SHIMADZU APPLICATION NEWS

LAAN-A-G-E011

● GAS CHROMATOGRAPHY

No.G250

Determination of Free and Total Glycerin in Biodiesel Methyl Esters –ASTM D6584 and EN14105–

There is rising concern with respect to global warming and the reduction of CO_2 emissions, and the use of plant-derived oils as a raw material for production of fuel for diesel engines (biodiesel) is spreading worldwide. Production of biodiesel generally involves reacting methanol with the oil, causing a trans-esterification reaction to produce fatty acid methyl esters. A residual byproduct of the manufacturing process includes free glycerine and mono-, di- and triglycerides. In the United States and Europe, there are standards and prescribed analytical methods for regulating the quality of biodiesel. In this Application News we introduce the analytical methods, ASTM D6584 and EN 14105, as they are now specified as of March 2007.

■ Analytical Method

There are differences in the standard solution concentrations and column temperature conditions, etc. in the ASTM and EN methods. However, which two specific internal standards are added to the sample, derivatization is conducted using N-Methyl-N-trimethylsilyltrifluoroacetamide (MSTFA), and analysis is conducted by the FID method with cool on-column injection into the capillary column. Tables 1 and 2 show the calibration standard stock solutions and standard solution concentrations used for generating the calibration curves, Figures # 1 and 2 show the sample preparation procedures, and Tables 3 and 4 show the analytical conditions with respect to the ASTM and EN methods, respectively. A column that can support a maximum temperature of 400 ˚C is used. Although the derivatized sample should remain stable for several hours, it is necessary to conduct analysis quickly since the sample will not remain stable for a long period.

In this Application News, the actual sample was prepared according to the ASTM sample preparation method, and analysis was conducted using the ASTM and EN analytical conditions, respectively. Since no triglyceride peak was detected with the actual sample used here, an arrow is shown in the elution position of the triolein standard. In order to conduct analysis under the ASTM column-heating conditions, a high-power oven (230 V) GC model is essential.
Moreover, we also introduce here analysis examples with different length columns using the simple OCI with the GC-2010.

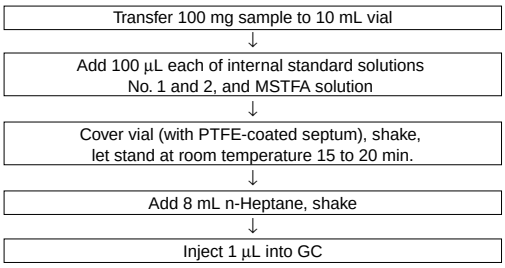

Fig.1 Sample Preparation – ASTM D6584

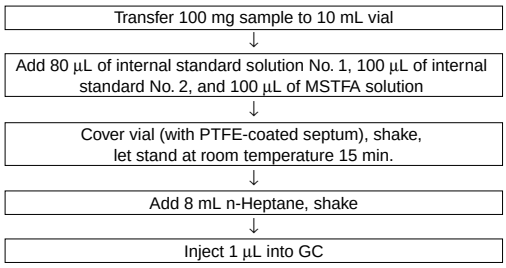

Fig.2 Sample Preparation – EN14105

Table 1 Preparation of Calibration Standard Stock Solutions and Standard Solutions - ASTM D6584

	Calibration Standard Stock Solution Concentrations (mg/mL) Solvent: Pyridine	Standard Solutions (Standard Stock Solution Addition Amount (µL))				
		No.1	No.2	No.3	No.4	No.5
Glycerine	0.5	10	30	50	70	100
1-Mono[cis-9-octadecenoyl] -rac-glycerol (monoolein)	5	20	50	100	150	200
1,3-Di[cis-octadecenoyl]glycerol (diolein)	5	10	20	40	70	100
1,2,3-Tri[cis-9-octadecenoyl] glycerol (triolein)	5	10	20	40	70	100
(S)-(-)-1,2,4-Butanetriol (Internal Standard 1)	1	100	100	100	100	100
1,2,3-Tridecabolylglycerol (Tricaprin) (Internal Standard 2)	8	100	100	100	100	100

Prepare by transferring each sample to 10 mL vial, add derivatization reagent similarly as with sample.

