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GC Brevis™ GC-2050

Application News

Quantification of H_2 and Hydrocarbons in CO_2 Using TCD-to-Jetanizer™-FID Series Connection

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User Benefits

- Gas analysis including hydrogen, carbon monoxide, hydrocarbons, methanol, and other species can be conducted.
- Nitrogen, an alternative carrier gas to helium, can be used as the carrier gas.
- The newly introduced GI-30 automatic gas injector enables automatic and reproducible analysis of gas samples.

■ Introduction

Carbon dioxide (CO_2), known as a greenhouse gas, is also an abundant carbon resource. Therefore, reactions that reduce CO_2 using, for example, water to convert it into useful compounds are attracting attention from the viewpoint of carbon neutrality. The products include hydrocarbons such as methane (CH_4), alcohols, and carbon monoxide (CO). Hydrogen (H_2) may also be produced as a by-product.

In this Application News, we used nitrogen as the carrier gas and connected a TCD and a Jetanizer-FID in series to simultaneously analyze H_2, CO, and light hydrocarbons. By using an inlet split, alcohols such as methanol (MeOH) could also be analyzed concurrently.

■ System Configuration

For target analytes consisting of H_2, CO, and hydrocarbons, possible detectors include a BID or a serially connected TCD and Jetanizer-FID. BID can detect all compounds except helium and neon but requires helium as the carrier gas. In contrast, TCD detects based on differences in thermal conductivity between analyte and carrier gas; using nitrogen as a carrier (which has low thermal conductivity) enables highly sensitive analysis of H_2, which has high thermal conductivity. The Jetanizer-FID, in which the nozzle of an FID is filled with a reduction catalyst, detects organic compounds and can also convert CO and CO_2 to CH_4 for detection.

If alcohols such as MeOH are included among the analytes, a column capable of separating inorganic gases (H_2, CO) and hydrocarbons must be used together with a column for separating alcohols. Conventionally, this requires multiple GCs or complex valve systems to change flow paths. However, by employing an inlet split, a single GC can measure both kinds of compounds without a valve system (see: Application News No.01-00964-EN).

Fig. 1 shows a schematic of the series connection of TCD and Jetanizer-FID. The analytical column is connected to the TCD, and from the TCD vent a restriction capillary and an inert metal column connect to the Jetanizer-FID. In this configuration some piping is unheated, which is advantageous for analysis of low-boiling compounds such as gases. Sample injection used the auto gas injector GI-30 and a sample vaporization chamber with low atmospheric leak (SPI). Fig. 2 shows a schematic of the analysis system when alcohols such as MeOH are included among the analytes. The SH-Q-BOND column separates hydrocarbons and alcohols, while the MICROPACKED-ST column separates H_2 and CO (patent pending).

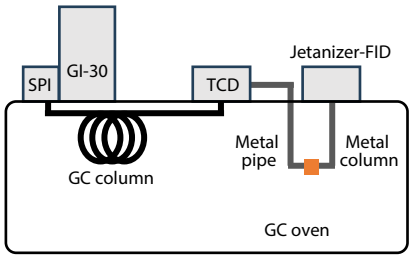

Fig. 1 System configuration of TCD-to-Jetanizer-FID Series Connection

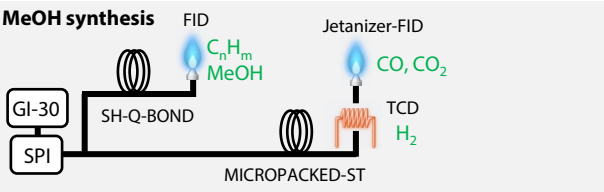

Fig. 2 System configuration for MeOH synthesis

■ Analysis of H_2, CO and Hydrocarbons

When the analytes are H_2, CO, and hydrocarbons up to C3, the MICROPACKED-ST column is suitable. In this work, gas produced from a CO_2-to-hydrocarbon conversion reaction using a copper catalyst — specifically CO, CH_4, C_2H_4, and H_2 — were measured using an analytical system in which TCD and Jetanizer-FID were connected in series. Analysis conditions are shown in Table 1.

