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Application News

Brevis™ GC-2050 Gas Chromatograph

Analysis of Benzene and Toluene by Brevis GC-2050 Using ASTM D3606

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User Benefits

- Quantitation of benzene and toluene in fuels based on ASTM D3606 is possible.
- Highly accurate backflush analysis is possible by using the SMI flow device.
- The compact design of the Brevis GC-2050 enables space-saving in the laboratory.

■ Introduction

Benzene and toluene are widely used as feedstocks for chemical products, but due to concerns about their effects on human health, the permissible concentrations of these two compounds are specified in various regulations. ASTM D3606 [1] provides two quantification methods (Procedures A and B) for benzene and toluene in automotive fuels. The corresponding concentrations of benzene and toluene are 0.12-5.2 Vol% and 0.4-19.7 Vol% when using Procedure A and 0.10-5.0 Vol% and 2.0-20.0 Vol% when using Procedure B.

In this Application News article, benzene and toluene were quantified by Procedure A in ASTM D3606. Satisfactory linearity of the calibration curves and reproducibility of the quantitation values could be obtained for both compounds.

■ System Configuration and Analysis Conditions

Table 1 shows the system configuration and analysis conditions. The compact Brevis GC-2050, with a width of about 35 cm, can contribute to space-saving in the laboratory while also demonstrating high analytical performance. In procedure A, benzene and toluene are measured with a backflush system using a capillary column. Backflush has the advantage of shortening the analysis time. Fig. 1 shows a schematic diagram of the backflush system. In addition to the FID detector (FID1) connected to the Wax analytical column, a second FID detector (FID2) which is connected to the restrictor tube, is used for monitoring to determine the timing of backflushing. The gas that flows through the columns is supplied from the injection port (SPL) and digital flow controller (AUX-APC). This is connected to discs called an SMI Flow Disc and 2-DET Splitter, which are used to split the flow to the two detectors. The SMI Flow Disc is a flow device for capillary analysis, and has the features of minimal leakage, a low dead volume, a low heat capacity, and inertness. For this reason, the device has the advantages that the temperature inside the device easily follows the temperature of the column oven, and it is also possible to analyze components with high adsorptivity. Before backflushing, the SPL pressure is set high, and during the backflush operation, the gas in the pre-column is made to flow in the reverse direction (backflushed) by changing the pressures of the SPL and AUX-APC. In this experiment, the initial backflush time was set to 3.1 min to match the elution time of toluene (Fig. 2).

Table 1 System Configuration and Analysis Conditions

Model	: Brevis GC-2050/AOC-30i
<AOC-20i>	
Injection Volume	: 0.5 µL
<Brevis GC-2050 >	
Injection Port	: SPL
Injection Temp.	: 200 ˚C
Inlet Pressure	: 297.1 kPa (Initial), 20 kPa (Backflush)
Injection Mode	: Split
Split Ratio	: 100
Carrier Gas	: He
Column Flow Rate	
(Pre-Column)	: 3.5 mL/min (Before Backflush), -1.77 mL/min (Backflush)
(Analytical Column)	: 2.58 mL/min
Purge Flow	: 3 mL/min
Carrier Gas Control	: Pressure mode
Backflush Device	: SMI Flow Disc, 2-DET Splitter*1
AUX-APC	: He 150 kPa (Before Backflush, Backflush)
Initial Backflush Time	: 3.1 min
Pre-Column	: SH-1 (P/N: 221-75725-30) (30 m × 0.25 mm I.D. × 0.5 µm)
Analytical Column	: SH-Wax (P/N: 221-75897-60) (60 m × 0.32 mm I.D. × 1 µm)
Restrictor Tube	: 42.5 cm × 0.10 mm I.D. (P/N: 227-35023-04)
Column Oven Temp.	: 75 ˚C (8 min) → 5 ˚C/min → 85 ˚C (3 min) → 40 ˚C/min → 140 ˚C (0.4 min) (Total: 14.78 min)
Detector	: FID × 2 (FID1, FID2)
Detector Temp.	: 200 ˚C
Makeup Gas	: N_2 24 mL/min
Detector Gas	: H_2 32 mL/min, Air 200 mL/min

*1 P/N of device: 222-31009 / P/N of total detector splitting system including necessary components: 222-31001-43.

