0000	8.42
	Nitrogen	24.3	1.0000	9.73
Versa	Helium	24.6	1.0000	6.95
	Nitrogen	24.5	0.9999	4.82

Using either helium or nitrogen as carrier gas provides excellent resolution and linearity when using the HT3 and Versa headspace samplers.

The methanol peak areas of the 20 unwashed biodiesel samples were used to calculate repeatability (r) and reproducibility (R). The repeatability (r) value is used to determine if the absolute difference between two independent test results, using the same equipment on identical samples, passes the method requirement.

The reproducibility (R) value from the method is used to determine if the absolute difference between two independent test results, using different equipment on identical samples, passes the method requirements.

Table 4. Repeatability and Reproducibility Data for Biodiesel Methanol Assay Following EN 14110

Repeatability (r)				
Instrument	**Carrier Gas**	**%RSD (n= 20)**	**Calculated**	**Actual**
HT3	Helium	2.36	0.0034	0.0011
	Nitrogen	3.50	0.0032	0.0013
Versa	Helium	0.76	0.0035	0.0003
	Nitrogen	2.11	0.0035	0.0010
Reproducibility (R) (%RSD = 40)				
HT3 vs Versa	Helium	3.28	0.0059	0.0006
	Nitrogen	17.8	0.0057	0.0031

The calculated mean values of the 20 samples were used to determine the maximum and minimum values following the method equations for r and R. The percent Relative Standard Deviation (%RSD) was also determined for the 20 samples. The r and R data was evaluated to determine if the 20 sample values fell within the method requirements.

Figure 3 shows the repeatability (r) data graphs for each instrument and its associated supply gas. Table 4 lists the %RSD and the repeatability and reproducibility values for the instruments, and their associated supply gases. Figure 4 shows the reproducibility (R) data graphs comparing the HT3 to the Versa with each supply gas.

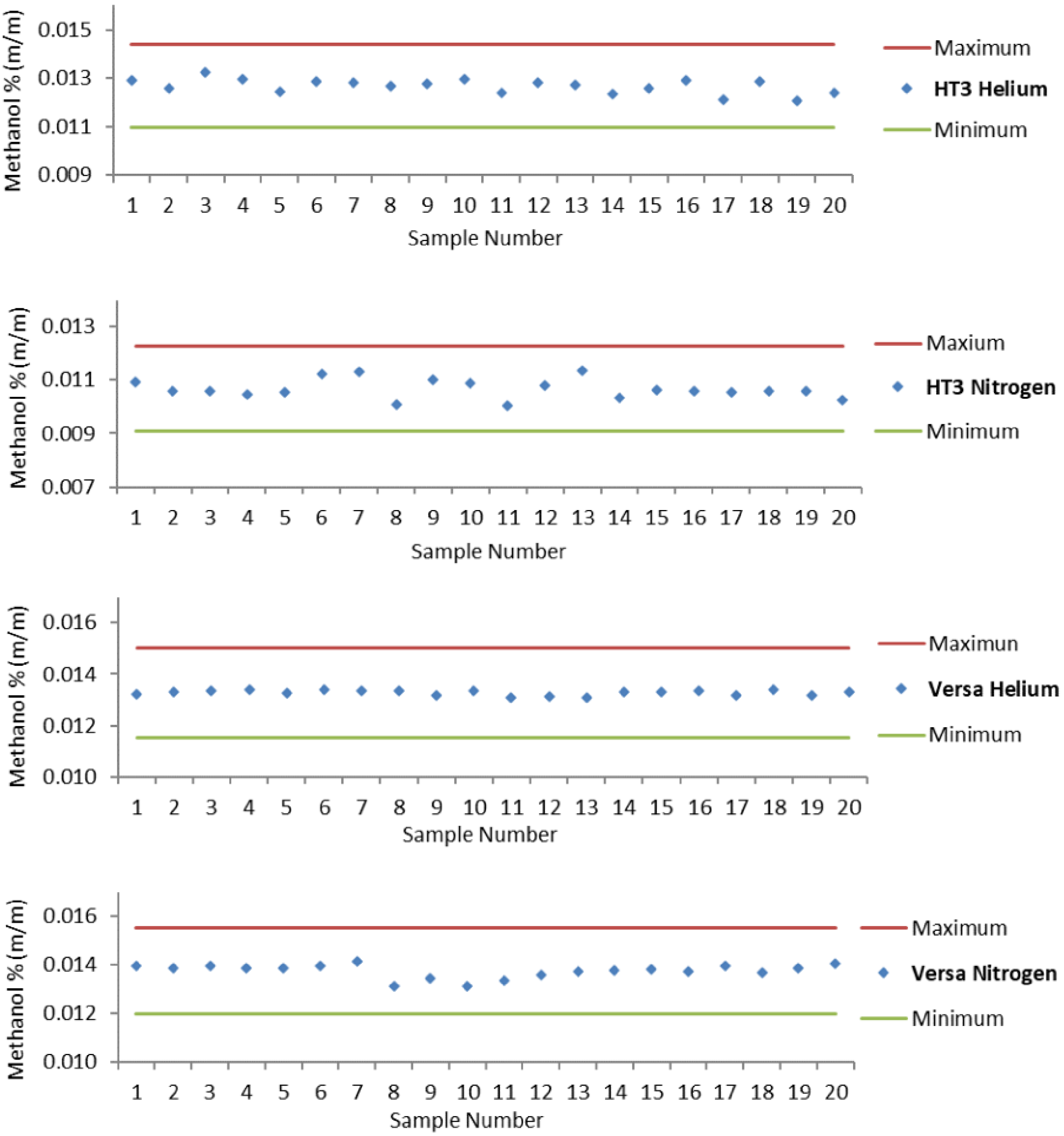

Figure 3. Graphs of Repeatability Data (r) for the HT3 with Helium and Nitrogen and Versa with Helium and Nitrogen (top to bottom) for 20 Biodiesel Samples Including the Method Maximum and Minimum Ranges

