

Application News

Assessment of Jetanizer™ and Quantitative Analysis of CO₂ and CH₄ in the Atmosphere

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User Benefits

- ◆ Simplification of the analytical system for CO and CO₂ utilizing the Jetanizer coupling with GC-FID.
- ◆ Low-cost system achieved with adding the Jetanizer to FID-2030 that is already working.
- ◆ N₂ as carrier gas available.

Introduction

More and more research and development projects are focusing on being "Carbon Neutral", which is the pursuit of zero Greenhouse gas production from human industrial activity. Greenhouse gas includes Carbon Dioxide (CO₂) and Methane (CH₄). In addition, high-purity hydrogen requires high-sensitive analytical system for the impurities such as CO, CO₂, and CH₄. Therefore, easy quantification methods for these gases are required in various fields for becoming "Carbon Neutral". While TCD and BID are excellent for the analysis of inorganic gases, they both have difficulties with these applications. Highly sensitive analysis is not possible in TCD, and carrier gas is limited to Helium in BID. A methanizer can be installed to utilize FID for CO and CO₂ analysis. A traditional methanizer uses a Nickel (Ni) catalyst in a hydrogen rich environment to reduce CO and CO₂ to CH₄ for analysis by FID. This setup requires an additional heater and gas line for installation. The Ni catalyst is also highly sensitive to oxidation by oxygen. The Jetanizer uses a novel, oxygen durable catalyst in the FID nozzle. The hydrogen for the FID flame provides the hydrogen rich environment for reduction and the FID heater is utilized for heating the catalyst. Thus, the whole system is durable for oxygen, simple to install, and can expand its usefulness to wider fields. This article introduces how the Jetanizer on the GC-2030 is useful for analysis of CO, CO₂ and CH₄.

Jetanizer

The Jetanizer is a compact Methanizer for FID developed from Activated Research Company. Highly efficient conversion of CO/CO₂ into CH₄ can be achieved with a catalyst inside FID nozzle. No extra line or heating device must be equipped. Exchanging FID nozzle is the only hardware change for the analysis. Fig. 1 shows an image of the Jetanizer. The insertion depth of the capillary column is shortened to 45 mm to avoid interfering with the catalyst inside the nozzle (usually the tip length is 72 mm).

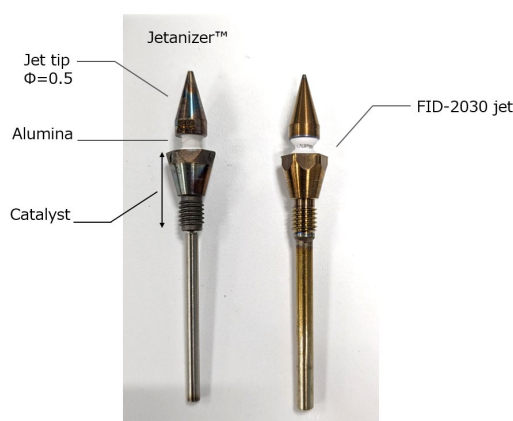


Fig. 1 Jetanizer™

Analytical Condition

Analytical evaluation was performed with our GC-2030(FID) that employs a gas sampling valve. The Jetanizer is installed in the same way as the FID-2030 nozzle. A metal guard column was connected to the end of the capillary column because the Jetanizer operating temperature is 400°C. Schematic illustration of the whole analytical system is shown in Fig. 2. A packed GC column was also evaluated for more loading capability. Table 1 shows the concentration of the standard gas samples (base gas was N₂). Table 2 shows the analytical condition

Table 1 Concentration of the standard gas samples

	1 (ppm)	25 (ppm)	100 (ppm)	0.1 (%)	1 (%)	25 (%)
CO	1.00	25.2	100	0.101	1.02	24.8
CO ₂	0.99	25.4	100	0.100	0.999	25.1
CH ₄	0.98	24.6	98.2	0.0996	0.994	25.1