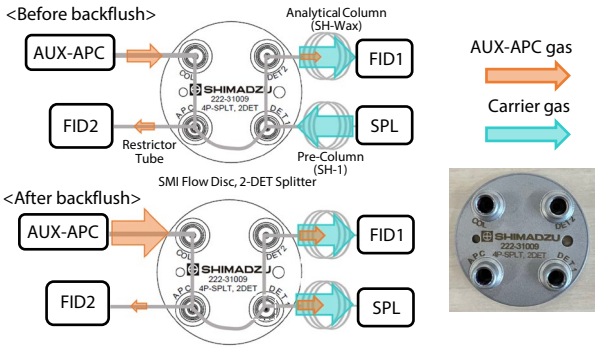


Fig. 1 Schematic Diagram of Backflush System

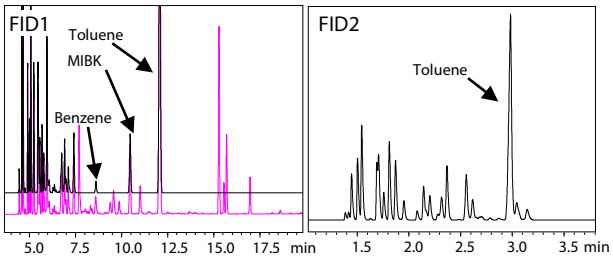
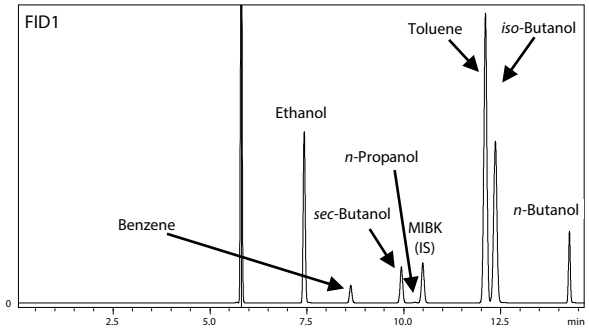


Fig. 2 Chromatograms of Gasoline with Backflush (Black) and without Backflush (Pink)

■ Confirmation of Separation

Using 2,2,4-trimethylpentane (isooctane) as a dilution solvent and 4 Vol% methyl isobutyl ketone (MIBK) as an internal standard substance, a solution for confirmation of separation was prepared by mixing the compounds at the following concentrations (Vol%). Ethanol: 20 %, benzene: 1 %, *sec*-butanol: 4 %, *n*-propanol: 0.1 %, toluene: 20 %, *iso*-butanol: 20 %, *n*-butanol: 5 %. Fig. 3 shows the chromatogram and the calculated degrees of separation (resolution). The compounds benzene, MIBK, and toluene all satisfied the standard resolution, and the separation of the other compounds was also satisfactory. When using butanol-blended gasoline, a sufficient analysis time and temperature for elution of the isomer *n*-butanol is required.



Degree of separation (resolution)	Measured value	Reference value
Ethanol/benzene	11.5	2
Benzene/*sec*-Butanol	11.1	2
n-Propanol/MIBK	1.68	1.5
Toluene/*iso*-Butanol	1.68	0.6

Fig. 3 Chromatogram of Solution for Confirmation of Separation and Degrees of Separation

■ Preparation of Calibration Curves

Seven types of standard solutions for use in calibration (Mix 1 to Mix 7) were prepared by mixing benzene and toluene to obtain the concentrations in Table 2, using isooctane as the dilution solvent and 1 Vol% MIBK as the internal standard substance. Fig. 4 shows the chromatograms and the prepared calibration curves. Coefficients of correlation R^2 = 0.999 or higher were obtained for both benzene and toluene, confirming that the calibration curves for these compounds satisfied the standard.