Table 2 Preparation of Calibration Standard Stock Solutions and Standard Solutions - EN14105

	Calibration Standard Stock Solution Concentrations (mg/mL) Solvent: Pyridine	Standard Solutions (Standard Stock Solution Addition Amount (µL))			
		No.1	No.2	No.3	No.4
Glycerine	0.5	10	40	70	100
1-Mono[cis-9-octadecenoyl] -rac-glycerol (monoolein)	5	50	120	190	250
1,3-Di[cis-octadecenoyl]glycerol (diolein)	5	10	40	70	100
1,2,3-Tri[cis-9-octadecenoyl] glycerol (triolein)	5	10	30	60	80
(S)-(-)-1,2,4-Butanetriol (Internal Standard 1)	1	80	80	80	80
1,2,3-Tridecabolylglycerol (Tricaprin) (Internal Standard 2)	8	100	100	100	100

Prepare by transferring each sample to 10 mL vial, add derivatization reagent similarly as with sample.

Table 3 Analytical Conditions - ASTM D6584

Column	: 5 % Phenylpolydimethylsiloxane 10 m or 15 m × 0.32 mmI.D. df=0.1 µm (Max.Temp. > 400 ˚C)
Guard column	: 2-5 m × 0.53 mmI.D.
Injector	: Cool on-column injection
Sample size	: 1 µL
Column Temperature	: 50 ˚C (1 min)-15 ˚C/min-180 ˚C-7 ˚C/min-230 ˚C -30 ˚C/min-380 ˚C (10 min)
Detector	: FID, 380 ˚C
Carrier Gas	: H_2 or He, 3 mL/min at 50 ˚C

Table 4 Analytical Conditions - EN14105

Column	: 100 % Dimethylpolysiloxane or 95 %Dimethyl -5 %Diphenylpolysiloxane 10 m × 0.32 mmI.D. df=0.1 µm (Max.Temp. > 400 ˚C)
Injector	: On-column injector or equivalent device
Sample size	: 1 µL
Column Temperature	: 50 ˚C (1min)-15 ˚C/min-180 ˚C-7 ˚C/min-230 ˚C -10 ˚C/min-370 ˚C (5 min)
Detector	: FID, 380 ˚C
Carrier Gas	: H_2 or He, 80 kPa

■ Biodiesel Analysis - ASTM D6584

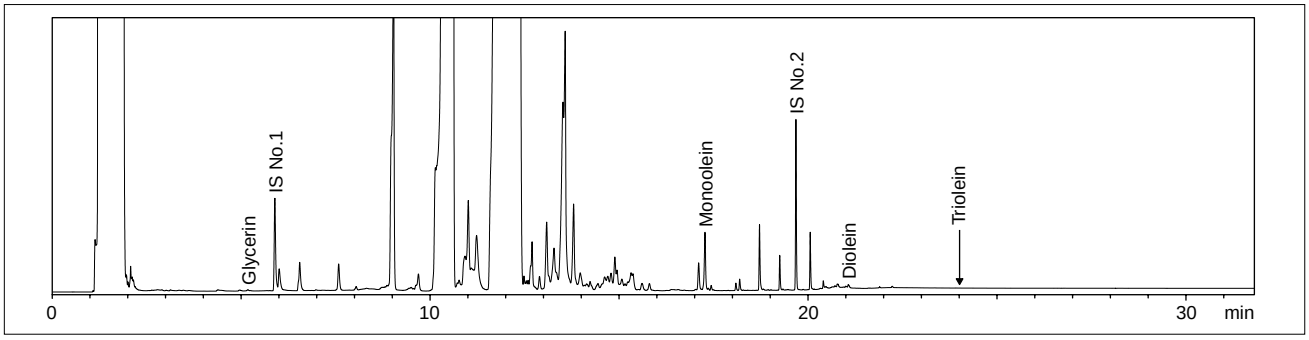

Fig.3 Chromatogram of Sample (Column ZB-5HT 15 m, Guard Column 5 m)

