

Determination of Organic Impurities in Bioethanol Using JIS K2190

Kei Usui, Toyohito Wada, Emiko Shimbo

User Benefits

- ◆ Determination of methanol and organic impurities in bioethanol can be conducted in accordance with JIS K2190.
- ◆ Using GC with inlet splitting allows simultaneous analysis on two different columns.
- ◆ GC/MS analysis enables separation of coeluting compounds by their mass spectra, providing high-confidence identification.

Introduction

To achieve carbon neutrality, practical use of bioethanol fuel produced from feedstocks such as sugarcane and corn is undergoing. To avoid competition with food resources, worldwide efforts are accelerating toward next-generation bioethanol fuel derived from non-food sources. In Japan, seven leading companies involved in automotive and fuel production formed the raBit (Research Association of Biomass Innovation for Next Generation Automobile Fuels) to advance technology research for next-generation bioethanol fuel. raBit conducts research aimed at efficiently producing automotive bioethanol fuel to realize a carbon-neutral society. Shimadzu participates as a supporting member and contributes analytical-technology cooperation to promote R&D.

Impurities occurring during bioethanol fuel production¹⁾ and the purity of product ethanol²⁾ affect bioethanol fuel quality and therefore require careful control. ASTM D4806 specifies denatured ethanol used as automotive fuel. In Japan, JIS K2190 specifies requirements for ethanol used as automotive fuel or as feedstock for ETBE (ethyl tert-butyl ether), a gasoline additive.

In this application news, analysis of organic impurities in bioethanol in accordance with JIS K2190 using the Brevis GC-2050 was conducted. The standard requires the use of two columns with different stationary phases, which normally requires two separate analyses per sample. By using an inlet split, analyses on two columns can be obtained in a single run, enabling more efficient quality control of bioethanol. We also present results from a simple GC/MS single-column configuration.

System Configuration and Analysis Conditions

Fig. 1 and Table 1 show the system configuration and analysis conditions. To split the inlet, an INJ2-way branch unit (P/N: 221-75231-41) was used. For details on inlet splitting, see [Application News No. 01-00661-EN](#). Brevis GC-2050 is compact (350 mm width) yet accommodates two standard-size columns, making it effective for reducing GC footprint and improving productivity.

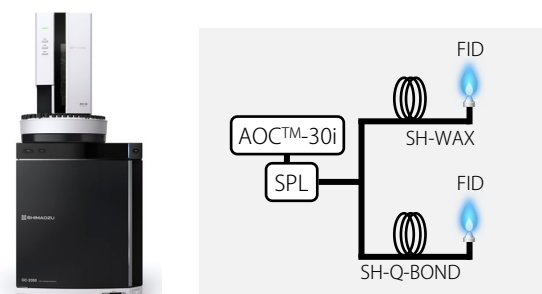


Fig. 1 Brevis™ GC-2050 and system configuration

Table 1 System configuration and analysis conditions of GC

GC Model	: Brevis GC-2050 / AOC-30 ^{†1}
Injection Volume	: 1 µL
Injection Port	: SPL
Injection Temp.	: 200°C
Flow Control Mode	: Constant linear velocity mode (Column1, 40 cm/s) (Hz)
Purge Flow	: 3 mL/min
Split ratio	: 15
Column Oven Temp. Program	: 50°C (2 min) → 10°C/min → 200°C (10 min)
Column1	: SH-Q-BOND (30 m × 0.32 mm I.D. × 10 µm) (P/N: 221-75764-30)
Column2	: SH-WAX (30 m × 0.32 mm I.D. × 0.50 µm) (P/N: 221-75896-30)
Detector1,2	: FID
Detector Temp.	: 200°C
Makeup Gas	: N ₂ 24 L/min
Detector Gas	: H ₂ 32 L/min, Air 200 L/min

^{†1} Requires an INJ2-way branch unit (PN: 221-75231-41).
The unit consists of a two-way branched adapter (a multi-column hanger and two INJ nuts).

Measurement of Standard Samples

Standard samples were measured to create calibration curves. Four standard mixtures (Standard1–4) were prepared as shown in Table 2. Standard1–3 contain compounds listed in JIS K2190. Standard4 contains compounds not listed in JIS K2190 but anticipated as possible impurities; these were also measured. Each standard mixture was prepared at three concentrations: 0.010 g/L, 0.10 g/L, and 1.0 g/L.

