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GC Analysis of Biodiesels: Compliance With International Standards Using a Single System

The last decade has seen increased interest worldwide in alternative fuels. Although biodiesels are still a minor part of the liquid biofuels transportation market, biodiesel consumption is escalating quickly. Accompanying this market growth, regulations described in EN 14214 and ASTM D6751 and referenced analytical methods for ensuring quality are also changing at a rapid pace. Laboratories find themselves continually challenged to keep up with method compliance without inundating laboratories with the multitude of equipment required to run an expanding set of methods for quality control and process management. This article discusses developments in GC methods for biodiesel analysis, and demonstrates a comprehensive solution to achieving regulatory compliance with biodiesel specifications.

Analytical methods for biodiesel blends

Analytical methods required for various biodiesel blend qualities are listed in Figure 1 with their respective analytical solutions. All methods based on GC are highlighted. Combining any of these methods in one instrumental solution reduces the number of instruments in the laboratory that are required to meet analytical method compliance, as demonstrated by the first generation of GC-based biodiesel solutions brought to market.

Recently, however, international standards organizations have implemented some key changes in biodiesel methods, and older solutions are no longer able to meet the new requirements satisfactorily. These amendments include EN 14103:2011, EN 14105:2011, and ASTM D6584-10 updates, and additional methods such as EN 15779 for Polyunsaturated Fatty Acids and prEN 16300 for iodine value determination.

The changes call for new equipment to comply with all of these methods. For instance, the scope change for EN 14103:2011 to include animal fats and cooking oils now also mandates column oven programming similar to EN 14105 and ASTM D6584-10 instead of the isothermal program required in previous versions of EN 14103. The obvious combination of two columns in one programmable oven does not provide a solution, just as maximum operating conditions for the typical wax-type column required for fatty acid methyl ester (FAME) analysis in EN 14103 do not allow the high-temperature conditions required for triglycerides analysis in the other methods.

As simple as it may sound, the alternative of swapping columns when switching methods using a single conventional oven cannot be considered a real solution when multiple methods need to be performed efficiently. Frequent changes to the system negatively affect long-term analytical performance and are prone to human error and material variations. Also, they require additional calibrations and thus add time to result delivery. Swapping columns on a frequent basis is costly, takes more time, and can compromise performance.

GC analysis of biodiesels using a dual programmable oven

Adding a secondary temperature-controlled oven zone is the ideal solution, because it allows all biodiesel methods to be combined within a single GC system without the limitations described above. It eliminates the purchasing and operating costs for a second instrument and permits optimal availability and time to result. *Figure 2* shows the additional secondary column oven that makes the next-generation AC Analytical Controls® Biodiesel All in One Analyzer (**PAC**, Houston, TX) a true "all-in-one" hardware solution that is compliant with all of the latest biodiesel standards.

The analyzer uses an **Agilent** 7890A Series GC (Santa Clara, CA) with electronic pneumatics control (EPC), **AC** proprietary temperature programmed inlet, split/splitless inlet, two capillary columns, secondary programmable oven, and two flame ionization detectors (FIDs). The back channel is configured for method EN 14103 (including prEN 16300), EN 15779, and EN 14110 with an optional headspace sampler; the front channel is configured for method EN 14105 and ASTM D6584. Included biodiesel-specific software provides all the calculations required for each method, including a pass/fail check against the latest specifications. It allows chemists to judge sample quality immediately upon run completion, without the need for various manual calculations or comparison with specifications.

Biodiesel analyzer application overview

Method EN 14103:2011—Determination of ester and linolenic ester methyl ester content in FAME

The scope of this method was to verify that the ester content of FAME is >90% and the linolenic ester content is between 1 and 15% (m/m). In EN 14103:2011, the ester content is now integrated as C6:0 to C24:1 using a column oven programmed run (*Figure 3*). Linolenic acid ester is also determined and reported

