Application News

Brevis™ GC-2050 Gas Chromatograph

Analysis of Denatured Fuel Ethanol with Brevis GC-2050 Using ASTM D5501

Kei Usui

User Benefits

- The compact design of the Brevis GC-2050 enables space-saving in the laboratory.
- As an alternative gas for helium, hydrogen can be used as the carrier gas.
- Analysis of ethanol and methanol in fuels based on ASTM D5501 is possible.

■ Introduction

Bioethanol has attracted attention as a form of renewable energy which can be obtained from biomass such as corn and sugar cane. ASTM D5501 provides a test method for determination of the concentrations of ethanol and methanol in fuels for concentrations of ethanol from 20 to 100 wt% and concentrations of methanol from 0.01 to 0.6 wt%.

In this Application News article, measurements of the purity of ethanol containing gasoline as a denaturant as specified in ASTM D5501 were carried out with a Brevis GC-2050 gas chromatograph, using helium and hydrogen as the carrier gases.

■ System Configuration and Analysis Conditions

Table 1 shows the system configuration and analysis conditions. Because rapid heating at 30 °C/min in the column oven is necessary, a 200 V power source was used. Although more than 100 peaks are generally eluted in analyses of gasoline, use of a 150 m column makes it possible to separate components with retention times near those of ethanol and methanol without using a CRG unit (column oven low temperature control device). In addition, the compact Brevis GC-2050, with a width of approximately 35 cm, demonstrates high analytical performance while also saving space in the laboratory.

■ Sample Preparation

The following three types of samples (1) to (3) were prepared.

(1) Sample for confirmation of splitter linearity (linearity mixture)
Ten types of paraffins, including *n*-paraffins with carbon numbers from 5 to 11: C5 to C11, 2,4-dimethylpentane, 2,4-dimethylhexane, and isooctane (2,2,4-trimethylpentane), were mixed.

(2) Standard solutions for calibration (calibration mixtures)
Methanol, ethanol, heptane (C7), and isooctane were mixed so as to obtain the concentrations in Table 2.

(3) Samples for purity test
A simulated denatured fuel ethanol was prepared by mixing methanol, ethanol, and commercially-available gasoline at a ratio of approximately 0.1 : 95 : 4.9 wt%, respectively.

■ Splitter Linearity Test

Splitter linearity tests were conducted as provided in ASTM D5501 using helium and hydrogen as the carrier gases. Fig. 1 shows the chromatograms, and Table 3 shows the test results. The test confirmed that the relative differences of the paraffins were ≤3 % in all cases.

■ Calculation of Relative Mass Response Factor (RMRF)

The relative mass response factor (RMRF) relative to heptane (C7) was calculated at each concentration of methanol and ethanol. Table 4 shows the results. The average value of RMRF at each concentration was used in determination of ethanol and methanol in the purity test.

Table 1 System Configuration and Analysis Conditions

Model	: Brevis GC-2050 (200 V)/AOC-30i
<AOC-30i>	
Injection Volume	: 0.2 µL
Syringe	: Xtra Life Microsyringe (P/N: 227-35400-01)
<Brevis GC-2050 >	
Injection Port	: SPL
Injection Temp.	: 300 °C
Injection Mode	: Split
Split Ratio	: 200
Carrier Gas	: He or H_2
Purge Flow	: 3 mL/min
Carrier Gas Control	: Constant linear velocity mode (24 cm/s)
Column	: SH-1 PONA (P/N: 227-36361-01) (150 m × 0.25 mm I.D. × 1.00 µm)
Column Oven Temp.	: 60 °C (15 min) → 30 °C/min → 250 °C (23 min)
Detector	: FID
Detector Temp.	: 300 °C
Makeup Gas	: N_2 30 mL/min
Detector Gas	: H_2 30 mL/min, Air 300 mL/min
Filter Time Constant	: 100 ms

Table 2 Mixing Ratios of Standard Solutions for Calibration

(wt%)

