GC Analysis of Total Fatty Acid Methyl Esters (FAME) and Methyl Linolenate in Biodiesel Using the Revised EN14103:2011 Method

Application Note

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Abstract

An Agilent 7890 Series GC was configured to run the newly revised European method EN14103:2011 for the determination of FAME content in finished B100 biodiesel. Four different types of biodiesel samples were manually prepared and analyzed using this system. For each biodiesel type, the total FAME and methyl linolenate contents were determined with precision exceeding the method's specifications.

Introduction

In 2011, the European Committee for Standardization (CEN) updated two important GC methods used to measure the quality of finished biodiesel. The first method, EN14105:2011, is used to separate and quantify glycerol and glycerin impurities in finished biodiesel.[1] A recent application note describes the operation and performance of the 7890 Series GC with this method.[2] The second updated GC method is EN14103:2011 and is used to quantify the total FAME content and the methyl linolenate content in finished biodiesel.[3] This method was revised to improve overall analysis precision and provide better chromatographic performance with biodiesel samples containing animal fats and mixed biodiesel feedstocks. This application note describes the operation and performance of the 7890 Series GC with the EN14103:2011 method.

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Experimental

Sample Preparation

Four different types of B100 biodesel were prepared for this analysis; soybean, rapeseed, coconut, and a rapeseed/coconut blend (50/50 volume). Approximately 100 mg of each sample was weighed into individual 12-mL vials followed by the addition of approximately 100 mg of the internal standard, methyl nonadecanoate (C19:0). The weights of the samples and the internal standards were recorded to the nearest 0.1 mg. Each sample plus the internal standard was then dissolved in 10 mL of toluene. Duplicates of the biodiesel samples were prepared to measure the reproducibility of the analysis.

GC Analysis

A 7890 Series GC was configured according to the requirements of the method. This configuration is shown in Table 1. The 7890 Series GC operating conditions were set according to the method and are shown in Table 2. Before the biodiesel samples were analyzed, a mixed sample of 21 FAMEs between methyl hexanoate (C6:0) and methyl nervonate (C24:1) were dissolved in toluene and run on the 7890 Series GC. The resulting chromatogram showed the elution order of the methyl ester peaks typically found in biodiesel samples. The biodiesel sample duplicates were then analyzed by injecting 1 µL of each sample onto the GC and recording the resulting chromatogram. The total ester and methyl linolenate contents were then calculated using the integrated peak areas of the FAMEs identified in the samples.

Table 1. Agilent 7890A Series GC Configuration for EN 14103:2011

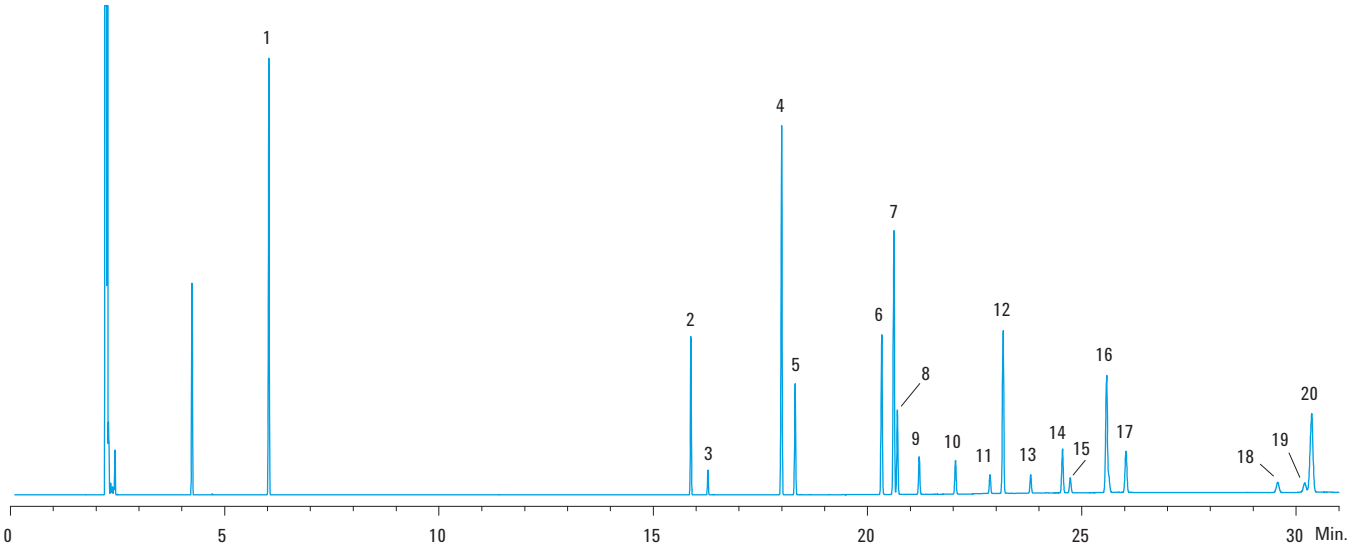
Standard Agilent 7890A Series GC Hardware	
G3440A	Agilent 7890A Series GC
Option 112	100 psi split/splitless Inlet with EPC control
Option 211	Capillary FID with EPC control
G4513A	Agilent 7693 Autoinjector
19091N-133	HP-INNOWax Column, 30 m × 0.25 mm, 0.25 µm