Table 2 Preparation of standard samples

		SH-Q-BOND	SH-WAX
Standard1	Methanol	✓	
	2-Propanol	✓	
	Cyclohexane		
Standard2	n-Pentane		✓
	Cyclohexane		✓
	1-Propanol		✓
	1-Butanol		✓
	2-Butanol		✓
	2-Methylpropan-1-ol		✓
	2-Methylbutan-1-ol		✓
	Acetone		✓
Standard3	Acetaldehyde	✓	
Standard4	1-Pentanol		✓
	3-Methylbutan-1-ol		✓
	Furfural	✓	
	Ethyl acetate	✓	

* Compounds marked with "✓" were used for quantitation on the indicated column.

Fig. 2 shows chromatograms of the standard mixtures. On the SH-Q-BOND column, peaks for an alcohol and cyclohexane in Standard2 overlapped; therefore, cyclohexane quantitation was performed on SH-WAX. Table 3 shows correlation coefficients for each compound's calibration curve; all compounds exhibited good linearity with correlation coefficients ≥ 0.999 .

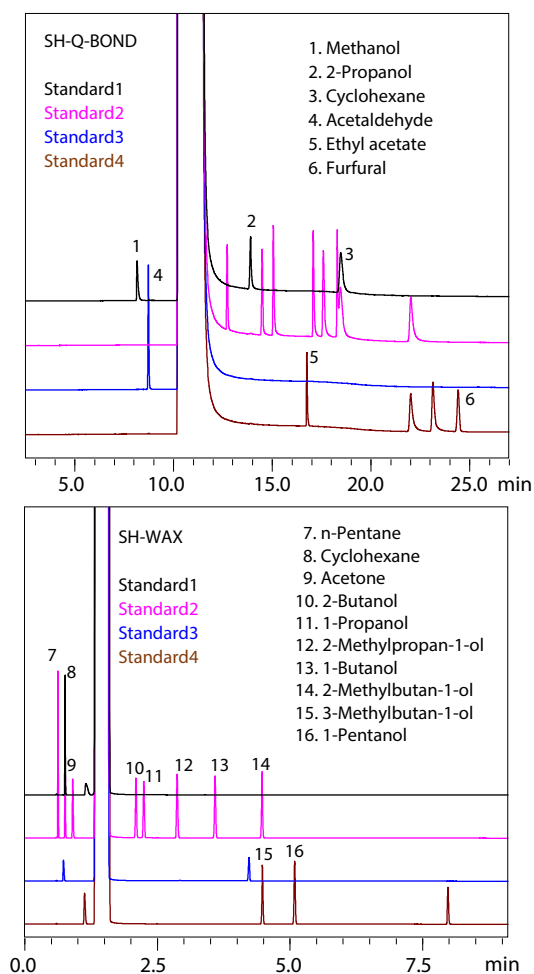


Fig. 2 Chromatograms of standards (0.10 g/L)

Table 3 Correlation coefficients of calibration curves

Methanol	0.99994	2-Methylbutan-1-ol	0.99993
2-Propanol	0.99990	Acetone	0.99998
n-Pentane	0.99992	Acetaldehyde	0.99982
Cyclohexane	>0.99999	1-Pentanol	0.99993
1-Propanol	0.99994	3-Methylbutan-1-ol	0.99993
1-Butanol	0.99993	Furfural	0.99997
2-Butanol	0.99994	Ethyl acetate	0.99998
2-Methylpropan-1-ol	0.99994		

■ Measurement of Bioethanol Samples

Organic impurities in bioethanol produced using genetically engineered yeast supplied by raBit were analyzed. Three samples were taken from the plant tank: the first draw (bottom), middle draw, and final draw. Because the tank is drawn from the lower portion, specific gravity and impurity content were expected to vary with draw timing. Water content measurements confirmed differences: first, middle, and last draws had 0.299%, 0.221%, and 0.232% water, respectively, with the first draw (from the lower part) showing the highest water content.

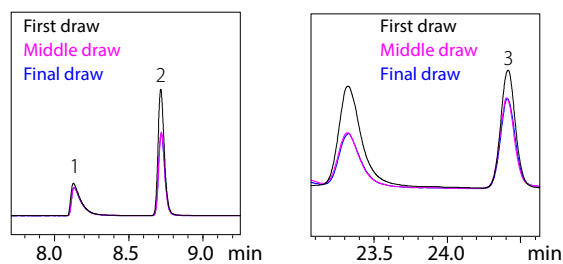


Fig. 3 Chromatograms of bioethanol
(1: Methanol, 2: Acetaldehyde, 3: Furfural)