Table 2 Concentration of Standard Solutions for Calibration (Unit: Vol%)

	Mix1	Mix2	Mix3	Mix4	Mix5	Mix6	Mix7
Benzene	5	2.5	1.25	0.67	0.33	0.12	0.06
Toluene	20	15	10	5	2.5	1	0.5

■ Confirmation of S/N Ratio

The S/N ratio of benzene was confirmed using the standard solution for calibration Mix 7. As a result, S/N = 437.14 was obtained, satisfying the reference value of S/N = 50.

■ Confirmation of Repeatability and Reproducibility

ASTM D3606 specifies the permissible differences for repeatability and reproducibility. First, in order to confirm repeatability, 6 repeated measurements were carried out using the standard solution for calibration Mix 4 (Table 3). The permissible difference obtained from the averaged quantitation values of benzene and toluene in these repeated measurements satisfied the 95 % confidence interval (reference values: benzene → 0.003, toluene → 0.009).

To investigate reproducibility, a standard substance for the Japan Petroleum Institute (JPI) component test (Tokyo Chemical Industry Co., Ltd.: S0429) was measured. Table 4 shows the differences between the quantitation values and the certified values. It was found that both repeatability and reproducibility satisfy the standards.

Table 3 Repeatability (Unit: Vol%)

	Benzene	Toluene
Run	Measured value	Measured value
1	0.65	4.97
2	0.65	4.97
3	0.65	4.96
4	0.65	4.96
5	0.65	4.96
6	0.65	4.96
Average value	0.65	4.96
Permissible difference	0.03	0.10
Standard deviation	0.001	0.003
Reference value (2.77 * Standard deviation)	0.003	0.009

Table 4 Reproducibility Using Standard Substance (Unit: Vol%)

Component	Certified value of component certified standard substance	Quantitation value	Difference with average value	Permissible difference of reproducibility
Benzene	0.5	0.55	0.025	0.11
Toluene	16.2	16.24	0.02	0.78

■ Conclusion

Using the Brevis GC-2050, an analysis of benzene and toluene as specified in ASTM D3606 was conducted. The analysis time could be shortened by using a backflush system. As the quantitation values of benzene and toluene were within the standard range for both reproducibility and repeatability, satisfactory results were obtained.

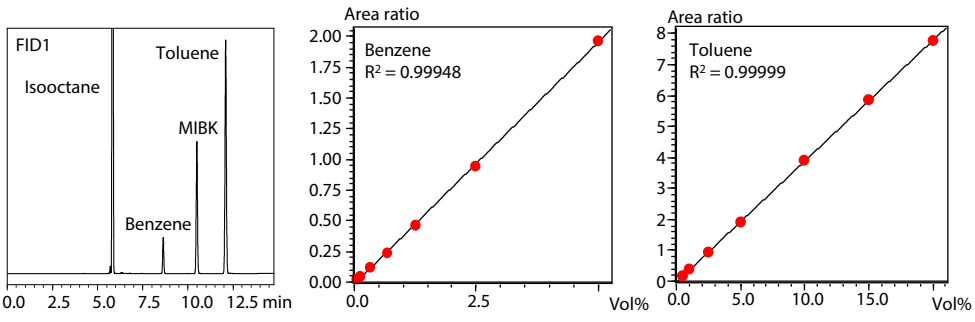


Fig. 4 Chromatograms and Calibration Curves of Standard Solution for Calibration (Mix 4)

<References>

1) ASTM D3606-22 : Standard Test Method for Determination of Benzene and Toluene in Spark Ignition Fuels by Gas Chromatography (2022)

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