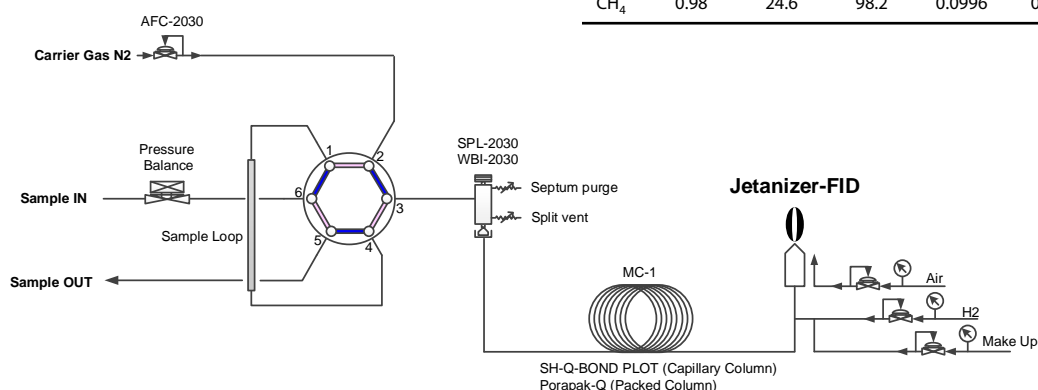


Fig. 2 Schematic illustration of the analytical system

Table 2 Analytical Condition

Model	: Nexis GC-2030
Gas Sampler	: MGS-2030 + 1 mL Loop
Inj. Temp.	: 250 °C
Inj. Mode	: ① Split 1:5 ② Direct
Carrier Gas	: N ₂
Column Flow	: ① 40 cm/sec ② 40 mL/min
Column	: ① SH-Q-BOND PLOT Column (30 m × 0.53 mm I.D., 20 μm) ② Porapak-Q 50/80 (2 m × 2 mm I.D.)
Column Temp.	: 40 °C
Detector	: FID + Jetanizer (column insertion depth : 45 mm)
FID Temp.	: 400 °C
Makeup Gas	: ① N ₂ , 24 mL/min ② N ₂ , 4 mL/min
H ₂ Flow	: 32 mL/min
Air Flow	: 250 mL/min

①:with capillary column ②:with packed column

■ Fundamental Performance of Jetanizer

Repeatability of the peak area, linearity of the calibration curve, and the converting efficiency (C.E.) into Methane were evaluated with the standard gas samples shown in Table 1. Fig. 3-1 shows a chromatogram of 0.1% standard gas sample with capillary column and Fig. 3-2 shows the one with packed column. Each Limit of Detection (LOD) value was calculated with S/N from 1 ppm standard gas sample. Table 3 shows the result.

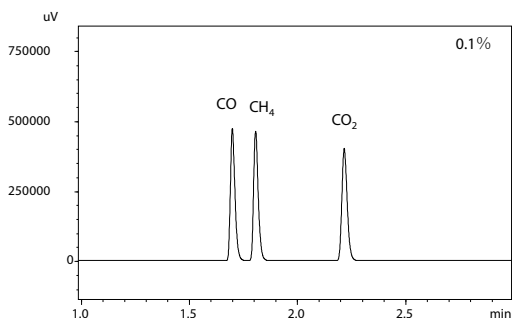


Fig. 3-1 chromatogram of 0.1% sample with capillary column

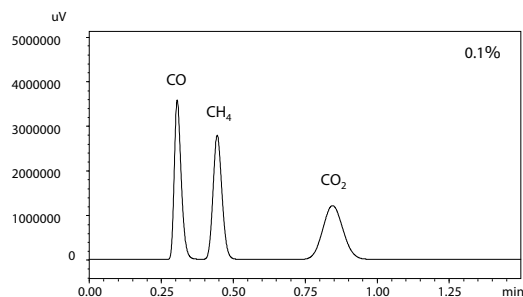


Fig. 3-2 chromatogram of 0.1% sample with packed column

Table 3 LOD of CO, CH₄, CO₂

	CO	CO ₂	CH ₄
Capillary column	0.34 ppm	0.37 ppm	0.27 ppm
Packed column	0.08 ppm	0.10 ppm	0.17 ppm

