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QUALITY

Conducting Glycerin Analysis with a Turnkey Gas Chromatography System

By David Armstrong and Tim Ruppel

Shortly after Minnesota mandated that all diesel fuel sold in the state contain 2 percent biodiesel blended with petroleum diesel, the weather turned cold and truckers and bus drivers began complaining that the biodiesel blend was clogging fuel filters. This resulted in the mandate being lifted for a total of 51 days. The Agricultural Utilization Research Institute (AURI) researched the problem and found that while biodiesel was not the only contributor to the clogging problem, it was indeed one of the contributors. Unfortunately for proponents of biodiesel, it appeared that it was the 2 percent biodiesel blended into the fuel mixture that received most of the blame for the problem.

This example and others similar to it bring to light the importance of measuring free and total glycerin in biodiesel that is to be used as a motor

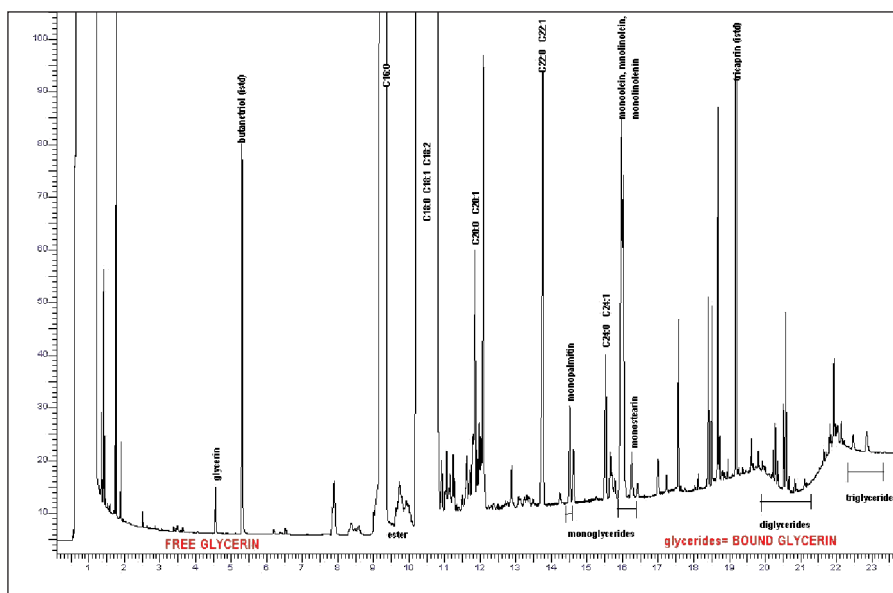


Figure 1. A chromatogram of B100 shows the peaks for free and bound glycerin.

fuel. ASTM D 6584 and EN 14105 methods both prescribe gas chromatography (GC) as the method for

this analysis. For someone who has spent years working with GC, configuring a system to perform such an analy-

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sis may not seem like a daunting task. For novices at this technique, the array of letters such as PPC (programmable pressure control), POC (programmable on column) and FID (flame ionization detector) can be more than just mildly bewildering. Some of the latest technologies feature out-of-the-box pre-configured systems for performing a specific analysis like free and total glycerin in biodiesel. These systems provide a supply of consumables to analyze samples and often special training courses are available for the inexperienced chromatographer.

Having a GC system come pre-configured is most helpful, but let's not forget that standards and samples also must be prepared for introduction into the GC. Fortunately, this operation is quite straightforward and can be performed by an operator with basic laboratory skills.

