SHIMADZU

Application Notes

Gas Chromatography

Analysis of Methyl Laurate Content In Low Concentration Biodiesel Blends (B1, B2) with Multidimensional Gas Chromatography System (Part II)

Introduction

Direct determination of C12ME (lauric acid methyl ester) in low concentration biodiesel blends, such as B1 and B2, was demonstrated by using dual-oven MDGC system without sample preparation. A low dead-volume inert "switching unit" is used in the system, interfacing the 1st and the 2nd dimension separation. The biodiesel blend was first subjected to the primary separation by using a non-polar column. The unresolved target analyte, C12ME, was then selectively heart-cut and re-injected for the 2nd dimension separation by a polar column that is operated by independent temperature programs of the 2nd oven. The remaining non-targeted high boiling point components in the non-polar column were subsequently back-flushed and purged out at high oven temperature setting of the 1st oven. The middle bore capillary MDGC approach showed accurate and repeatable qualitative and quantitative data. Fast MDGC method utilizing narrow bore capillary columns was also investigated for this application.

Experimental

B100 CME was produced from a commercial coconut oil, prepared in the laboratory by transesterification process. The transesterification process converts the triglycerides in the oil into Fatty Acid Methyl Esters (FAMEs) by using a catalyst (NaOH) and methanol as reagent.[1] The C12ME content in the laboratory-made CME was determined by GCMS to be ~33%. Four diesel samples, named as SS, ES, PS and CS, were obtained from different brands in the market and were used as matrices of the spiked samples. The biodiesel blends that are fortified with 1% of laboratory-made CME are designated B1SS, B1ES, B1PS and B1CS in the following discussion.

Instruments and Analysis Conditions

An MDGC/GCMS-2010 equipped with a liquid auto-injector, AOC-20i and a set of GC/GCMS/MDGCsolution Workstation were used for this experiment. The analysis conditions for both Conventional MDGC (using a pair of 0.25mm I.D. columns) and Fast MDGC (using a pair of 0.10mm I.D. columns) are listed in Table 1.