■ Repeatability of the Peak Area and Efficiency of Methane Conversion

CO and CO₂ cannot be directly detected with FID. Converting them into CH₄ with the Jetanizer is crucial for the analysis and its efficiency is highly influential to the analysis.

C.E. can be calculated with peak area (A) and concentration (C) of CO/ CO₂ and CH₄. The relation between them can be described as formula (1). The area repeatability %RSD and C.E. of each sample are shown in Table 4-1 and Table 4-2.

$$C.E. (\%) = \frac{A(\text{CO or CO}_2)}{A(\text{CH}_4)} * \frac{C(\text{CH}_4)}{C(\text{CO or CO}_2)} * 100 \quad (1)$$

Table 4-1 Repeatability of peak area (n=10) and the C.E. when using capillary column

	CO		CO ₂		CH ₄
	%RSD	C.E.	%RSD	C.E.	%RSD
1 ppm	2.11	97.6	2.23	100.3	2.48
25 ppm	0.39	98.4	1.03	97.8	0.74
100 ppm	0.29	100.2	0.35	100.2	0.28
0.1 %	0.08	99.0	0.09	99.2	0.09
1 %	0.17	99.8	0.21	100.2	0.16
25 %	0.33	100.9	0.41	100.0	0.33

Table 4-1 Repeatability of peak area (n=10) and the C.E. when using capillary column

	CO		CO ₂		CH ₄
	%RSD	C.E.	%RSD	C.E.	%RSD
1 ppm	1.18	104.9	1.58	124.5	0.93
25 ppm	0.27	98.2	0.31	95.5	0.28
100 ppm	0.05	99.3	0.09	97.6	0.05
0.1 %	0.05	98.5	0.05	98.4	0.05
1 %	0.15	98.7	0.16	101.0	0.16
25 %	0.13	68.7	0.12	94.6	0.11

Sufficient repeatability and C.E. were obtained when using capillary column for both CO and CO₂. In packed column analysis, the repeatability and C.E. was sufficient except for CO in 25% standard gas sample. Here, the C.E. limited to 68.7% which is likely due to overloading the catalyst. In such case, reducing the volume of the sample injection should be an effective and direct solution. Slowing down the flow rate could also solve the low C.E. because the sample volume touching the catalyst per a unit of time should be decreased.

■ Linearity of the Calibration Curve

Fig. 4-1, 4-2, and 4-3 shows the calibration curves for CO, CO₂ and CH₄, respectively. Calibration point of 25% standard gas sample was excluded in packed column. The coefficients of determination (R²) were more than 0.9999 for all CO, CO₂ and CH₄ when using capillary column. The R² for CO, CO₂ and CH₄ were 0.9988, 0.9994 and 0.9996, respectively. Fig. 5 shows relative response factors (RRFs) from 1ppm to 25% standard gas samples when using capillary column. Contamination from the air slightly influenced the RRFs when the sample was 1ppm. The RRFs for CO, CO₂ and CH₄ were consistent for all other standard concentrations.