Table 2. GC Conditions for Determination of Ester and Linoleic Acid Methyl Ester Content (EN14103:2011)

Split/Splitless inlet	
Temperature	250 °C
Split flow	100 mL/min
Column 2 flow	Helium at 1 mL/min constant flow
Column temperature	60 °C for 2 min 10 °C /min to 200 °C 5 °C/min to 240 °C Hold 240 °C for 7 min
Flame ionization detector	250 °C

Results and Discussion

The retention times and elution order of 21 methyl esters from C6:0 to C24:1 are shown in Figure 1. All of the FAMEs were chromatographically resolved with the exception of methyl behenate (C22:0) and methyl eicosapentaenoate (C20:5), which co-elute at approximately 25.582 minutes. In general, the FAMEs elute in order of increasing carbon number, however, the polyunsaturated esters, methyl behenate (C20:5) and methyl docosahexaenoate (C22:6) exhibited longer retention times since these compounds have greater polarity compared to same carbon number FAMEs that are saturated or have fewer double bonds.



Peak no.	Name		RT (min.)
1	methyl hexanoate	C6:0	6.031
2	methyl myristate	C14:0	15.878
3	methyl myristoleate	C14:1	16.275
4	methyl palmitate	C16:0	17.996
5	methyl palmitoleate	C16:1	18.311
6	methyl stearate	C18:0	20.332
7	methyl oleate (9)	C18:1	20.617
8	methyl oleate (11)	C18:1	20.697
9	methyl linoleate	C18:2	21.205
10	methyl linolenate	C18:3	22.052

Peak no.	Name		RT (min.)
11	methyl arachidate	C20:0	22.857
12	methyl eicosonate	C20:1	23.166
13	methyl eicosadienoate	C20:2	23.808
14	methyl arachidonate	C20:4	24.551
15	methyl eicosatrienoate	C20:3	24.730
16	methyl behenate and methyl eicosapentaenoate	C22:0 C20:5	25.582
17	methyl erucate	C22:1	26.031
18	methyl lignocerate	C24:0	29.574
19	methyl nervonate	C24:1	30.203
20	methyl docosahexaenoate	C22:6	30.365

Figure 1. Retention times and elution order of C6:0 to C24:1 FAMEs.

The chromatogram in Figure 2 shows a typical analysis of FAMEs in a soybean biodiesel sample. The internal standard, methyl nonadecanoate (C19:0), was well resolved from the C16 and C18 FAMEs typically found in this type of biodiesel. The inset chromatogram shows the peaks in this sample identified as methyl linolenate (C18:3) isomers. The area responses of these three peaks were summed when reporting the total methyl linolenate content. The chromatograms in Figure 3 show the other biodiesel samples analyzed for this work.