	Mix1	Mix2	Mix3	Mix4	Mix5
Methanol	0.6	0.5	0.3	0.2	0.1
Ethanol	20.0	50.0	75.0	90.0	99.4
C7	10.0	10.0	10.0	4.0	0.5
Isooctane	69.4	39.5	14.7	5.8	0.0

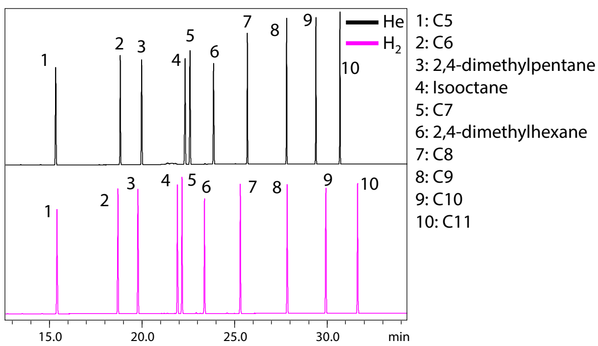

Fig. 1 Chromatograms of Samples for Splitter Linearity Test

Table 3 Results of Splitter Linearity Test

	Compound	Known wt%	He Calc wt%	He Relative difference*(%)	H_2 Calc wt%	H_2 Relative difference*(%)
1	C5	9.40	9.14	-2.8	9.16	-2.6
2	C6	9.34	9.27	-0.7	9.28	-0.6
3	2,4-dimethyl Pentane	9.90	9.81	-0.9	9.82	-0.8
4	Isooctane	10.55	10.80	2.3	10.72	1.5
5	C7	10.45	10.53	0.7	10.43	-0.2
6	2,4-dimethyl hexane	9.38	9.36	-0.1	9.27	-1.1
7	C8	9.78	9.94	1.6	9.84	0.6
8	C9	10.38	10.47	0.8	10.47	0.9
9	C10	10.01	10.01	0.0	10.11	1.0
10	C11	10.81	10.68	-1.2	10.90	0.9

* ASTM D5501 criterion: Within ±3 % relative

■ Ethanol Purity Test

The above-mentioned purity test samples were measured. Gasoline components other than methanol and ethanol were calculated assuming RMRF = 1. Fig. 2 shows the chromatograms when using helium and hydrogen as the carrier gas, and Table 5 shows the results and repeatability for the analysis of methanol and ethanol. It was found that the results satisfied the repeatability limit specified in ASTM D5501 in 16 successive tests regardless of whether helium or hydrogen was used as the carrier gas.

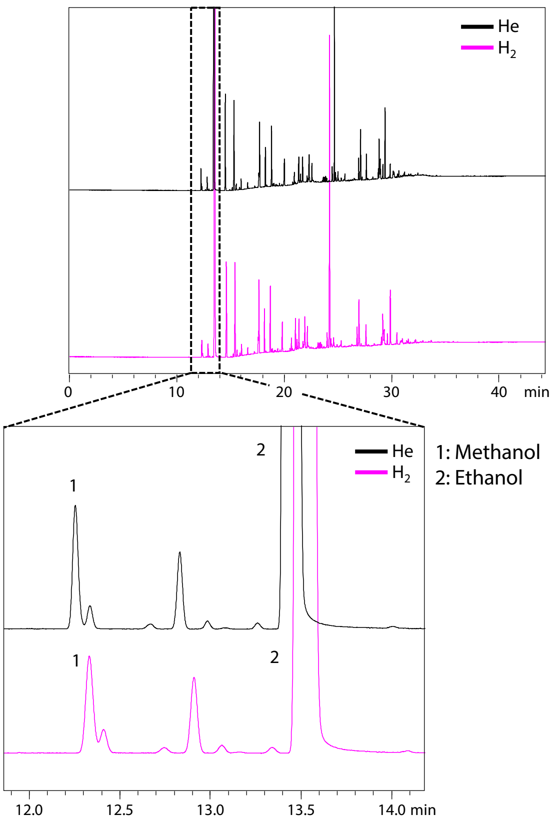

Fig. 2 Chromatograms of Purity Test Samples
(Top: Total Chromatogram, Bottom: Enlargement)