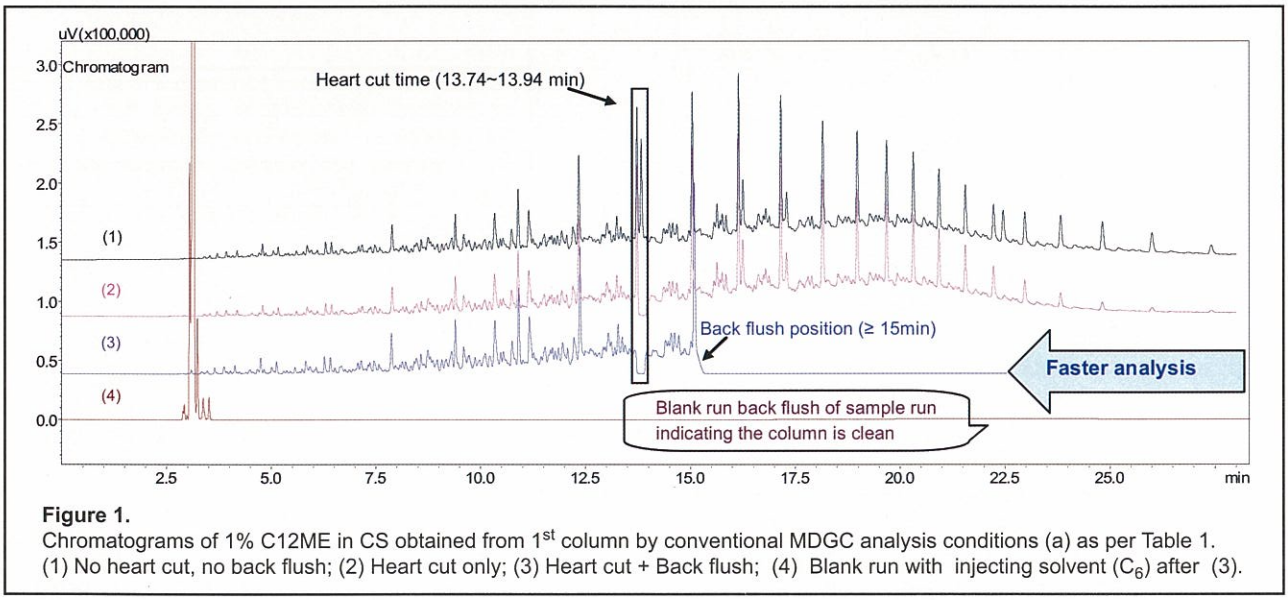

Figure 1.
Chromatograms of 1% C12ME in CS obtained from 1st column by conventional MDGC analysis conditions (a) as per Table 1.
(1) No heart cut, no back flush; (2) Heart cut only; (3) Heart cut + Back flush; (4) Blank run with injecting solvent (C_6) after (3).

Table 1. Analysis Conditions of MDGC.

Analytical conditions	Conventional MDGC (a)	Fast MDGC (b)
1st instrument		
1st Column		
type	Rtx-1; non-polar (Resteks Corp., USA)	DB-5 ; low polarity (J&W, USA)
dimension	30 m x 0.25 mm I.D., df=0.25 µm	10 m x 0.10 mm I.D., df=0.10 um
Oven temperature		
Initial temperature	70°C (0 min)	
Program 1	70°C @ 10°C/min ~ 220°C (0 min)	70°C @ 30°C/min ~ 180°C (0 min)
Program 2	220°C @35°C/min ~300°C (11min/6min @ backflush)	180°C@50°C/min ~ 300°C (4min)
Carrier gas	He	
without back flush	190 kPa	700 kPa
with back flush	190 kPa (15min) @ -400 kPa/min~10 kPa (7 min)	700 kPa (4.25min) @ -400 kPa/min~10 kPa (4.10min)
Switching gas	He, 120 kPa	He, 500 kPa
heart cut time	13.74 ~13.94 min	3.96 ~ 4.14 min
INJ temperature	250°C	
FID temperature	320°C	
Injection		
mode	Split	
split ratio	100	200
volume	0.2 µL	
2nd instrument		
2nd Column		
type	Stabilwax; polar (Resteks Corp., USA)	DB-Wax; polar (J&W, USA)
dimension	30 m x 0.25 mm I.D., df=0.25 µm	10 m x 0.10 mm I.D., df=0.10 µm
Oven temperature		
Initial temperature	50°C (15 min)	50°C (4 min)
Program 1	50°C @ 30°C/min ~ 220°C (2 min)	50°C @50°C/min ~ 230°C (1.4 min)
GC I/F temperature	230°C	
DET, qMS		
I/f temperature	250°C	
IS, temperature	EI, 200°C	
Acquisition	Scan, M/Z 40~350	
Scan speed	1666 amu/sec	3333 amu/sec

Results

Conventional MDGC

Fig. 1 shows the chromatograms of 1% C12ME spiked into CS (diesel sample) obtained from the 1st column analyzed under conditions (a) shown in Table 1. The unresolved C12ME elution band (13.74~13.94 min) for heart-cutting, and the back flushed position (@15 min) were determined. By back-flushing out the unwanted high boiling points matrix components from the split line of the injector, the analysis time of the 1st column could be reduced by 5.5 min (from 28 min shortened to 22.5 min); and it is possible to align with the analysis time of 2nd column. Blank run was done by injecting solvent (hexanes) after the sample analyses. A clean baseline (chromatogram (4) in Fig. 1) indicated that the back-flushing successfully eliminated the carryover of the late-eluting compounds with reduced analysis cycle time.