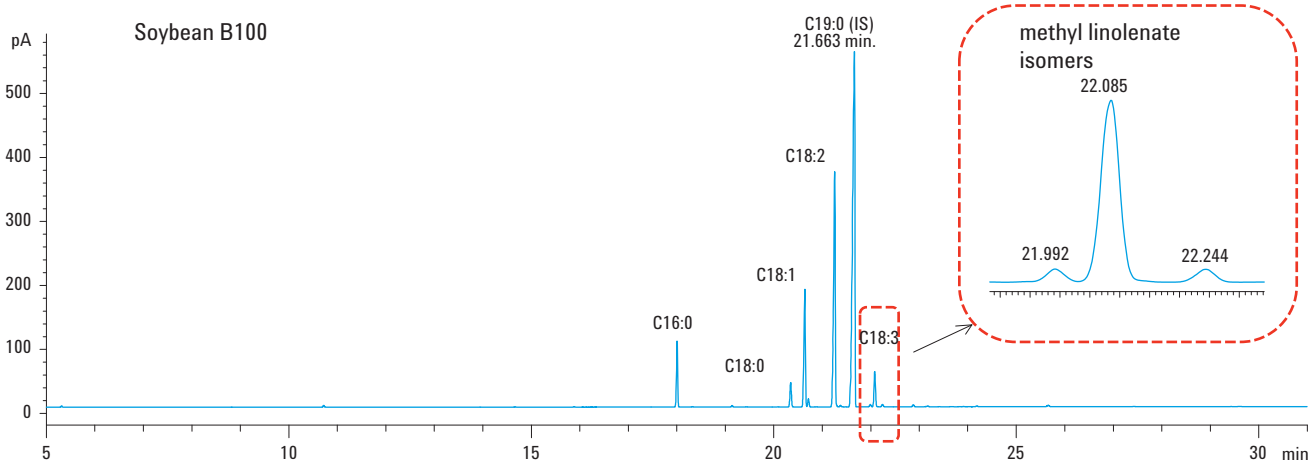


Figure 2. Analysis of total FAMEs in soybean B100 biodiesel. The inset chromatogram shows the three isomers of methyl linolenate.