Table 4 Calculation of Relative Mass Response Factor (RMRF)

	Methanol Concentration (wt%)	Methanol RMRF He	Methanol RMRF H_2	Ethanol Concentration (wt%)	Ethanol RMRF He	Ethanol RMRF H_2
Mix1	0.6	3.10	3.18	20.0	2.09	2.08
Mix2	0.5	2.99	3.05	50.0	2.05	2.04
Mix3	0.3	2.98	2.98	75.0	2.04	2.01
Mix4	0.2	2.92	2.92	90.0	1.97	1.93
Mix5	0.1	2.70	2.70	99.4	1.84	1.82
	Ave. RMRF	2.94	2.96	Ave. RMRF	2.00	1.98

Table 5 Quantitative Analysis of Methanol and Ethanol (wt%)

Run	He Methanol Measured value	He Methanol Difference*	He Ethanol Measured value	He Ethanol Difference*	H_2 Methanol Measured value	H_2 Methanol Difference*	H_2 Ethanol Measured value	H_2 Ethanol Difference*
1	0.178	0.000	95.624	0.024	0.172	-0.001	95.589	0.030
2	0.180	0.001	95.604	0.004	0.174	0.001	95.597	0.038
3	0.179	0.000	95.612	0.012	0.172	-0.001	95.591	0.032
4	0.179	0.000	95.578	-0.022	0.173	-0.001	95.555	-0.004
5	0.179	0.000	95.614	0.014	0.173	-0.001	95.572	0.013
6	0.178	0.000	95.610	0.010	0.172	-0.002	95.583	0.024
7	0.179	0.000	95.575	-0.025	0.173	0.000	95.517	-0.042
8	0.178	0.000	95.547	-0.053	0.174	0.000	95.528	-0.032
9	0.179	0.000	95.567	-0.033	0.175	0.001	95.527	-0.032
10	0.178	0.000	95.585	-0.015	0.174	0.001	95.553	-0.006
11	0.179	0.000	95.548	-0.052	0.173	0.000	95.550	-0.009
12	0.178	0.000	95.559	-0.041	0.174	0.000	95.544	-0.015
13	0.178	0.000	95.658	0.058	0.174	0.001	95.552	-0.007
14	0.178	-0.001	95.675	0.075	0.174	0.000	95.570	0.011
15	0.179	0.000	95.630	0.030	0.173	0.000	95.574	0.015
16	0.180	0.001	95.614	0.014	0.174	0.001	95.543	-0.016
Average value	0.179		95.600		0.173		95.559	
Repeat-ability limit		0.008		0.142		0.007		0.142

* (Measured value) – (Average value)

■ Conclusion

Ethanol purity tests were carried out as provided in ASTM D5501 using a Brevis GC-2050 gas chromatograph. The splitter linearity test showed no inlet discrimination so that accurate qualitative analysis could be made for denatured fuel ethanol with the wide boiling range components regardless of whether helium or hydrogen was used as the carrier gas.

<References>

1) ASTM D5501-20 : Standard Test Method for Determination of Ethanol and Methanol Content in Fuels Containing Greater than 20 % Ethanol by Gas Chromatography (2020)

SHIMADZU
Shimadzu Corporation
www.shimadzu.com/an/

01-00706-EN First Edition: Jul. 2024

> Please fill out the survey

Related Products Some products may be updated to newer models.

> Brevis™ GC-2050

Gas Chromatograph

Related Solutions

- Clean Energy
- Biomass-SCJ
- Hydrocarbon Processing Industry (Petrochemical, Ch
- Chemicals

- Price Inquiry
- Product Inquiry
- Technical Service / Support Inquiry
- Other Inquiry