Table 1 Analysis conditions of CO and hydrocarbons

GC Model	:	Brevis GC-2050 / GI-30*1
Loop Volume	:	1 mL
Injection Port	:	SPI
Injection Temp.	:	150 ℃
Flow Control Mode	:	Constant Inlet Pressure mode (220 kPa) (N_2)
Purge Flow	:	3 mL/min
Split ratio	:	4
Column Oven Temp. Program	:	35 ℃(2.5 min) → 20 ℃/min → 245 ℃
Column	:	MICROPACKED-ST (2 m × 1.0 mm I.D.) (P/N：M00-00002-659) (250 m×0.50mmI.D., df=15µm entered to calculate flowrate)
Detector1	:	TCD
Detector Temp.	:	260 ℃
Makeup Gas	:	2.0 L/min
Reference Gas	:	50 L/min
Detector2	:	Jetanizer-FID
Detector Temp.	:	400 ℃
Makeup Gas	:	N_2 24 L/min
Detector Gas	:	H_2 32 L/min、Air 250 L/min

*1 Requires a metal column (PN: 221-57812-07), a union (PN: 221-53393-01), a ferrule (PN: 221-53177-04), a metal column (PN: 221-35023-20).

Calibration curves were prepared by collecting gases into vacuum sampling bottle at the following concentrations. CO_2 was used as the balance gas.

- H_2: 100, 1,000, 10,000 ppm
- CO, CH_4, C_2H_4: 1, 10, 100, 1,000 ppm

Because nitrogen was used as the carrier gas, sensitivity of CO and hydrocarbons in the TCD is low; therefore, Jetanizer-FID was used for quantitation of CO, CH_4, and C_2H_4. The calibration curves (Fig. 3) exhibited excellent linearity ($R^2 \geq 0.999$ for all compounds). Table 2 lists the S/N at the lowest calibration concentration. H_2 showed sufficient sensitivity at 100 ppm, and the other compounds showed sufficient sensitivity at 1 ppm.

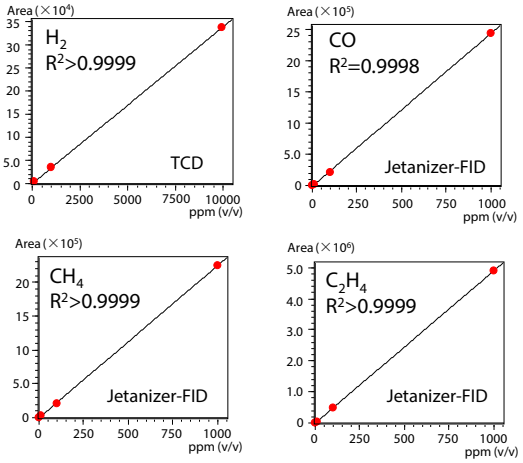

Fig. 3 Calibration curves of H_2, CO, CH_4, and C_2H_4

Table 2 S/N values for H_2, CO, CH_4, and C_2H_4

	Conc.(ppm)	S/N
H_2	100	97.2
CO	1	41.5
CH_4	1	55.3
C_2H_4	1	57.1

A chromatogram of a catalytic reaction sample is shown in Fig. 4. All compounds were well-separated. Table 3 summarizes the quantified values and area reproducibility (%RSD) for six consecutive measurements. Although the sample contained impurities such as water vapor, good area reproducibility was obtained for all compounds.

