Methanol in Biodiesel by EN14110 with the HT3 and Versa Automated Headspace Analyzers

Application Note

Versa

HT3

Abstract

With the rising prices of fossil fuels, more emphasis is being put on renewable resources and green technologies. Alternative fuel sources, such as biodiesel, have become more and more viable. B-100 biodiesel, one of these alternative sources, is manufactured through the transesterification of renewable oils with methanol and must meet quality specifications found in ASTM D6751-12[1] and EN 14214[2].

One of these qualifications, methanol content, is determined by EN 14110[3], a headspace-gas chromatography method. This application note will present data for two different automated headspace vial samplers to meet the performance criteria outlined in EN Method 14110.

Introduction

Dr. Rudolph Diesel patented the first compression ignition engine in 1893, with the intention of using vegetable oils as a source of combustion. Additional advances in the use of vegetable oils as fuel were made in 1937 by a Belgium inventor who converted vegetable oils into fatty acid methyl esters by transesterification. Despite these early advances, widely available, low-cost petroleum-based diesel fuel has historically discouraged continuing research in biodiesel technology.

It was not until the 1970's oil crises that increased concern over the cost and availability of petroleum-based fuels, led once again to biodiesel alternatives. Followed closely in the 1980s by increased environmental awareness, a desire for energy self-sufficiency, and agricultural overproduction, biodiesel, coupled with transesterification, experienced a resurgence that has grown into today's biodiesel markets.[4]

This application note will demonstrate the versatility of the Teledyne Tekmar 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. This poster will include data from both headspace systems using two different GC carrier gases: helium and nitrogen.

Procedure B of the EN 14110 method, which employs automated headspace injections, will be used due to the automated sampling capability of the Versa and the HT3. (Procedure A of the EN 14110 method is typically used with manual headspace injections.) A sample containing methanol and 2-propanol will be used to ensure that the GC system meets the minimum resolution requirement of the method.

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Experimental-Instrument Conditions

The HT3 and Versa Automated Headspace Analyzers were connected to a GC/FID for this study. A Restek Rxi®-624Sil MS column with a gradient bake out was used with helium or nitrogen as the carrier gas. Table 1 displays the HT3 and Versa automated headspace vial sampler parameters, while Table 2 displays the GC/FID parameters. An optional 0.5 mL loop was used in the HT3 and Versa in accordance with the method parameters. If the standard 1 mL loop is used, the sample volume should be correspondingly reduced to 1 mL.

Teledyne Tekmar HT3 and Versa Parameters		
Variable	**HT3 Values**	**Versa Values**
Constant Heat Time	On	
GC Cycle Time	23.00 min	23.00 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)
Platen/Sample Temp	80 °C	80 °C
Platen Temp Equil Time	1.00 min	0.10 min
Sample Equil Time	45.00 min	45.00 min
Pressurize	10 psig	10 psig
Pressurize Time	2.00 min	2.00 min
Pressurize Equil Time	0.20 min	0.20 min
Loop Fill Pressure	7 psig	7 psig
Loop Fill Time	2.00 min	2.00 min
Inject Time	1.00 min	1.00 min

Table 1: HT3 and Versa Automated Headspace Conditions

GC/FID Parameters	
Column	Rxi-624Sil MS, 30m, 0.32mm ID, 1.8µm dF
Oven Program	40 °C for 5 min, 35 °C/min to 280 °C for 2 min, run time 13.86 min
Inlet:	Temperature 150 °C, Split Ratio 20:1, Constant Velocity 40.0 cm/sec, Purge Flow 0.5 mL/min
FID	Temperature 280 °C, Hydrogen 40 mL/min, Air 400 mL/min, Makeup 30.0 mL/min

Table 2: GC / FID Parameters

Standard Preparation

A sample of biodiesel was used as a reference fatty acid methyl ester (FAME). An initial test of the sample indicated that it contained approximately 0.02% methanol, resulting in interference with the calibration curve. Subsequently, this reference was cleaned following recommendations in the method, and reanalyzed. Secondary analysis of the sample was found to contain approximately 0.0005% methanol, not sufficient to 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.