For preparation of the standards, it is recommended to use a biodiesel calibration standards kit that contains reference solutions that meet the specifications called for in ASTM D 6584 and EN 14105. A set of calibration standards containing external and internal standards can be created using the kit, a pipette and the solvent heptane. The external samples will be used to build a calibration curve on the GC and the internal standards will be added to the sample itself. All external standards can be made up in autosampler vials. Sample preparation is stated in ASTM D 6584 and requires only a few steps. In a 10 milliliter (ml) septa vial, add 100 mil-

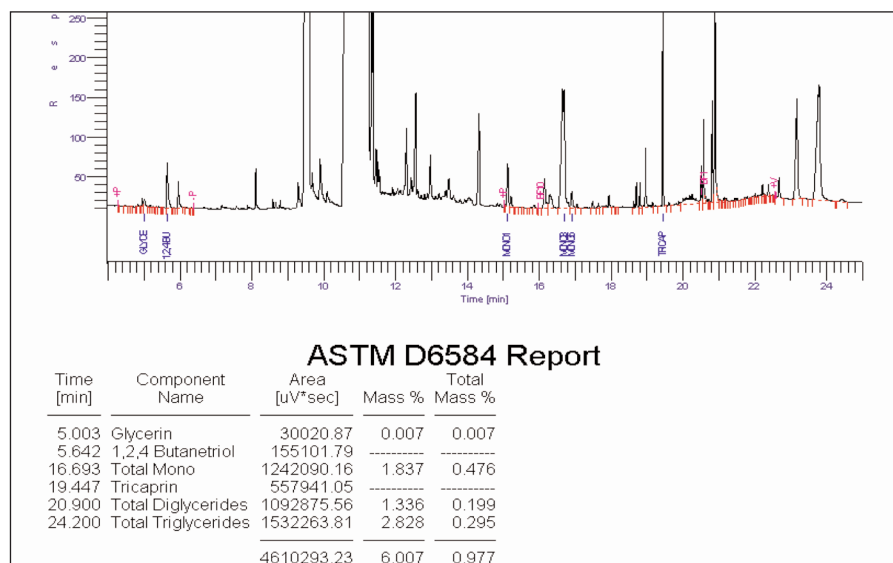


Figure 2. A report generated from PerkinElmer's trademarked TotalChrom software shows the values for free glycerin (glycerin) and bound glycerin (total mono, total diglycerides and total triglycerides).

ligrams of biodiesel, 100 microliters (μ l) of the internal standard, 100 μ l of the derivitizing solution, shake and allow to react for 20 minutes. Dilute with eight ml of heptane and shake to mix. This solution is now ready for analysis and can be transferred to an autosampler vial. The five external standards and the samples to be analyzed can be loaded into the autosampler tray and the analysis begun.

The biodiesel sample will provide a chromatogram that will appear much like the one shown in Figure 1. Peak identification algorithms built into the system's software show that the free glycerin is a single peak that elutes in about 4.5 minutes. The bound glyc-

erides elute later and appear as three separate families of peaks. It is a good idea to compare the chromatogram from your sample to that generated from the external standards to be sure that the peaks of interest are eluting at the proper time.

At this point the software provided with the turnkey biodiesel GC system can become very helpful to identify the peak or peaks for each of these values and then calculate the concentration of each component based upon the intensity of the peak.

Free glycerin is quite easy to calculate since the GC is actually measuring glycerin itself, and the value determined by the GC can be directly reported as

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Laboratories interested in archiving their analyses or generating certificates of analysis will find that there are several new laboratory information management system products that serve this purpose very well. These biofuels specific data handling packages can collect data from all instruments in the laboratory either directly or indirectly and can use those data to provide high quality reports.