Property	CEN/ISO	ASTM	B100	B5	B7	B20
FAME content	EN 14103		AC All-in-one biodiesel			
Density at 15 °C	EN ISO 12185	D4052	VIDA	VIDA	VIDA	VIDA
Viscosity at 40 °C	EN ISO 3104	D445	HVM 472/HVU 481	HVM 472/HVU 481	HVM 472/HVU 481	HVM 472/HVU 481
Flash point	EN ISO 2719	D93	HFP 339/HFP 360/HFP 370/FP 93/ AC Simdis	HFP 339/HFP 360/HFP 370/FP 93/ AC Simdis	HFP 339/HFP 360/HFP 370/FP 93/ AC Simdis	HFP 339/HFP 360/HFP 370/FP 93/ AC Simdis
Cetane number	EN ISO 5165	D613	CID 510**	CID 510**	CID 510**	CID 510**
Iodine value	prEN 16300		AC All-in-one biodiesel			
Linolenic acid methyl ester	EN 14103		AC All-in-one biodiesel			
PUFA (> 4 double bonds)	EN 15779		AC All-in-one biodiesel			
Methanol content	EN 14110		AC All-in-one biodiesel			
Monoglyceride content	EN 14105		AC All-in-one biodiesel			
Diglyceride content	EN 14105		AC All-in-one biodiesel			
Triglyceride content	EN 14105		AC All-in-one biodiesel			
Free glycerol	EN 14105	D6584	AC All-in-one biodiesel			
	EN 14106		AC All-in-one biodiesel			
Total glycerol	EN 14105	D6584	AC All-in-one biodiesel			
Sulfur content	EN ISO 20846	D5453	Multitek/CNS Simdis*	Multitek/CNS Simdis*	Multitek/CNS Simdis*	Multitek/CNS Simdis*
Cloud Point		D2500	CPP 5Gs/HCP 852/MPP 5Gs	CPP 5Gs/HCP 852/MPP 5Gs	CPP 5Gs/HCP 852/MPP 5Gs	CPP 5Gs/HCP 852/MPP 5Gs
Carbon Residue		D4530	MCRT 160	MCRT 160	MCRT 160	MCRT 160
Distillation Vacuum		D1160	HDV 632			
Distillation Atmospheric	ISO 3405	D86		Optidist/PMD	Optidist/PMD	Optidist/PMD
	ISO 3924	D2887		AC Simdis/ AC 8634	AC Simdis/ AC 8634	AC Simdis
CFPP	EN 116 / prEN 16329			FPP 5Gs/HCP 842	FPP 5Gs/HCP 842	FPP 5Gs/HCP 842
PAH	EN 12916			Applicated HPLC	Applicated HPLC	Applicated HPLC
Aromaticity				Applicated GC	Applicated GC	Applicated GC
		Notes:	* CNS SIMDIS unofficial method, but will provide comparable data			
			** Correlation to ASTM D613			

Figure 1 – Biodiesel analysis requirements. (All instruments are from **PAC***, Rotterdam, The Netherlands.)*

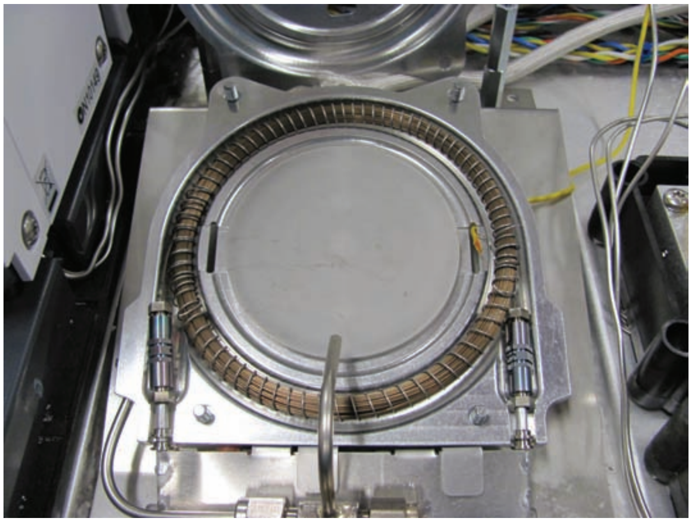

Figure 2 – Biodiesel All in One secondary programmable column oven.

separately. As can be seen in Figure 3, the internal standard has changed from C17:0 to C19:0 in EN 14103:2011 to allow this method to be used for animal source biodiesel. Since C17:0 FAME is present as a component itself in samples containing animal sources, using it as an internal standard would lead to biased results. Other changes to the method involve a sample preparation procedure and the solvent now being toluene instead of heptane.

Relatively new to EN 14214 is the included iodine value calculation according to prEN 16300, using data from EN 14103.