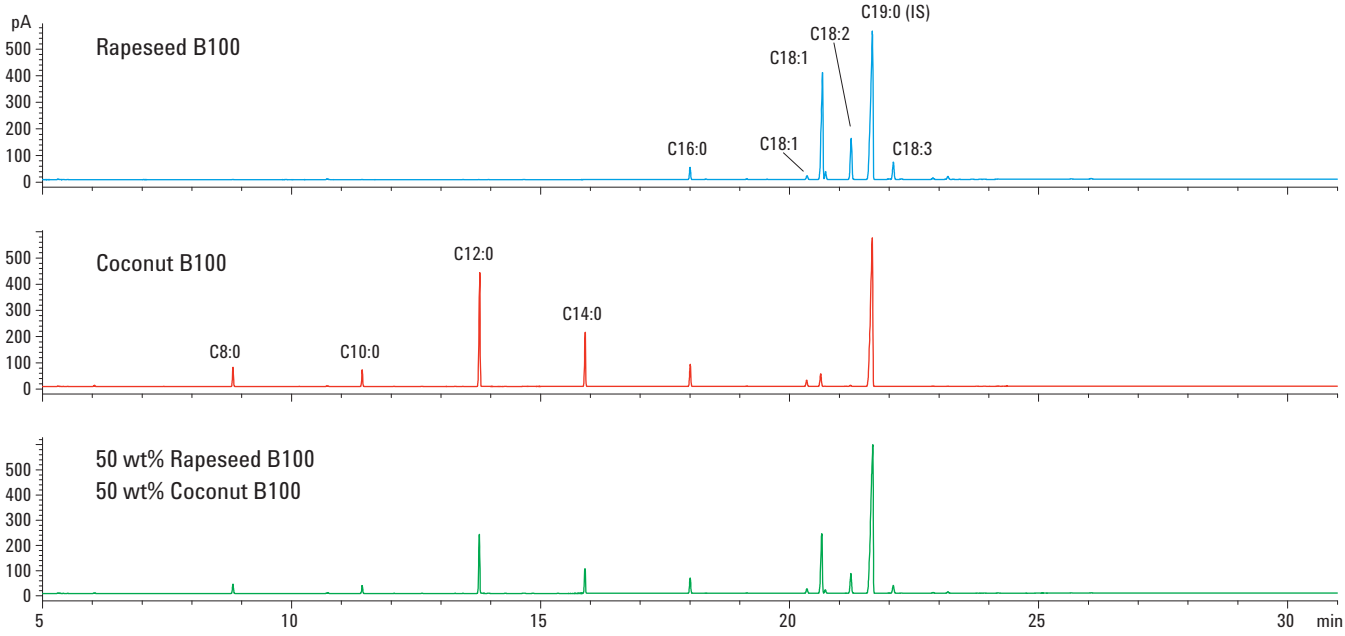


Figure 3. Analysis of total FAMEs and methyl linolenate in rapeseed B100, coconut B100 and a 50/50 wt% mixture of rapeseed and coconut B100 biodiesels.

Data analysis and reporting was performed using the calculations outlined in the EN14103:0211 method. The reference response factor was determined for each biodiesel sample using the recorded weight and area of the C19:0 peak. The areas of the other FAME peaks were then combined and the total FAME content was calculated using the C19:0 reference response factor and the recorded weight of the sample. The weight percent of methyl linolenate was reported separately using the combined areas of the three C18:3 peaks.

Tables 3 and 4 show the total FAME content and the methyl linolenate content reported for each biodiesel sample duplicate. With these results, we were able to determine the single user precision of the measurements. Single user precision is also known as repeatability (r). Repeatability is the difference between two test results obtained by the same operator using the same equipment on identical test material. The EN14103 method provides repeatability statements for the total FAME content and the methyl linolenate content. To use this statement, the absolute value of the difference between the duplicate sample results were taken and compared to the maximum difference required by the method. As shown in Tables 2 and 3, each sample analysis meets the method's repeatability specifications for the total FAME content and the methyl linolenate content.

Table 3. Total FAME Content and Precision of Four Biodiesel Samples Analyzed Using the Revised EN14103:2011 Method

	Total FAME (wt%)		**Repeatability (wt%)**	
Sample	Run 1	Run 2	r	r (spec)*
Soybean	97.4	97.1	0.3	1.01
Rapeseed	95.6	95.4	0.2	1.01
Coconut	87.0	87.2	0.2	1.01
Rape/Coco (50/50)	91.1	91.3	0.2	1.01

* r (spec) is the maximum repeatability specified by the EN14103:2011 method.

Table 4. Methyl Linolenate Content and Precision of Four Biodiesel samples Analyzed Using the Revised EN14103:2011 Method

	C18:3 (wt%)		**Repeatability (wt%)**	
Sample	Run 1	Run 2	r	r (spec)*
Soybean	7.3	7.3	0.0	0.2
Rapeseed	8.3	8.4	0.1	0.2
Coconut	0.0	0.0	0.0	0.0
Rape/Coco (50/50)	4.1	4.1	0.0	0.1

* r (spec) is the maximum repeatability specified by the EN14103:2011 method.

Conclusion

The 7890 Series GC was configured to run the revised EN14103:2011 method for the determination of total FAME content and methyl linolenate content in B100 biodiesel. Duplicates of four different type of biodiesel were manually prepared according to the method's protocols followed by GC analysis. Each sample was successfully analyzed and the results showed precision exceeding the requirements of the EN14103:2011 method.

References

1. DIN EN14105:2011-07 "Fat and oil derivatives – Fatty Acid Methyl Esters (FAME) – Determination of free and total glycerol and mono-, di-, and triglyceride contents", European Committee for Standardization, Management Centre: Avenue Marnix 17: B-1000 Brussels.
2. "Agilent 7696A WorkBench Automated Sample Preparation for the GC Analysis of Biodiesel Using Method EN14105:2011", James D. McCurry, Agilent Technologies, Publication Number 5990-9893EN, February 24, 2012.
3. DIN EN14103:2011 "Fat and oil derivatives – Fatty Acid Methyl Esters (FAME) – Determination of ester and linolenic acid methyl ester content", European Committee for Standardization, Management Centre: Avenue Marnix 17: B-1000 Brussels.

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