Property	ASTM Method	Units	ASTM D-6751-06 ^{E1} Standards	SoyGold Standard Ranges
Flash Point	D93	Degrees °C	130 min.	162-174
Water & Sediment	D2709	% vol.	0.050 max.	0.005-0.04
Kinematic Viscosity, 40 °C	D445	mm ² /sec.	1.9 – 6.0	4.062-4.141
Sulfated Ash	D874	% mass	0.020 max.	0.003-0.010
Total Sulfur S15 Grade S 500 Grade	D5453	% mass PPM PPM	0.05 max. 15 max. 500 max.	0.0002-0.0005 2-5 2-5
Copper Strip Corrosion	D130		No. 3 max.	1A
Cetane	D613		47 min.	48.4-49.7
Cloud Point	D2500	Degrees °C Degrees °F	Report Report	0.0-2.2 32.0-35.6
Carbon Residue 100% sample	D4530	% mass	0.050 max.	0.008-0.010
Acid Number	D664	mg KOH/gm	0.50 max.	0.08-0.20
Free Glycerine	D6584	% mass	0.020 max.	0.001-0.01
Total Glycerine	D6584	% mass	0.240 max.	0.050-0.15
Phosphorus Content	D4951	% mass	0.001 max.	0.0002-0.0005
Distillation Temperature, Atmospheric Equivalent Temperature, 90% Recovered	D1160	Degrees °C Degrees °F	360 max. 680 max.	350 662
Sodium and Potassium, Combined	UOP391	ppm	5ppm max	<2

Figure 3. A certificate of analysis of a biodiesel sample generated from PerkinElmer's trademarked Labworks Green

the free glycerin. The peaks used for bound glycerin determinations are actually peaks for various glycerides (monoglyceride, diglyceride and triglyceride), which are glycerin with additional hydrocarbon chains attached. ASTM D 6584 provides the factors needed to convert the values for glycerides in the accepted values for glycerin. The software contains these factors and automatically performs the calculation. The software then takes one more step as it adds the free glycerin value to those

values calculated for the bound glycerin and determines a total glycerin value. Figure 2 (found on page 96) is an example of a report of the values for free and bound glycerin.

Laboratories interested in archiving their analyses or generating certificates of analysis will find that there are several new laboratory information management system products that serve this purpose very well. These biofuels-specific data handling packages can collect data from all instruments in

the laboratory—either directly or indirectly—and can use those data to provide high-quality reports. As can be seen from the example of a report shown in Figure 3 (found on pages 98 & 99), complete data including the property, ASTM method (EN methods can also be entered), units, limit set by the method, and the standard range of the method can all be built into a report. The appropriate data from your laboratory can then be added alongside this information so that the reviewer

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Property	ASTM Method	Units	Non-ASTM Standards	SoyGold Standard Ranges
Specific Gravity Density@60°F	D4052	Sp. Gr. Pounds/Gallon API° Lbs/ Cu. Ft	Report	0.8843 7.3695 28.56 55.1578
Soap		PPM	Report	ND
Rancimat@110 ° C	EN14112	Hours	3.0	3.0-6.0
NACE Corrosion@72°F	TM0172-2001		B+ min.	A-B++
HAZE RATING @60° F	D4176		2	2
Voluntary Filtration Method	D6217 Modified (B)	Seconds	360 max.	20-200

METALS/OTHER*	ICP	PPM		
Ca + Mg		PPM	5	<0.50
Cu-Copper		PPM	Report	<0.10
Na-Sodium		PPM	Report	<1.00
Ca-Calcium		PPM	Report	<0.15
Mg Magnesium		PPM	Report	<0.15
P-Phosphorous		PPM	Report	<1.60
Fe-Iron		PPM	Report	<0.20
Ni-Nickel		PPM	Report	<0.30
K-Potassium		PPM	Report	<1.00

Analyzing biodiesel for free and total glycerin in compliance with ASTM 6584 and EN 14105 methods is not a trivial undertaking.

will know at a glance how the sample results compare to the criteria set by the method.

Conclusion

Analyzing biodiesel for free and total glycerin in compliance with ASTM 6584 and EN 14105 methods is not a trivial undertaking. This task can be made much easier through the use of a turnkey GC biodiesel system that is preconfigured with all of the hardware and software needed to perform this analysis almost immediately upon

installation. Ready-made standards can be commercially obtained which further reduces the complexity of the analysis. Once the analysis is performed, data from the GC, as well as data from other tests instruments, can be entered into the data handling software for data reporting and archiving.

For more information on preconfigured turnkey systems and laboratory information management system solutions tailored for the biofuels industry, visit www.perkinelmer.com/biofuels. ■

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