Table 4 Concentration of impurities in bioethanol

Compound	Conc. of impurities (g/L)		
	First draw	Middle draw	Final draw
Methanol	0.137	0.118	0.117
2-Propanol	0.020	0.019	0.019
n-Pentane	-	-	-
Cyclohexane	0.039	0.023	0.022
1-Propanol	0.630	0.606	0.607
1-Butanol	0.017	0.014	0.014
2-Butanol	-	-	-
2-Methylpropan-1-ol	0.121	0.114	0.114
Acetone	-	-	-
Acetaldehyde	0.202	0.128	0.128
1-Pentanol	-	-	-
3-Methylbutan-1-ol ^{*1}	0.257	0.251	0.252
Furfural	0.092	0.071	0.072
Ethyl acetate	0.127	0.118	0.116

^{*1} 2-methyl-1-butanol and 3-methyl-1-butanol were coeluted in GC and thus quantified together as 3-methyl-1-butanol

■ Measurement of Bioethanol Samples Using GC/MS

Although GC/MS measurements are not specified in JIS, identification from mass spectra reduces misidentification. Table 5 shows an example of analysis conditions using an SH-624 column. 2-methyl-1-butanol and 3-methyl-1-butanol were coeluted on GC analysis; however, GC/MS could separate by mass spectra and allows quantitation of 2-methyl-1-butanol and 3-methyl-1-butanol (Figure 4).

Table 5 System configuration and analysis conditions of GC/MS

GC-MS Model	: GCMS-QP2020 NX / AOC-30i
Injection Volume	: 0.5 μ L
Injection Port	: SPL
Injection Temp.	: 240 $^{\circ}$ C
Flow Control Mode	: Constant linear velocity mode (45 cm/s) (He)
Purge Flow	: 3 mL/min
Split ratio	: 30
Column Oven Temp. Program	: 40 $^{\circ}$ C (5 min) \rightarrow 10 $^{\circ}$ C/min \rightarrow 220 $^{\circ}$ C (5 min)
Column	: SH-624 (30 m \times 0.25 mm I.D. \times 1.4 μ m) (P/N: 221-75863-30)
Ion Source Temp.	: 200 $^{\circ}$ C
Interface Temp.	: 220 $^{\circ}$ C
Measurement Mode	: Scan/SIM
Scan Range (m/z)	: 29-300

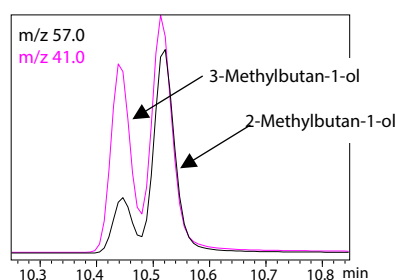


Fig. 4 MS chromatograms of 3-Methylbutan-1-ol and 2-Methylbutan-1-ol (each Compound: 0.05 g/L)

Calibration curves over 0.01–1.0 g/L were prepared similarly to the GC method. Fig. 5 shows GC/MS chromatograms of 0.01 g/L standards. Table 6 summarizes the quantitation ions, S/N at 0.01 g/L, and calibration correlation coefficients. S/N values were ≥ 10 for all compounds, indicating sufficient sensitivity. Except for the highly volatile acetaldehyde, all compounds showed correlation coefficients ≥ 0.999 .

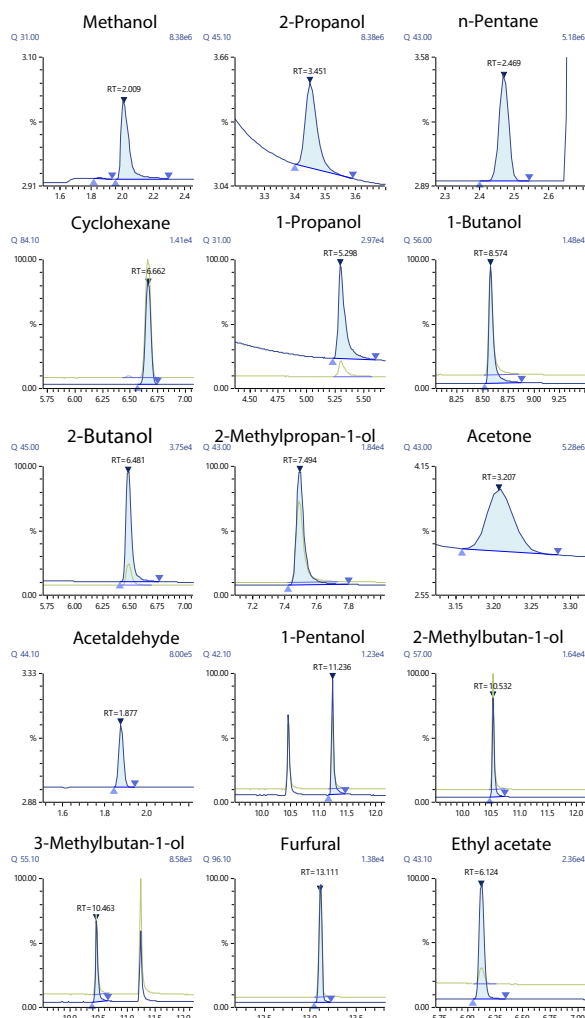


Fig. 5 GC/MS chromatograms of standards (0.01 g/L)