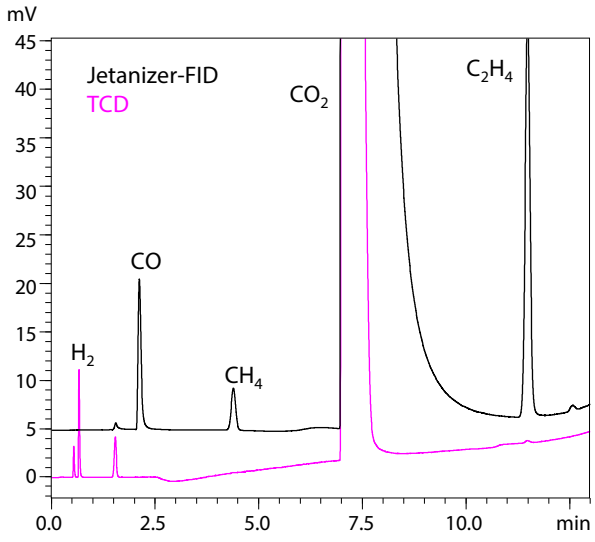

Fig. 4 Chromatograms of catalytic reaction sample
(black: Jetanizer-FID, pink: TCD)

Table 3 Conc. and area %RSD (n=6) of catalytic reaction sample*1

	Conc. (ppm)	Area %RSD
H_2	570.9	0.92
CO	36.8	0.64
CH_4	14.1	0.69
C_2H_4	71.1	0.60

*1 H_2: TCD, the other compounds: Jetanizer-FID

■ Measurement Using INJ2-way branch unit (MeOH synthesis)

To simulate MeOH synthesis, two gas samples with different concentrations (Sample I and II; Table 4) were prepared and analyzed. Analysis conditions are shown in Table 5. Because MeOH tends to be retained on the MICROPACKED-ST column, periodic column conditioning is required.

Table 4 Composition of Sample I and II

Sample I	Conc.(ppm)	Sample II	Conc.(ppm)
H_2	100,000	H_2	500
CO	100,000	CO	5
CH_4	100	CH_4	5
C_2H_2	100	C_2H_4	5
MeOH	100	C_2H_6	5
CO_2	Balance	C_3H_6	5
		C_3H_8	5
		MeOH	5
		CO_2	Balance

Table 5 Analysis conditions for MeOH synthesis

GC Model	:	Brevis GC-2050 / GI-30 *1
Loop Volume	:	1 mL
Injection Port	:	SPI
Injection Temp.	:	150℃
Flow Control Mode	:	Linear velocity mode (N_2) (Column1 : 50 cm/s (4.0 min) → 25 cm/s • min → 100℃(5.5 min)) *2
Purge Flow	:	3 mL/min
Split Ratio	:	15
Column Oven Temp. Program	:	60℃(1.5 min)→ 25℃/min → 250℃(2.1 min)*2
Column1	:	SH-Q-BOND (30 m × 0.32 mm I.D. × 10 µm) (P/N : 221-75764-30)
Detector1	:	FID
Detector Temp.	:	250℃
Makeup Gas	:	N_2 24 L/min
Detector Gas	:	H_2 32 L/min、Air 200 L/min
Column2	:	MICROPACKED-ST (1 m × 1.0 mm I.D.) (P/N : M00-00002-657)
Detector2	:	TCD
Detector Temp.	:	260℃
Makeup Gas	:	2.0 L/min
Reference Gas	:	50 L/min
Detector3	:	Jetanizer-FID
Detector Temp.	:	400℃
Makeup Gas	:	N_2 10 L/min
Detector Gas	:	H_2 32 L/min、Air 250 L/min

*1 Requires a metal column (PN: 221-57812-07), a union (PN: 221-53393-01), a ferrule (PN: 221-53177-04), a metal column (PN: 221-35023-20), an INJ2-way branch unit (P/N: 221-75231-41).
The unit consists of a two-way branched adapter (a multi-column hanger and two INJ nuts).
*2 Analysis time of sample I is 7 minutes.