Method EN 14105:2011—Determination of free and total glycerol and mono-, di-, and triglyceride content in FAME

The scope of this method was to determine the free and total glycerol and residual mono-, di-, and triglyceride content in FAME prepared from rapeseed, sunflower, soybean, palm, animal oils, fats, and a mixture of these.

The sample was analyzed on the Biodiesel All in One Analyzer after silylating with N-methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA). After derivatization, the sample was injected directly on the polydimethylsiloxane (PDMS) column; quantification of glycerol was performed against 1,2,4-butanetriol as internal standard. Mono-, di-, and triglycerides were evaluated against new individual internal standards for each glyceride category. To calculate the bonded glycerin content of the sample, average conversion factors were applied to the mono-, di-, and triglycerides. New to this method is that column performance criteria must be calculated for every analysis.

Method EN 14110—Determination of methanol content in FAME

The scope of this method was to verify the methanol content of FAME from 0.01 to 0.5% (m/m). The sample with internal

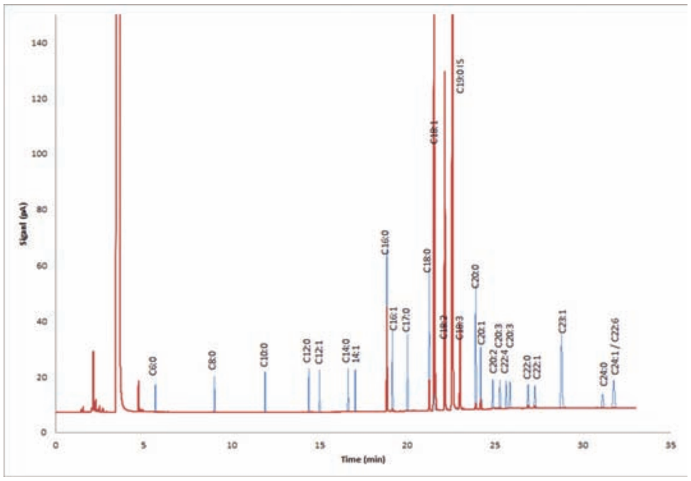

Figure 3 – Method EN 14103:2011. Blue trace: reference sample 00.03.037, C6:0–C24:1 esters in toluene. Red trace: typical rapeseed sample.

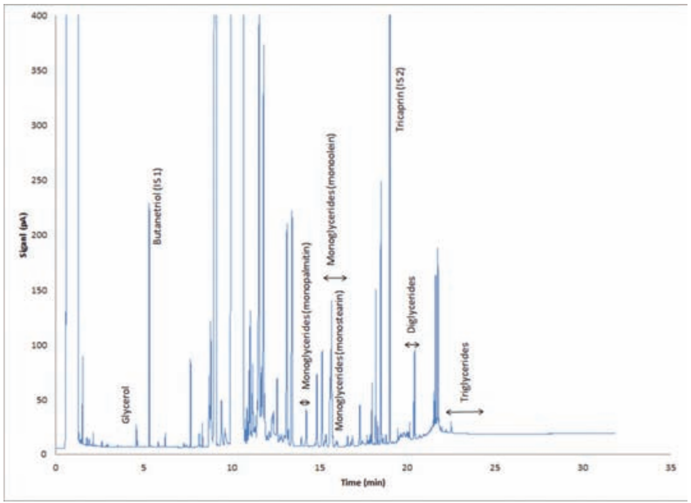

Figure 4 – Typical rapeseed sample chromatogram according to ASTM D6584.

standard (2-propanol) was prepared into a headspace vial and introduced into the back channel split inlet by either automatic or manual headspace sampling. The capillary wax column separated the individual components in an isothermal run and components were detected by flame ionization detection.

Method ASTM D6584-10a—Determination of free and total glycerin content in B-100 methyl esters

The scope of this method was to determinate the total glycerin from 0.05% (m/m) to 0.5% (m/m), and free glycerin, 0.005% (m/m) to 0.05% (m/m), in B-100. After derivatization with MSTFA, n-heptane was added to the sample. The final reaction mixture was directly injected. *Figure 4* shows a calibration standard for ASTM D6584-10a.