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Sample Preparation

Procedure B of the EN 14110 method was used. A sample containing methanol and 2-propanol was prepared as a resolution solution, as well as an external standard calibration. Sample and calibration solutions were prepared in 22 mL headspace vials for this evaluation. An additional 20 sample headspace vials of unwashed biodiesel were analyzed to demonstrate repeatability and reproducibility between the instruments and the supply/carrier gases.

Results

The resolution between methanol and 2-propanol was also calculated. Figure 1 shows a chromatogram of a resolution solution. Table 3 lists the calculated resolution values for the HT3 and the Versa, comparing helium and nitrogen.

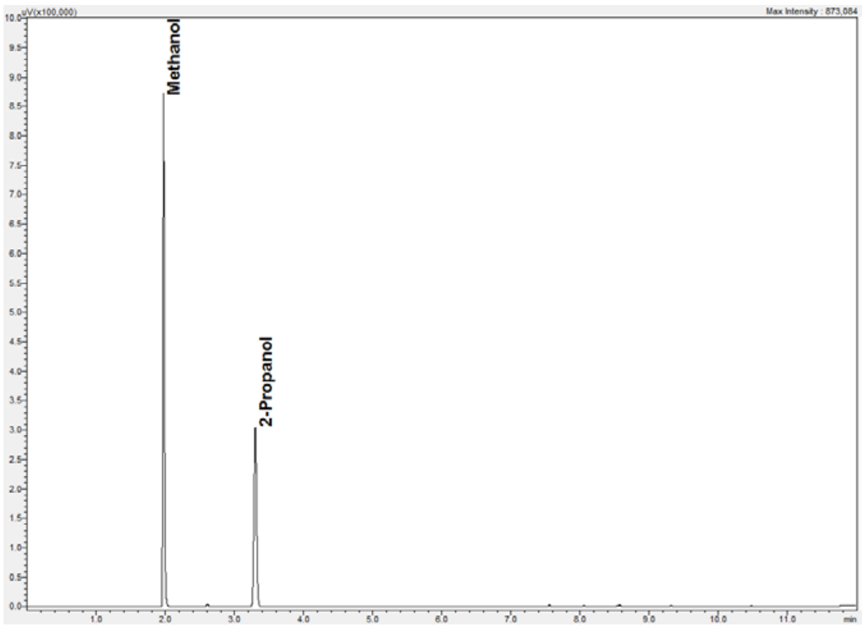

Figure 1: Chromatogram of the Resolution Solution

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

Instrument	Gas	Resolution	Correlation Coefficient (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

Table 3: Resolution and Calibration Data for Biodiesel Methanol Assay Following EN 14110.