■ Biodiesel Analysis - EN14105

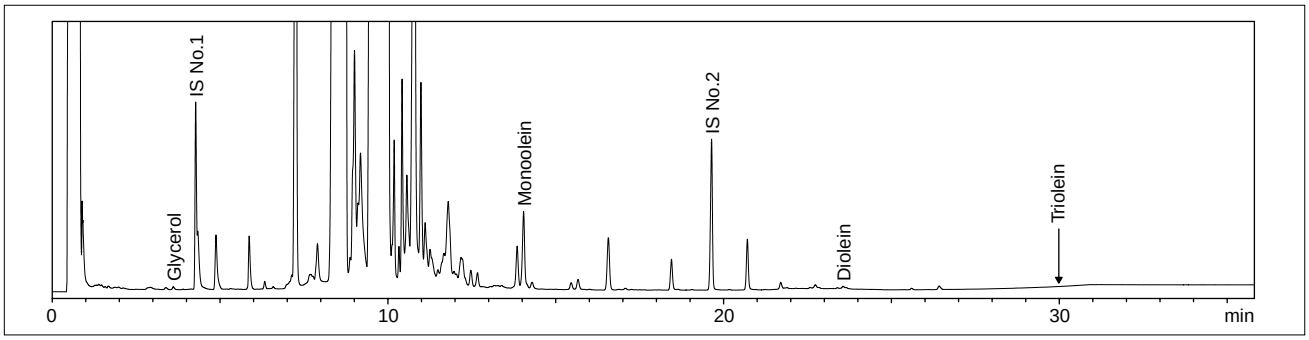

Fig.4 Chromatogram of Sample (Column ZB-5HT 10 m, Guard Column 5 m)

■ Biodiesel Analysis - Simple Cool on Column Injection Method

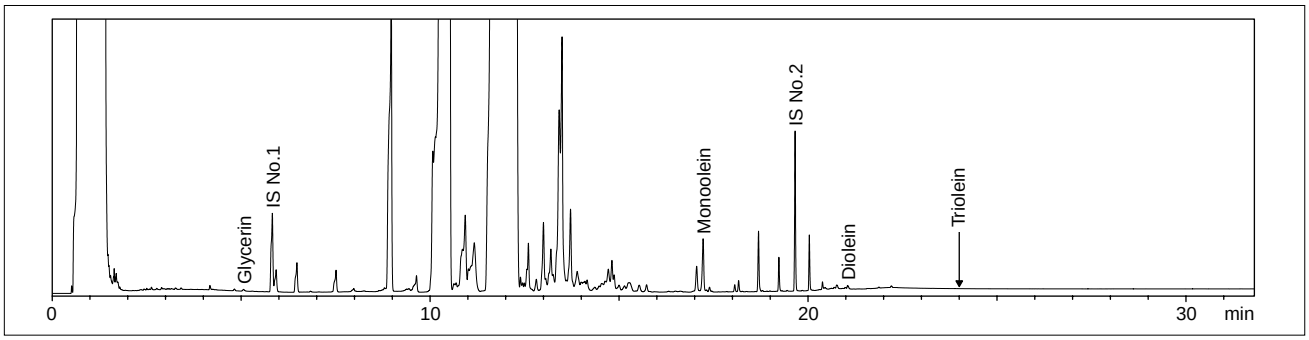

Fig.5 Chromatogram of Sample (Column ZB-5HT 15 m)

Table 5 Operating Conditions (Fig.3,4,5)

Column	: ZB-5HT 15 m × 0.32 mmI.D.df=0.1 µm + Guard column 5 m × 0.53 mmI.D. - (Fig.3) ZB-5HT 10 m × 0.32 mmI.D.df=0.1 µm + Guard column 5 m × 0.53 mmI.D. - (Fig.4) ZB-5HT 15 m × 0.32 mmI.D.df=0.1 µm - (Fig.5)
Injector	: Cool on-column injector
Sample size	: 1 µL
Column Temperature	: 50 ˚C (1 min) - 15 ˚C/min - 180 ˚C - 7 ˚C/min - 230 ˚C - 30 ˚C/min - 380 ˚C (10 min) - (Fig.3,5) 50 ˚C (1 min) - 15 ˚C/min - 180 ˚C - 7 ˚C/min - 230 ˚C - 10 ˚C/min - 370 ˚C (5 min) - (Fig.4)
Detector	: FID 380 ˚C
Injector Temperature	: 50 ˚C (0.1 min)-150 ˚C/min-380 ˚C (29.51 min) - (Fig.3,5) 50 ˚C (0.1 min)-150 ˚C/min-380 ˚C (33.51 min) - (Fig.4)
Carrier Gas	: He, 3 mL/min at 50 ˚C (52.9 cm/sec Constant Linear Velocity Mode) - (Fig.3,5) He, 80 kPa (120 cm/sec Constant Linear Velocity Mode) - (Fig.4)

NOTES:

✻This Application News has been produced and edited using information that was available when the data was acquired for each article. This Application News is subject to revision without prior notice.

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