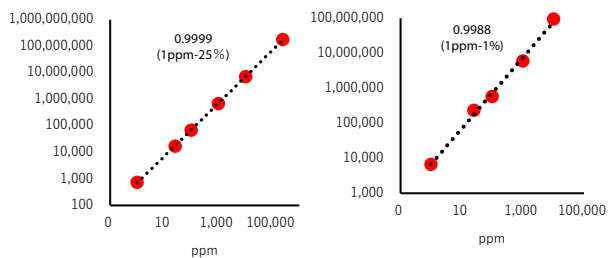


Fig. 4-1 Calibration curve of CO
(Left: capillary column Right: packed column)

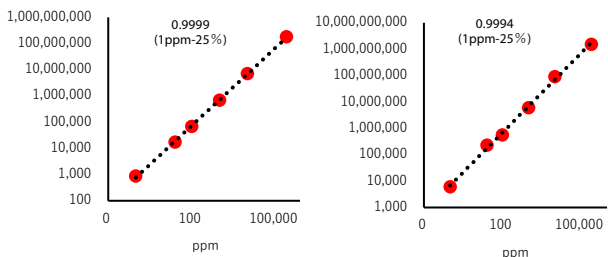


Fig. 4-2 Calibration curve of CO₂
(Left: capillary column Right: packed column)

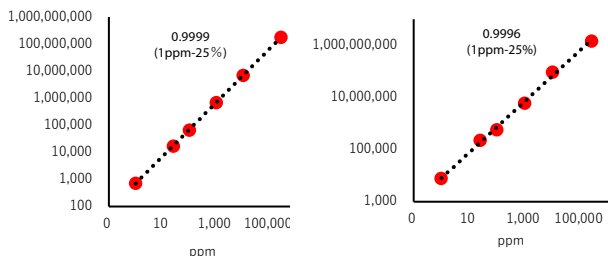


Fig. 4-3 Calibration curve of CH₄
(Left: capillary column Right: packed column)

■ Evaluation of Durability to Oxygen

Ni catalyst is vulnerable to oxygen damage; therefore, the analytical system must strictly exclude contamination of oxygen. The catalyst employed in the Jetanizer is durable for oxygen. For evaluating durability to oxygen, more than 3500 injections of air samples, containing approximately 20% oxygen, were completed. Periodically during the air sample injections, 0.1% standard gas sample was injected. Fig. 6 shows the CO₂/CH₄ value of each injection. Sensitivity fluctuation was not observed even after more than a total volume of 3.5 L of air was injected. The Jetanizer catalyst should be stable for exposure to oxygen.

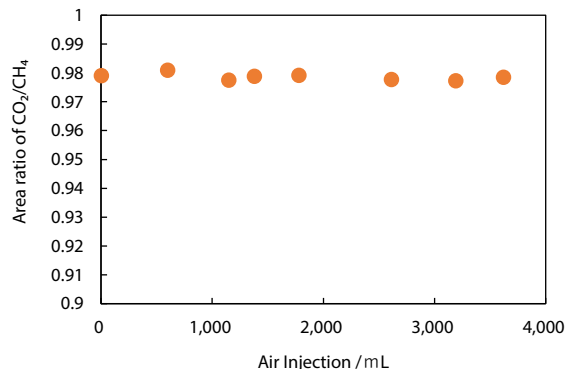


Fig. 6 CO₂/CH₄ value of 0.1% standard gas sample

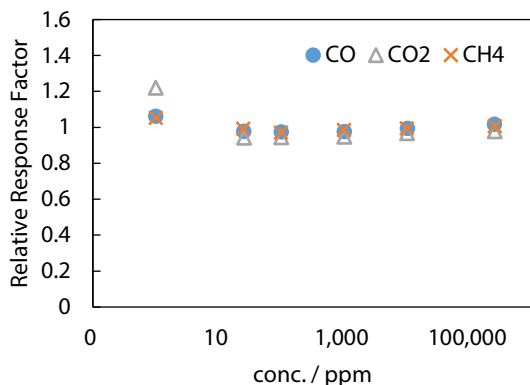


Fig. 5 Relative reference factors when using capillary column

■ Quantification of CO₂ and CH₄ in the Air

Oxygen may produce a baseline deflection when eluting to the Jetanizer in air samples. Column selection for avoiding coelution is important in such cases. MICROPACKED-ST is an option for obtaining full separation of O₂, CH₄ and CO₂.