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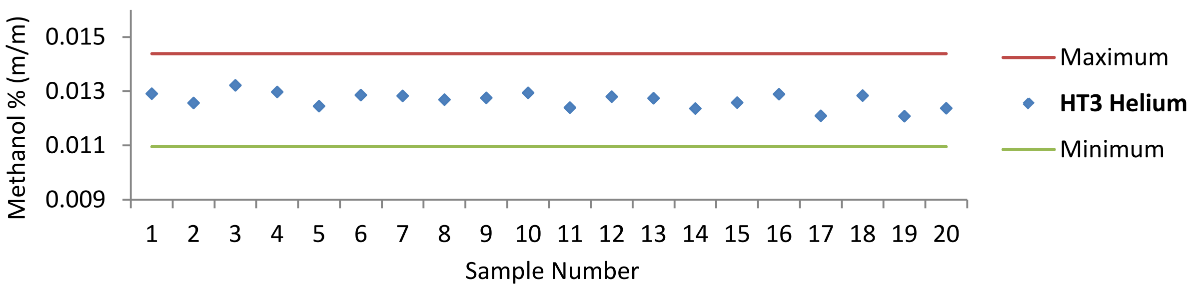
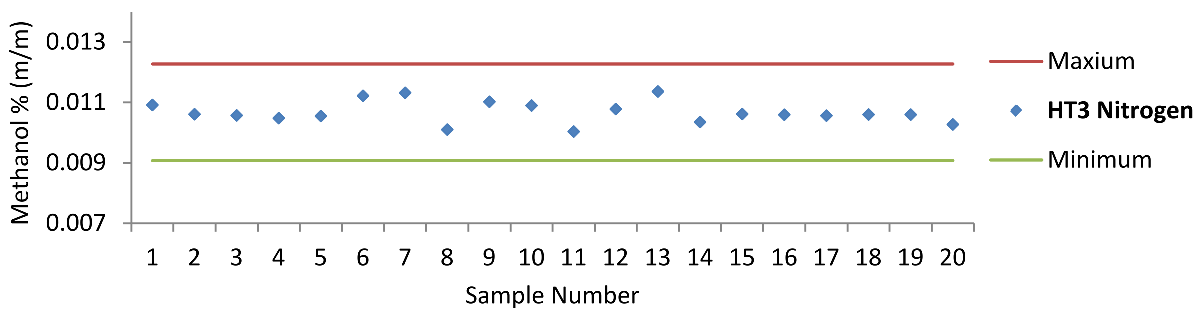
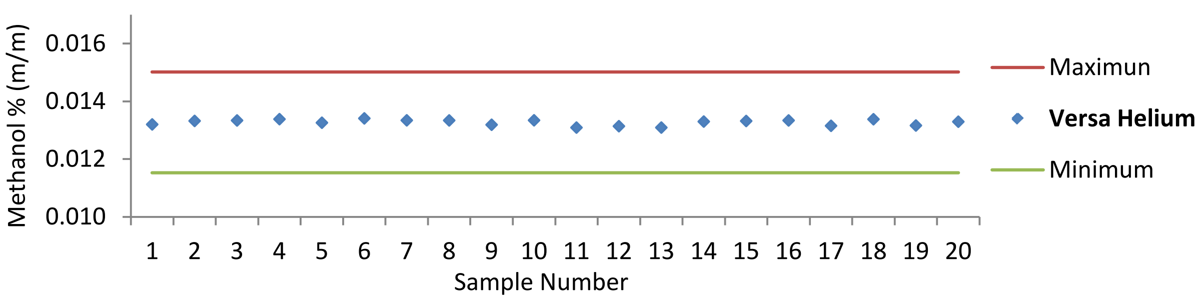
The methanol peak areas of the 20 unwashed biodiesel samples were used to calculate repeatability (r) and reproducibility (R). The repeatability (r) value is used to determine if the absolute difference between two independent test results, using the same equipment on identical samples, passes the method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

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 2 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 3 shows the reproducibility (R) data graphs comparing the HT3 to the Versa with each supply gas.







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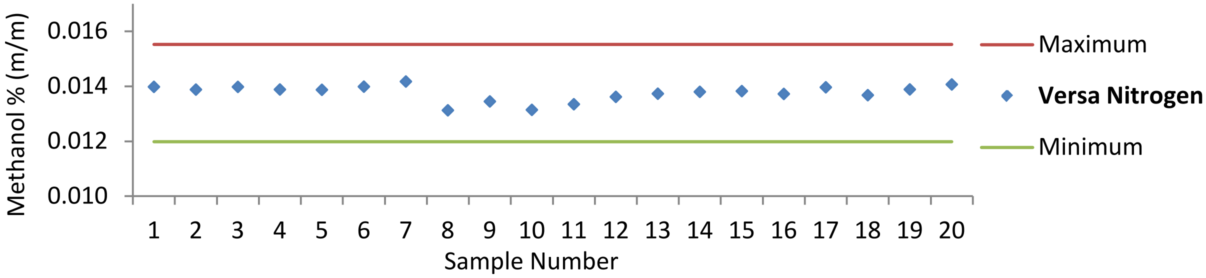