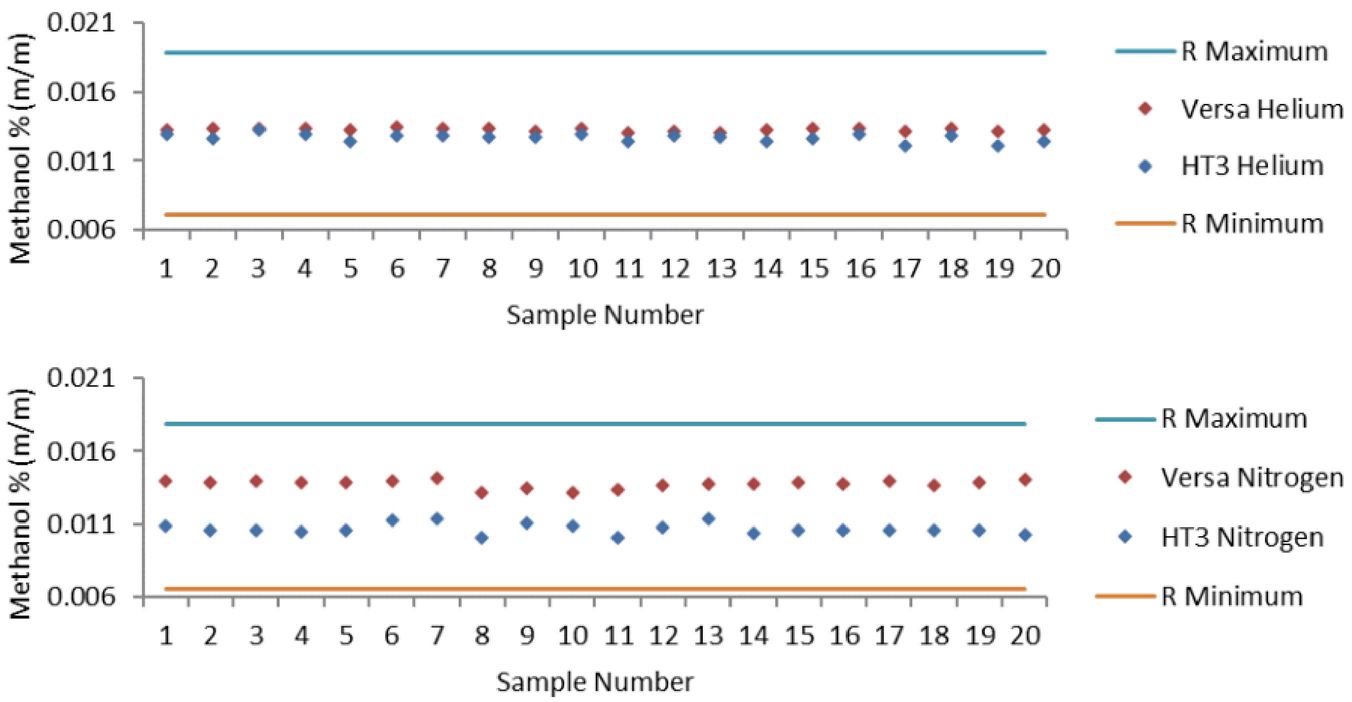

Figure 4. Graph of reproducibility (R) data comparing the HT3 and Versa % methanol value with helium (top) and nitrogen (bottom).

Conclusion

The identification of Methanol content, the crucial compound monitored in biodiesel fuels, will normally be determined using the headspace method EN 14110. Procedure B of this method uses an external standard and lends itself to the use of an automated headspace vial sampler. The HT3 and Versa automated headspace vial samplers successfully demonstrated their suitability to analyse methanol content in biodiesel.

The method resolution requirement was greatly exceeded, ranging from 24.3 to 24.7, using a 624-type column with either helium or nitrogen as the carrier gas and the supply gas for the HT3 and Versa. A temperature gradient GC method was used to clean off any possible interfering volatile compounds.

The method correlation coefficient requirement was also greatly exceeded (0.9999 or better), with either helium or nitrogen as the carrier gas and the supply gas for the HT3 and Versa. The %RSD values of the calibration (4.8 to 9.7) also surpassed the internal standard method requirement.

The repeatability values for the 20 biodiesel samples passed the method requirements using either helium or nitrogen as the carrier gas and the supply gas for the HT3 and Versa. This dependability, combined with the benefits of automation, and the ability to connect to most common GCs, makes the HT3 and Versa automated headspace vial samplers excellent choices when performing method EN 14110.

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