Fig. 2 shows that the unresolved C12ME elution band (from B1 biodiesel blends), re-injected from "switching unit", was well separated by the 2nd column. This is demonstrated by: (1) the peak shape similarity between the TIC (total ion chromatogram) and the mass chromatograms (m/z 74 & 87) of C12ME; (2) the satisfactory Similarity Index (SI) obtained when the mass spectrum of C12ME was searched against the private library as well as a public library (NIST05). The private library generated by the same GCMS instrument used in this experiment gave a better match as expected (refer to Table 2).

Table 2.

Similarity index (SI)[a] of C12ME mass spectra in biodiesel blends		
1% CME in	SI[b]	
diesel sample	Private Lib	NIST
B1SS	99	96
B1ES	99	96
B1PS	99	96
B1CS	99	96

[a] SI quantitatively expresses the difference between the mass spectra of an unknown and those registered in libraries. If the patterns of the two mass spectra are identical, the SI is 100.
[b]SI of measured C12ME spectra Vs in-house private library and commercial library, NIST05.

The Method Precision and Quantitative Analysis for Conventional MDGC

Diesel sample CS that was fortified with 0.5% C12ME was used to check the method precision. Seven replicate analyses were conducted under heart-cut and back-flush conditions. The data from the 2nd column (listed in Table 3) demonstrated excellent repeatability for both retention time (CVRT = 0.0017%) and peak areas (CV_{TIC} = 1.491%; CV_{MC} = 1.706%).

Table 3.

Summary of method precision in spiked sample[a] from 2nd column

C12ME	RT	Area (TIC)	Area (MC, M/Z=74)
1st	20.4612	992608	3946913
2nd	20.4603	979058	3900519
3rd	20.4605	1010134	4024136
4th	20.4612	988260	3923211
5th	20.4608	1007104	3998946
6th	20.4610	1018493	4059354
7th	20.4605	1015105	4076236
Avg.	20.4608	1001537	3989902
SD	0.0003	14932	68088
RSD (%)	0.0017	1.491	1.706

[a] Diesel sample, CS containing 0.5% C12ME

Two calibration curves were obtained by plotting the peak area of TIC and MC (mass chromatogram) of C12ME against the concentration (Fig. 3). Excellent linearity was obtained for both calibration curves for the concentration of C12ME in biodiesel blends in the range of 0.1~2.0% w/w; the coefficients of correlation (r^2) were better than 0.997 for both TIC and MC. The 2nd column quantitative results for C12ME in the fortified biodiesel blends (listed in Table 4) are very close to the actual amount of C12ME in the biodiesel blends, each of which contained 1% of the laboratory-made CME (containing 33% of C12ME). In addition, the quantitative results based on TIC and MC (m/z=74) from qMS detector are correlate well. This is another indication that the target analyte was well separated from the matrix components with high peak purity.

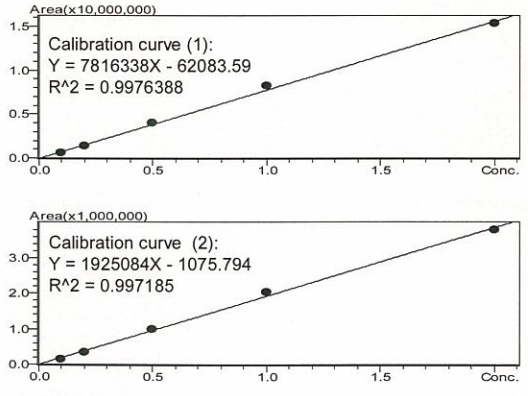

Figure 3. Calibration curves plot for C12ME's concentration (0.1~2.0%; w/w) Vs peak area of: **Upper:** TIC. **Lower:** MC (M/Z=74).

Table 4.

Quantitation results of C12ME in spiked samples[a] from 2nd column

Spiked sample	Concentration of C12ME , %(w/w)	
	TIC[b]	MC, M/Z 74[c]
B1SS	0.33	0.32
B1ES	0.25	0.25
B1PS	0.29	0.29
B1CS	0.30	0.30

[a] Diesel samples containing 1% CME, where the content of C12ME in lab made B100 CME was actually ~ 33 %.
[b] Concentration determined by peak area of TIC with calibration curve (1) of Fig. 3.
[c] Concentration determined by peak area MC with calibration curve (2) of Fig. 3.

