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Gas Chromatograph Nexis™ GC-2030

Application News

# Assessment of Jetanizer™ and Quantitative Analysis of $CO_2$ and $CH_4$ in the Atomosphere

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## User Benefits

- Simplification of the analytical system for CO and $CO_2$ utilizing the Jetanizer coupling with GC-FID.
- Low-cost system achieved with adding the Jetanizer to FID-2030 that is already working.
- $N_2$ 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 ($CO_2$) and Methane ($CH_4$). In addition, high-purity hydrogen requires high-sensitive analytical system for the impurities such as CO, $CO_2$, and $CH_4$. 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 $CO_2$ analysis. A traditional methanizer uses a Nickel (Ni) catalyst in a hydrogen rich environment to reduce CO and $CO_2$ to $CH_4$ 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, $CO_2$ and $CH_4$.

## ■ Jetanizer

The Jetanizer is a compact Methanizer for FID. Highly efficient conversion of CO/$CO_2$ into $CH_4$ 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).

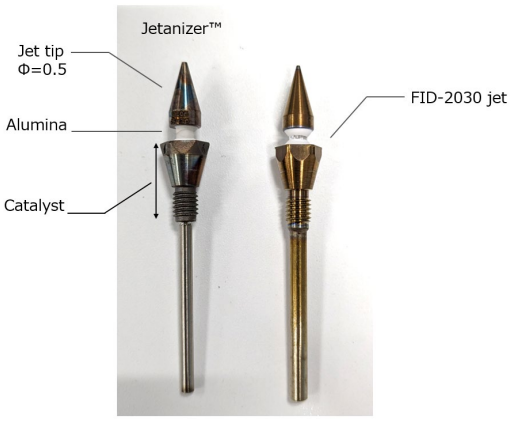


Fig. 1 Jetanizer™

## ■ 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℃. 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 $N_2$). 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 |

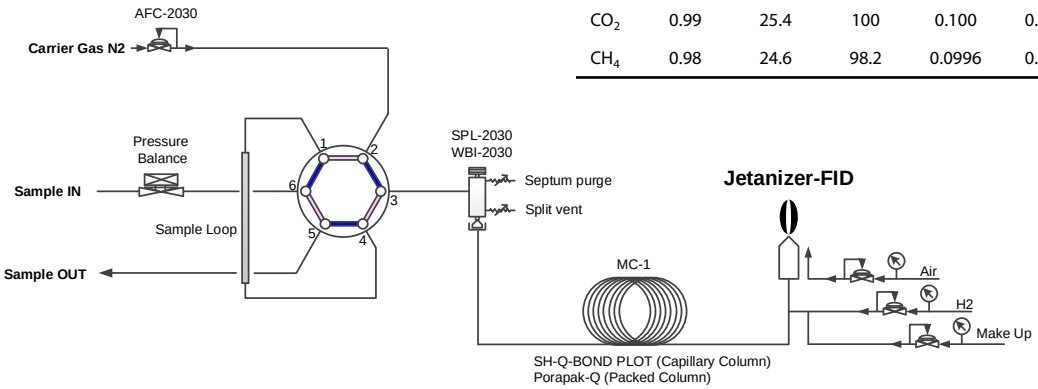


Fig. 2 Schematic illustration of the analytical system

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<br>② 40 mL/min |
| Column | : ① SH-Q-BOND PLOT Column (30 m × 0.53 mm I.D., 20 μm)<br>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.

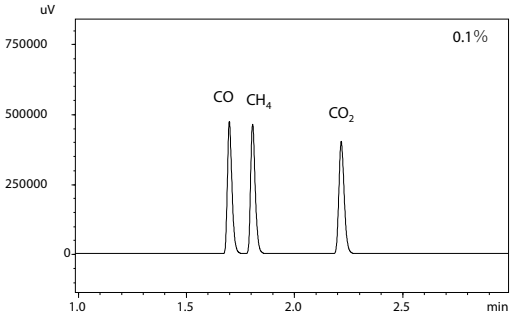


Fig. 3-1 chromatogram of 0.1% sample with capillary column

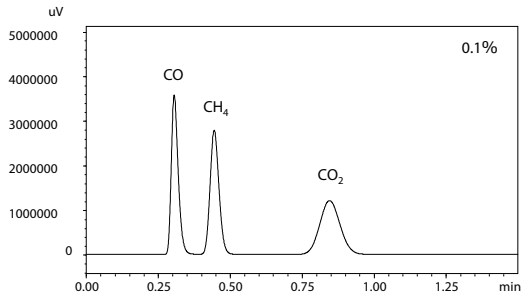


Fig. 3-2 chromatogram of 0.1%sample with packed column

Table 3 LOD of CO, $CH_4$, $CO_2$

| | 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 $CO_2$ cannot be directly detected with FID. Converting them into $CH_4$ 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/ $CO_2$ and $CH_4$ . 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.

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

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 $CO_2$. 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 CO, $CO_2$ and $CH_4$, 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, $CO_2$ and $CH_4$ when using capillary column. The R2 for CO, $CO_2$ and $CH_4$ 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, $CO_2$ and $CH_4$ were consistent for all other standard concentrations.