Chromatograms of samples I and II are shown in Fig. 5. In both samples, the FID produced sharp peaks for hydrocarbons and MeOH. Hydrocarbon peaks were also detected by Jetanizer-FID. Table 6 lists the area reproducibility (%RSD) for six consecutive injections. Methanol, which has low vapor pressure, showed %RSD of 0.91 at 5 ppm but deteriorated to 5.73 at 100 ppm. Other compounds showed %RSD less than 1 regardless of concentration, indicating good reproducibility.

■ Conclusion

By using TCD-to-Jetanizer-FID series connection it was possible to analyze H_2, CO, and other compounds simultaneously. H_2, CO, and hydrocarbons exhibited good area reproducibility (%RSD) across a range of concentrations. Furthermore, by employing an inlet split, MeOH could be quantified concurrently.

<Acknowledgements>

We are sincerely grateful to Dr. Shoko Kume of Hiroshima University for providing the sample.

<Related Applications>

1. Gas Analysis for CO_2 Conversion Using a GI-30 Auto Gas Injector, Application News No. 01-00964-EN

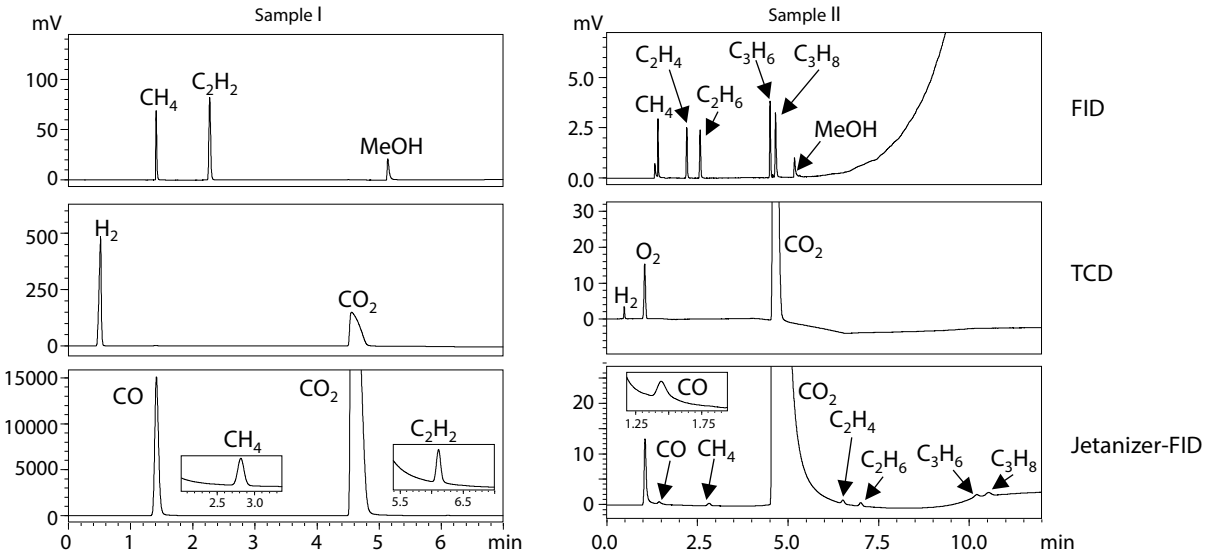

Fig. 5 Chromatograms of Samples I and II

Table 6 %RSD (n=6) of Samples I and II *1

Sample I		
	Conc.(ppm)	Area %RSD
H_2	100,000	0.11
CO	100,000	0.13
CH_4	100	0.10
C_2H_2	100	0.11
MeOH	100	5.73

Sample II		
	Conc.(ppm)	Area %RSD
H_2	500	0.40
CO	5	0.98
CH_4	5	0.34
C_2H_4	5	0.45
C_2H_6	5	0.64
C_3H_6	5	0.54
C_3H_8	5	0.62
MeOH	5	0.91

*1 H_2: TCD, CO: Jetanizer-FID, the other compounds: FID

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