The air sample was injected five times sequentially to the GC. Table 5 and Fig. 7 show the analytical condition and the obtained chromatogram, respectively. CH₄ and CO₂ were clearly separated from O₂. The CH₄ and CO₂ in the air were quantified using a single point calibration of a gas standard containing 100 ppm of CH₄ and 1000 ppm of CO₂ diluted with N₂. The result is shown in Table 6. CH₄ was 2.1 ppm and CO₂ was 419 ppm, respectively. The repeatability of the area (%RSD) was sufficient. The concentrations and repeatability are shown in Table 6.

Table 5 Analytical Condition

Model	: Nexis GC-2030
Gas Sampler	: MGS-2030 + 1 mL Loop
Inj. Temp.	: 150 °C
Inj. Mode	: Split 1:3
Carrier Gas	: N ₂ , constant flow mode (10 mL/min)
Column	: MICROPACKED-ST (1.0 m × 1.0 mm I.D.) (Input value to the software: 125 m × 0.50 mm I.D., df = 15 μm due to flow re-calculation)
Column Temp.	: 40 °C (1 min) → 40 °C/min → 200 °C (3 min)
Detector	: FID + Jetanizer (column insertion depth : 45 mm)
FID Temp.	: 400 °C
Makeup Gas	: N ₂ , 14 mL/min
H ₂ Flow	: 32 mL/min
Air Flow	: 250 mL/min

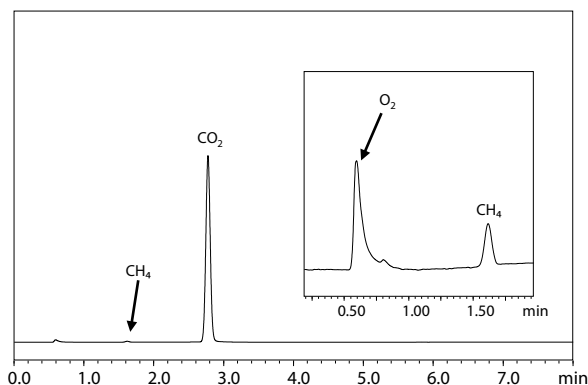


Fig. 7 Obtained chromatogram of the air sample

Table 6 Quantification(ppm) and repeatability (%RSD) result (n=5)

	CH ₄	CO ₂
Quantification (ppm)	2.1	419
Repeatability (%RSD)	0.49	0.51

■ Summary

Analytical performance of the Jetanizer was evaluated on GC-2030 (FID) coupling with gas sampling valve. Converting efficiency from CO/CO₂ to CH₄ was evaluated and obtained successful result. Fundamental analytical performance such as linearity and repeatability also shows sufficient result. Endurance for oxygen was also assessed with sequential injections of the air. The sensitivity remained stable even after 3500 air injections. CO₂ and CH₄ were quantified in the air sample.

The Jetanizer will be useful in the situation such that “the concentration is too small for TCD” and “BID is not available due to Helium shortage”.

■ Notice

Observe the following precautions when using the Jetanizer.

- * Column insertion depth must be 45 mm. Inserting over 45mm of capillary column may damage the catalyst inside or the column itself.
- * Flow rate of the air should be around 250 mL/min.
- * Too much column flow may extinguish the flame of FID.
- * Baseline or noise level may be higher than usual FID analysis.
- * Hydrocarbons with triple bond structure (such as acetylene), substances with sulfur (such as hydrogen sulfide), and substances with halogens may influence the Jetanizer mechanism.
- * Sample matrix gas of O₂ or H₂ may influence the shape of the flame after elution. Therefore, quantification may be interfered immediately after elution of O₂ and H₂. The target compounds should be distant from O₂ and H₂ in chromatogram.
- *The Jetanizer is not a product of Shimadzu. The product is out of our support coverage.
- * Contact to our salesperson for more information.

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