Determining the Ester and Linoleic Acid Methyl Ester Content to Comply with EN14103

Application

HPI

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Abstract

Gas chromatography with a split/splitless inlet and FID is used to determine the ester and linoleic acid methyl ester content of fatty acid methyl esters (FAME) intended for use as pure biofuel or as a blending component for heating and diesel fuels. The method is suitable for FAME containing methyl esters between C14 and C24. This application used the Agilent 6850 System and HP-INNOWax column; calibration was achieved with internal standards of methyl heptadecanoate. After analyzing several different types of biodiesel, excellent precision was obtained, exceeding the EN14103 method specifications.

Introduction

Biodiesel fuel is produced when a vegetable oil or an animal fat reacts with methanol in the presence of a catalyst to yield fatty acid methyl esters (FAME) and glycerin, which is removed. FAME is a pure biodiesel fuel called B100. A "green" fuel, biodiesel is biodegradable, nontoxic, and is essentially free of sulfur and aromatics. It is rapidly gaining momentum worldwide as an alternative fuel source for diesel engines.

Only biodiesel fuel meeting the specifications of ASTM D6751 or EN14214 is acceptable for use as a motor fuel. Several GC methods have been developed to determine if a biodiesel meets the specification. For example, EN14103 determines the ester and linoleic acid methyl ester content; EN14105 and ASTM D6584 determine free and total glycerin and mono-, di-, and triglyceride content; and EN14110 is for methanol. EN14106, which determines free glycerol, is not commonly used since 14105/ASTM D6584 provides more complete results.

Three major GC biodiesel solutions—EN14103, EN14105/ASTM D6584, and EN14110—were developed for the Agilent GC platform. This application describes the performance of EN14103 on the Agilent 6850 GC.

Experimental

The application was conducted with the Agilent 6850 GC with FID, split/splitless inlet, and

HP-INNOWax column (30 m × 320 µm id × 0.25 µm film of polyethylene glycol). A solution of methyl heptadecanoate in heptane (10 mg/mL or 5 mg/mL) was used as a calibration for quantification.

Gas Chromatographic Conditions

Inlet Temperature:	250°C
Split ratio:	80:1
Injection volume:	1µL
Column flow (He):	1.5 mL/min, constant flow mode
FID temperatures:	300°C
H_2 flow:	40 mL/min
Air flow:	400 mL/min
Make up (N_2):	40 mL/min
Oven program:	210 °C hold 9 min, to 230 °C at 20°C/min, hold 10 min
Column:	30m x 320mm x 0.25 µm HP-INNOWax (Part no. 19091N-113)
Calibration standard:	Solution of methyl heptadecancate in heptane (5 mg/mL)

Sample Preparation

Accurately weigh approximately 250mg of sample in 10-mL vial, and then add 5 mL of methyl heptadecanoate solution using a pipette.

Results and Discussion

Several samples of B100 biodiesel made from vegetable oils and animal oils were analyzed. Figure 1 and Figure 2 are the chromatograms of rapeseed oil and pork oil, respectively.

The HP-INNOWax column exhibits excellent separation for the methyl esters between C14 and C24, which obtain baseline separation. To achieve a satisfactory compromise between resolution and analysis time, esters between C14 and C20 were separated isothermally at 200 °C; esters between C22 and C24 were separated at 230 °C.

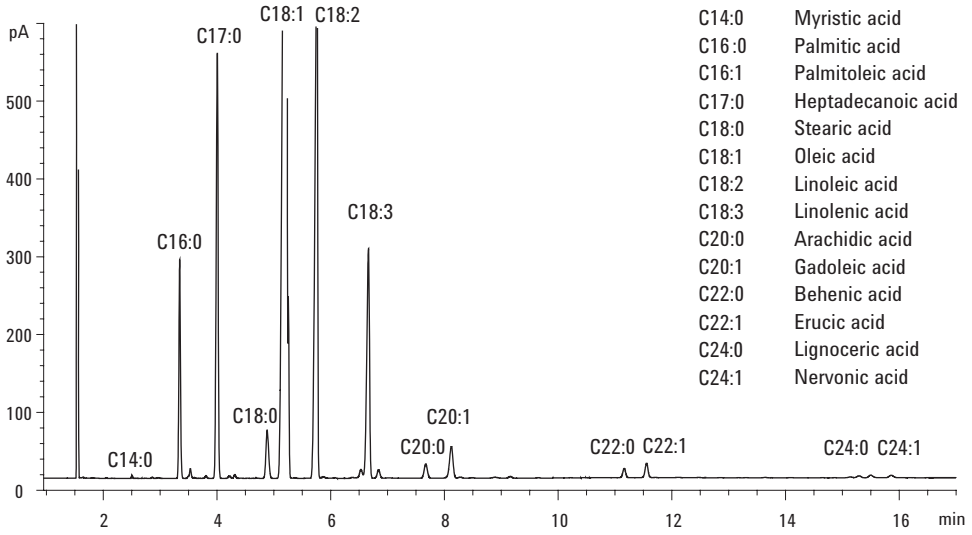

Figure 1. Chromatogram of rapeseed methyl esters.