Figure 2: Graphs of Repeatability Data (r) for the HT3 with Helium and Nitrogen and Versa with Helium and Nitrogen (top to bottom) for 20 Biodiesel Samples Including the Method Maximum and Minimum Ranges

Repeatability (r)				
Instrument	**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

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

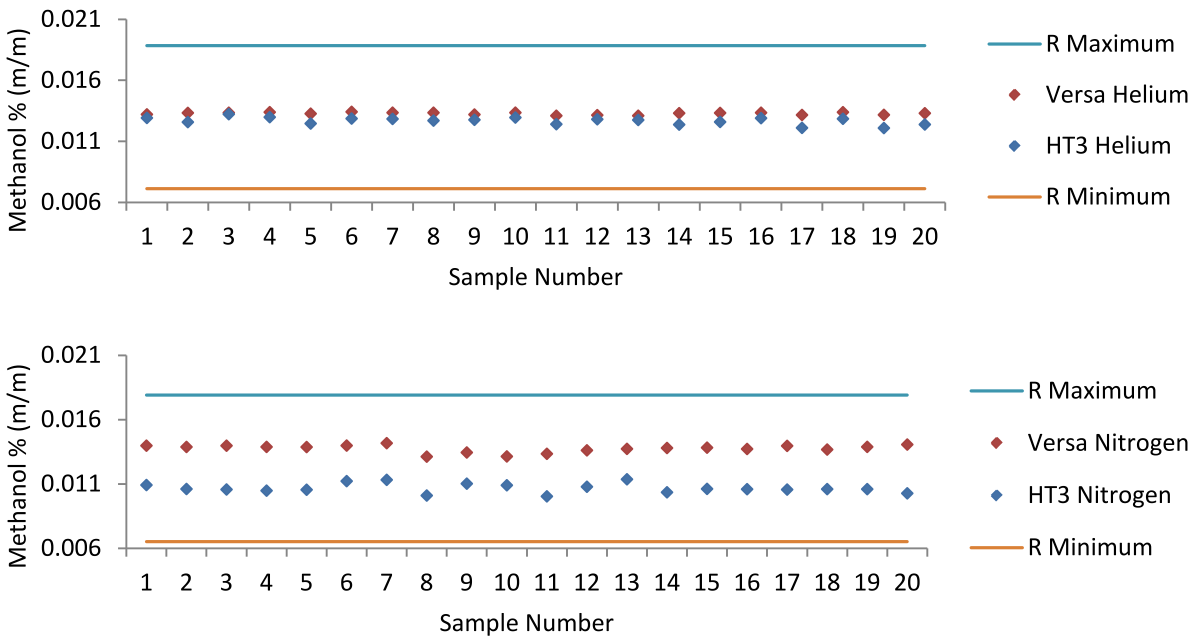

Figure 3: Graph of the Reproducibility Data (R) Comparing the HT3 and Versa % Methanol Value with Helium (Top) and Nitrogen (Bottom).

Conclusions

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 Teledyne Tekmar HT3 and Versa automated headspace vial samplers successfully demonstrated their suitability to analyze 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 and reproducibility 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.

References

1. ASTM D 6571-12. Standard specification for biodiesel fuel blend stock (B100) for middle distillate fuels. ASTM International. West Conshohocken PA.
2. EN 14214 Automotive fuels – Fatty Acids Methyl Esters (FAME) for diesel engines – requirements and test methods
3. EN 14110 Fat and oil derivatives – Fatty Acid Methyl Esters (FAME) – determination of methanol content
4. http://www.biodiesel.com/index.php/biodiesel/history_of_biodiesel_fuel

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