Fast MDGC

A fast MDGC method was developed for this application with a pair of 0.10mm ID columns (the analysis conditions are listed in Table 1. Both heart cut and back flush techniques were applied and the data are shown in Fig. 4 and 5. The total analysis time was 10 min, giving a 2.25 times speed gain compared with conventional MDGC method.

Method sensitivity of the Fast MDGC techniques is inferior compared with conventional middle bore capillary analysis.[2] Low sample loading capacity is the key restriction factor of thin film narrow bore column for detecting low concentration target analyte eluted within high concentration matrix (refer to Fig. 6). To increase method sensitivity, more samples could be introduced by compromising the resolution. However, for this particular application, C12ME content in B1 and B2 biodiesel blends typically ranges from 0.4~0.8%. The method developed here shows good signal-to-noise (S/N) ratio for the target analyte in this concentration range.

Conclusions

It has been demonstrated that C12ME in low concentration biodiesel blends, such as B1 or B2, could be well separated and accurately determined by using dual-oven MDGC system without sample preparation. Accurate and repeatable qualitative/quantitative data obtained from Conventional MDGC for middle bore capillary columns demonstrated the high efficiency heart cut and back flush mechanisms of the inert "switching unit" of Shimadzu dual-oven MDGC system. Thus, this system could serve as a reliable QC instrument for such application even if a FID is used as the detector in the 2nd instrument. Fast dual oven MDGC application with the same techniques could be performed by Shimadzu MDGC system as well. Despite the expected slight decrease in method sensitivity due to the low sample loading capacity of the thin film narrow bore capillary columns, it is sufficient for this particular application.

References

[1] http://journeytoforever.org/biodiesel_make.html
[2] L. Mondello, A. Casilli, P.Q. Tranchida, M. Furukawa, K. Komori, K. Miseki, P. Dugo, G. DugoJ. Chrommatogr. A, 1105 (2006) 14.

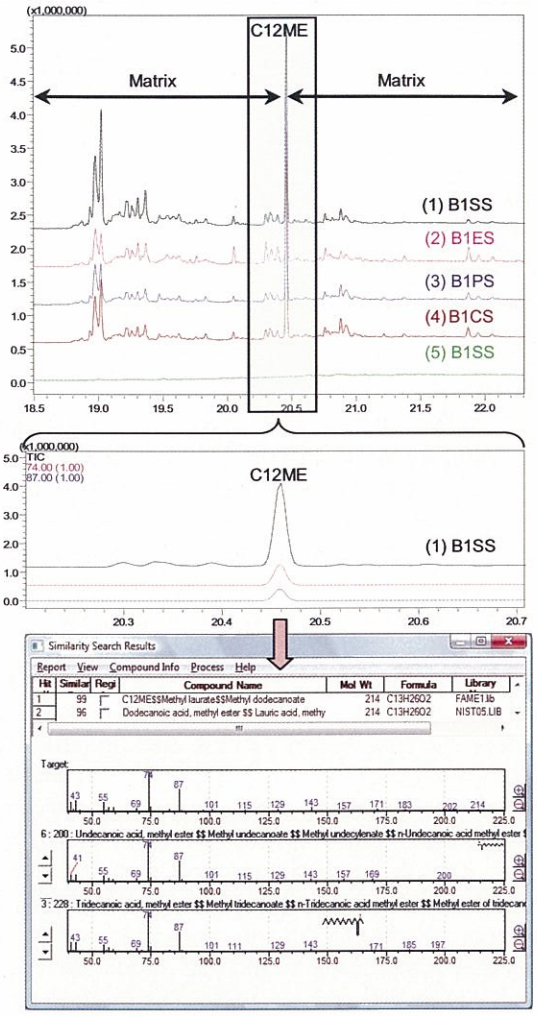

Figure 2. TIC of B1 biodiesel blends obtained from 2nd column by conventional MDGC conditions.
Upper: (1), (2), (3) & (4) obtained by Heart cut + Back flush; (5) No reinjection from 1st column (background TIC);
Middle: Enlargement of TIC (1);
Lower: Library search result of C12ME from TIC(1).