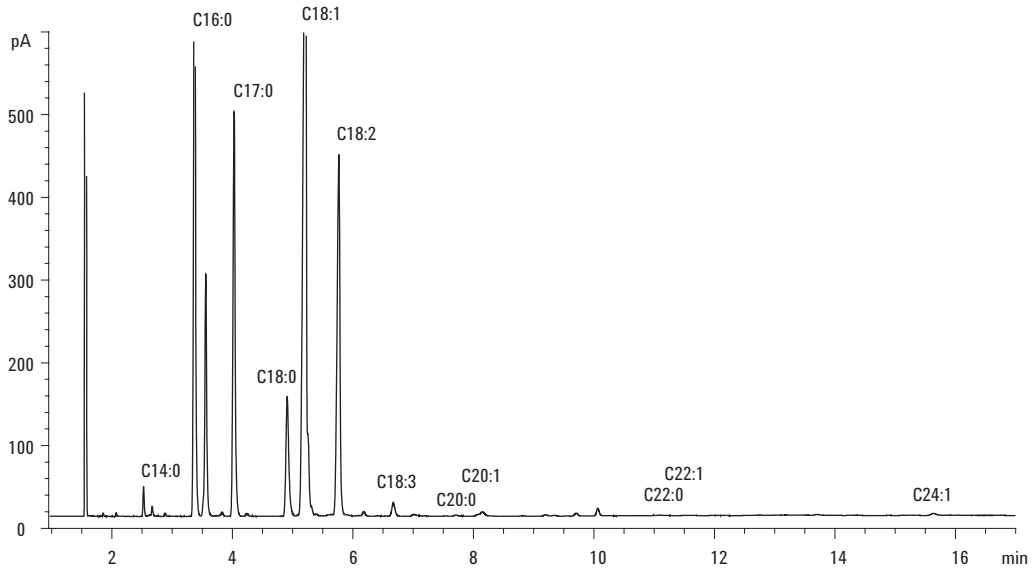

Figure 2. Chromatogram of pork methyl esters.

Quantitative results for different types of biodiesel fuel, such as rapeseed oil, soybean oil, chicken oil and pork oil are shown in Table 1. It can be seen that rapeseed oil contains a higher concentration of C18:1 (55.68% m/m) and soybean oil contains a higher concentration of C18:2 (48.66% m/m). The animal oils (chicken and pork) contain a higher concentration of C18:1; however, compared with vegetable oil, animal oil contains a higher concentration of C16:0.

Table 2 shows excellent repeatability, exceeding the specification of EN14103. The data in Table 3 demonstrate that most RSD% is within 1%.

Table 1. Observed FAME Composition in % (m/m) of Different Type Oil

		Average, % (m/m)			
Component FAME		**Rapeseed oil**	**Soybean oil**	**Chicken oil**	**Pork oil**
Myristic acid	C14:0	0.04	0.07	1.12	0.43
Palmitic acid	C16:0	4.12	9.90	17.63	15.62
Palmitoleic acid	C16:1	0.05	0.02	2.15	5.28
Stearic acid	C18:0	1.57	4.27	9.91	3.93
Oleic acid	C18:1	55.68	22.54	34.32	28.48
Linoleic acid	C18:2	17.82	48.66	7.38	11.87
Linolenic acid	C18:3	7.61	7.27	0.37	0.48
Arachidic acid	C20:0	0.56	0.32	0.14	0.05
Gadoleic acid	C20:1	1.31	0.18	0.73	0.29
Behenic acid	C22:0	0.32	0.32		
Erucic acid	C22:1	0.51			
Lignoceric acid	C24:0	0.15		0.08	
Nervonic acid	C24:1	0.16	0.16	0.15	0.15

Table 2. Repeatability* for Different Type Biodiesel

		Observed			
	EN14103 Spec (m/m)	Soybean (m/m)	Rapeseed (m/m)	Chicken (m/m)	Pork (m/m)
Ester content	1.6%(m/m)	0.065%(m/m)	0.254%(m/m)	0.021%(m/m)	0.098%(m/m)
C18:3 content	0.1%(m/m)	0.005%(m/m)	0.018%(m/m)	0.002%(m/m)	0.012%(m/m)

*The absolute difference between two independent single test results, obtained using the same method on identical test material in the same laboratory by the same operator using the same equipment with a short time interval.

Table 3. Relative Standard Deviation Data (RSD%) for FAME Analysis

		RSD%, %(m/m) (Average=5)			
Component FAME		Rapeseed oil	Soybean oil	Chicken oil	Pork oil
Myristic acid	C14:0	0.38	0.34	0.17	0.16
Palmitic acid	C16:0	0.05	0.01	0.05	0.03
Palmitoleic acid	C16:1	0.17	1.02	0.16	0.11
Stearic acid	C18:0	0.16	0.49	0.06	0.23
Oleic acid	C18:1	0.14	0.04	0.03	0.10
Linoleic acid	C18:2	0.14	0.02	0.03	0.47
Linolenic acid	C18:3	0.11	0.03	0.28	0.95
Arachidic acid	C20:0	0.35	0.16	0.32	1.55
Gadoleic acid	C20:1	0.46	1.05	0.20	0.63
Behenic acid	C22:0	0.34	0.49		
Erucic acid	C22:1	0.23			
Lignoceric acid	C24:0	1.31		1.14	
Nervonic acid	C24:1	1.15	1.31	1.49	0.89

Conclusions

The ester and linoleic acid methyl ester content present in the different types of biodiesel fuel produced from rapeseed, soybean, chicken, and pork were quantitatively analyzed using the Agilent 6850 System equipped with a split/splitless inlet, FID, and HP-INNOWax column. Calibration was achieved with internal standards, methyl heptadecanoate. The results show excellent repeatability, exceeding the specification of EN14103. The relative standard deviation is less than 1% for almost all methyl esters.

References

1. EN14103, "Fat and oil derivatives. Fatty acid methyl esters (FAME) Determination of ester and linolenic acid methyl ester contents."
2. ASTM D6751-03, "Standard specification for biodiesel fuel blend stock (B100) for middle distillate fuels."

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