Method EN 15779:2012—Determination of polyunsaturated fatty acid methyl esters

Algae are gaining interest as a potential source for biodiesel. Together with *Jathropa*, algae form one of the most interesting alternative biodiesel sources that do not interfere with the food chain. However, polyunsaturated fatty acid methyl esters (PUFAs) are more prominent in marine-based sources than land-based crops. These PUFAs exhibit lower oxidation stability and are more susceptible to polymerization reactions, which may ultimately contribute or even lead to engine fouling and fuel line or filter blocking.

Method EN 15779 is now mandated for the determination of PUFAs between 0.6% (m/m) and 1.5%. The maximum allowable concentration according to EN 14214 is 1.0%. By extend-

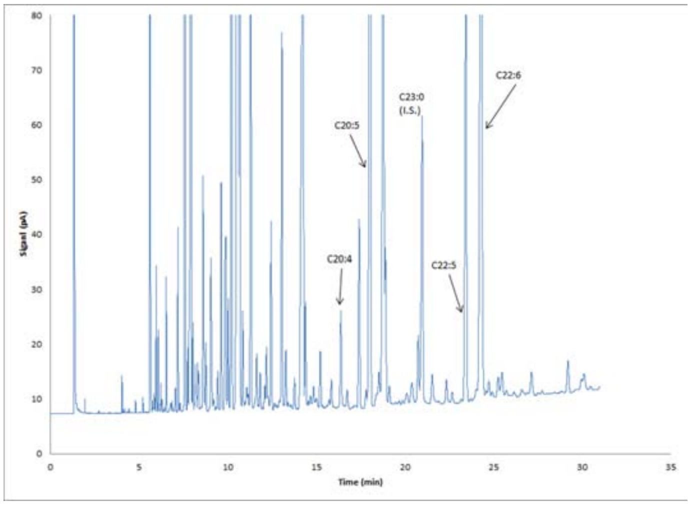

Figure 5 – Typical sample containing PUFA (marine source). Sample contains approximately 16.0% total PUFA methyl esters.

#	C20:4 (n-6)	C20:5 (n-3)	C22:5 (n-3)	C22:6 (n-3)	Total PUFA
1	0.25%	0.25%	0.27%	0.32%	1.09%
2	0.25%	0.25%	0.27%	0.32%	1.09%
3	0.25%	0.25%	0.27%	0.32%	1.09%
4	0.25%	0.25%	0.27%	0.33%	1.09%
5	0.25%	0.25%	0.27%	0.33%	1.09%
6	0.25%	0.25%	0.27%	0.32%	1.09%
7	0.25%	0.25%	0.27%	0.32%	1.09%
8	0.25%	0.25%	0.27%	0.32%	1.09%
Average (%)	**0.25%**	**0.25%**	**0.27%**	**0.32%**	**1.09%**
sd (%)	**0.00%**	**0.00%**	**0.00%**	**0.00%**	**0.00%**
RSD (%)	**0.23%**	**0.09%**	**0.30%**	**0.29%**	**0.15%**
Sample	**n.d.**	**n.d.**	**0.02%**	**0.07%**	**0.09%**

Figure 6 – Repeatability data for EN 15779 using typical sample spiked with 1% PUFA (0.25% each component).

ing the oven programming on the secondary programmable oven (the EN 14103:2011 channel), this method can also be run on the Biodiesel All in One system.

Figure 5 shows data from a typical marine source reference sample containing approximately 16% PUFA, with very clear peak separation and identification. In a repeatability study summarized in *Figure* 6, 1% PUFA (≈0.25% each) was added to an unknown sample. The data demonstrate low levels of C22:5 and C22:6 in the sample (0.02 and 0.07%, respectively), and confirm excellent repeatability for the secondary programmable oven.

Compliance with biodiesel specifications

With the popularity of alternative fuels on the rise, the need to accurately analyze biodiesel is also increasing. With international standards organizations making important changes in biodiesel methods, most existing solutions no longer meet the requirements or are inefficient. The Biodiesel All in One complies with EN 14214 and ASTM D6751 biodiesel specifications, including the latest additions, such as prEN 16300 for iodine value and EN 15779 for determination of polyunsaturated fatty acids. Using an innovative dual programmable oven concept, the analyzer runs all required gas chromatographic biodiesel methods in a single gas chromatograph without the need to modify the system or have multiple systems for the different methods. Therefore, it reduces costs and saves valuable laboratory space, while offering very high performance.

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