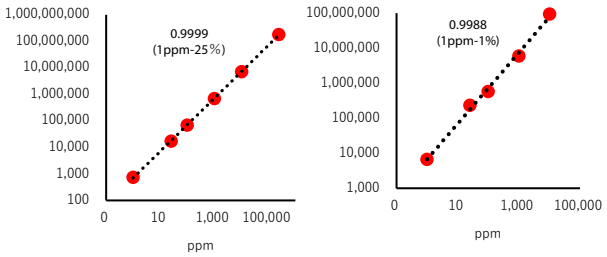


Fig. 4-1 Calibration curve of CO
(Left: capillary column Right: packed column)

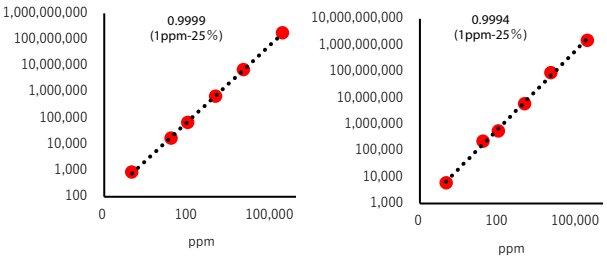


Fig. 4-2 Calibration curve of $CO_2$
(Left: capillary column Right: packed column)

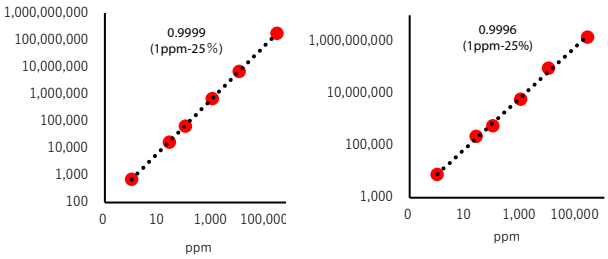


Fig. 4-3 Calibration curve of $CH_4$
(Left: capillary column Right: packed column)

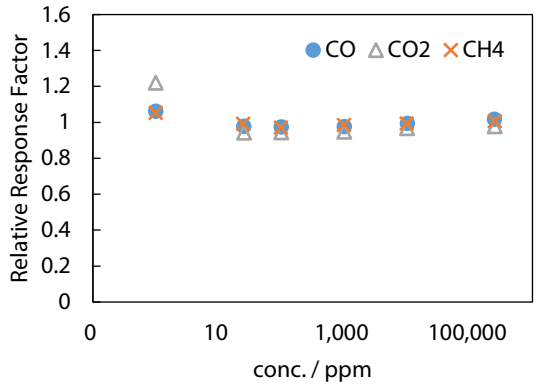


Fig. 5 Relative reference factors when using capillary column

## ■ 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 $CO_2$ /$CH_4$ 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.

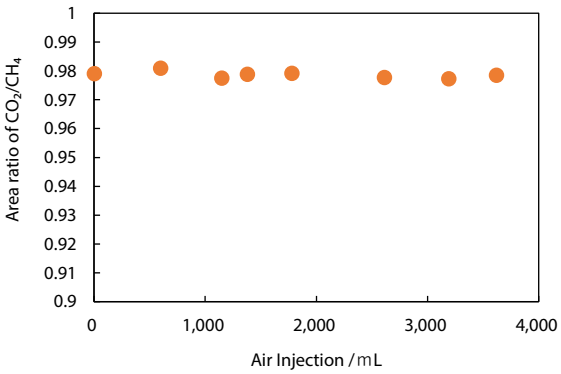


Fig. 6 $CO_2$ /$CH_4$ value of 0.1% standard gas sample

## ■ Quantification of $CO_2$ and $CH_4$ 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 , $CH_4$ and $CO_2$.

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. $CH_4$ and $CO_2$ were clearly separated from O2 . The $CH_4$ and $CO_2$ in the air were quantified using a single point calibration of a gas standard containing 100 ppm of $CH_4$ and 1000 ppm of $CO_2$ diluted with N2. The result is shown in Table 6. $CH_4$ was 2.1 ppm and $CO_2$ 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 |

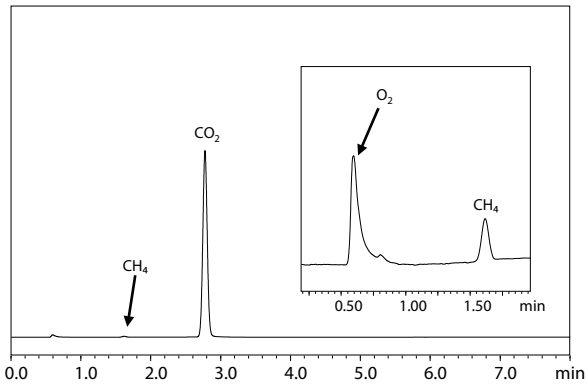


Fig. 7 Obtained chromatogram of the air sample

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/ $CO_2$ to $CH_4$ 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. $CO_2$ and $CH_4$ 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 $O_2$ or $H_2$ may influence the shape of the flame after elution. Therefore, quantification may be interfered immediately after elution of $O_2$ and $H_2$. The target compounds should be distant from $O_2$ and $H_2$ in chromatogram.
* Contact to our salesperson for more information.



01-00599B-EN
First Edition: Oct. 2023
Revision A : Apr. 2024
Revision B : Sep. 2024

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