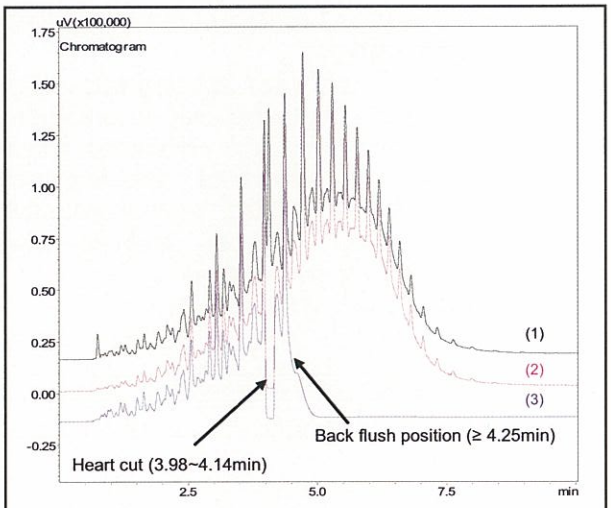

Figure 4. Chromatograms of 1% C12ME in CS obtained from 1st column by conventional Fast MDGC conditions listed in Table 1. (1) No heart cut, no back flush; (2) Heart cut only; (3) Heart cut + Back flush.

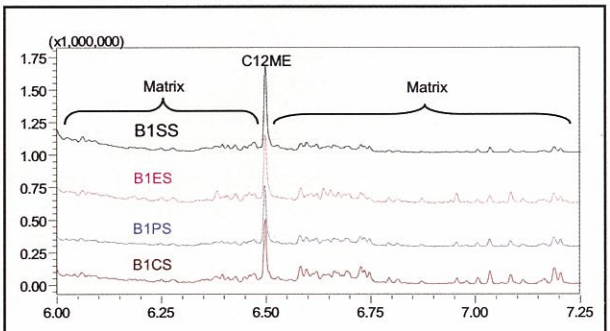

Figure 5. TIC of B1 biodiesel blends obtained from 2nd column by fast MDGC conditions as per Table 1.

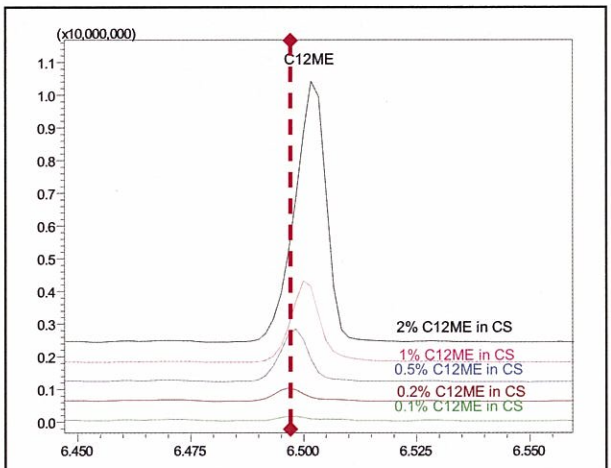

Figure 6. TIC of C12ME in CS obtained from 2nd column by fast MDGC conditions as per Table 1.

Author(s):
Hui-Loo Lai Chin, Novalina Lingga, Cynthia Lahey,
Shimadzu Asia Pacific Pte. Ltd., Singapore

Tai Jia Xing
Department of Chemistry,
National University of Singapore

SHIMADZU (Asia Pacific) Pte. Ltd.
Customer Support Centre
16 Science Park Drive #01-01, The Pasteur
Singapore Science Park I, Singapore 118227
http://www.shimadzu.com.sg
Tel: +(65) 6778-6280
Fax: +(65) 6778-2050

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