Table 6 GC/MS analysis of standard compounds

Compound	Quantitation ion	S/N (0.01 g/L)	Correlation coefficient
Methanol	31.0	567	0.99993
2-Propanol	45.1	59	0.99991
n-Pentane	43.0	1274	0.99991
Cyclohexane	84.1	725	0.99986
1-Propanol	31.0	101	0.99991
1-Butanol	56.0	1814	0.99992
2-Butanol	45.0	663	0.99990
2-Methylpropan-1-ol	43.0	1506	0.99992
Acetone	43.0	256	0.99985
Acetaldehyde	44.1	475	0.99817
1-Pentanol	42.1	582	0.99996
2-Methylbutan-1-ol	57.0	1084	0.99989
3-Methylbutan-1-ol	55.1	645	0.99998
Furfural	96.1	1217	0.99999
Ethyl acetate	43.1	797	>0.99999

Brevis and AOC are trademarks of Shimadzu Corporation or its affiliated companies in Japan and/or other countries.

■ Comparison of GC and GC/MS Results

Concentration of impurities in bioethanol using GC (two-column split-inlet method) and GC/MS (single-column) are compared. Results are shown in Table 7. For most compounds, GC and GC/MS yielded similar values.

Table 7 Concentration of impurities in bioethanol

Compound	Concentration (g/L)	
	GC	GC/MS
Methanol	0.028	0.025
2-Propanol	-	<0.010
n-Pentane	-	-
Cyclohexane	-	-
1-Propanol	0.013	<0.010
1-Butanol	-	<0.010
2-Butanol	-	-
2-Methylpropan-1-ol	0.010	<0.010
Acetone	-	-
Acetaldehyde	0.015	<0.010
1-Pentanol	-	-
2-Methylbutan-1-ol ^{*1}	-	-
3-Methylbutan-1-ol ^{*1}	0.018	0.015
Furfural	0.017	0.014
Ethyl acetate	0.020	0.017

*1 2-methyl-1-butanol and 3-methyl-1-butanol were coeluted in GC and thus quantified together as 3-methyl-1-butanol

■ Conclusion

GC analysis of organic impurities in bioethanol in accordance with JIS K2190 was performed. By splitting the inlet, results from two columns were obtained in a single analysis. For bioethanol samples drawn at different times from the tank, statistically meaningful differences were found in impurity concentrations, demonstrating that GC is suitable for quality control of bioethanol. Using GC/MS, all target compounds can be analyzed on a single column. Notably, GC/MS enabled separation and quantitation of 2-methyl-1-butanol and 3-methyl-1-butanol, which were difficult to separate by GC alone.

<Acknowledgements>

We are sincerely grateful to raBit (Research Association of Biomass Innovation for Next Generation Automobile Fuels) for providing samples and considering the analytical results.

<Related Applications>

1. Monitoring of Organic Acids in Biomass Fermentation Process and Yeast Cultivation Process, [Application News No. L588](#)
2. Analysis of Denatured Fuel Ethanol with Brevis GC-2050 Using ASTM D5501, [Application News No. 01-00706-EN](#)
3. Simultaneous Analysis of Greenhouse Gases Using Nitrogen Carrier Gas, [Application News No. 01-00661-EN](#)
4. Determination of Elemental Impurities in Bioethanol Using ICP-MS, [Application News No. 01-01021-EN](#)

➤ Please fill out the survey

Related Products

Some products may be updated to newer models.



➤ **Brevis GC-2050**
Gas Chromatograph



➤ **GCMS-QP2020 NX**
Gas Chromatograph Mass Spectrometer



➤ **AOC-30 Series**
Autoinjector / Autosampler

Related Solutions



➤ **Biomass Fuels**



➤ **Quality Control
(Biomass Fuels)**

➤ **Clean Energy**

➤ **Chemicals**

**Hydrocarbon
➤ Processing Industry
(Petrochemical, Ch**

➤ **Price Inquiry**

➤ **Product Inquiry**

➤ **Technical Service /
Support Inquiry**

➤ **Other Inquiry**