Application News

Gas Chromatograph Nexis™GC-2030

Simultaneous Analysis of Three Greenhouse Gas Components, CH_4, CO_2, and N_2O

Emiko Shimbo and Shinji Uchiyama

User Benefits

- The three major greenhouse gases, CH_4, CO_2, and N_2O can be analyzed using GC-BID.
- They are simultaneously analyzed with high sensitivity by BID-FID series connection, a simple GC configuration.
- ECD, which requires complicated procedures, is not required.

■ Introduction

In recent years, there has been a global demand to reduce greenhouse gas (GHG) emissions. To achieve "carbon neutrality," a state of net-zero carbon dioxide emissions, innovative researches and developments are ongoing in many countries.

The major GHGs include methane (CH_4), carbon dioxide (CO_2), nitrous oxide (N_2O), and chlorofluorocarbons, etc. The amount of CO_2 emission is the largest, but the Global Warming Potential (GWP) of CH_4 and N_2O is 25 and 298 times higher than that of CO_2, respectively.

ECD is generally utilized to analyze N_2O, but it is not sensitive to other GHGs and cannot be used for simultaneous analysis. Using a Dielectric-Barrier Discharge Ionization Detector (BID), most compounds, except helium and neon, can be detected with high sensitivity. In this article, simultaneous analysis of CH_4, CO_2, and N_2O with gas chromatograph Nexis GC-2030 is demonstrated.

■ Measurement Conditions

Three different methods of measurement were performed depending on the target components and their concentrations. Table 1 shows the conditions of each analysis, and Table 2 summarizes the differences. A gas sampler MGS-2030 was used to introduce the sample into the gas chromatograph through the inlet unit SPL-2030.

Table 1 Measurement Conditions

Model:	Nexis GC-2030
Gas Sampler:	MGS-2030 + 1 mL Loop
Injection Unit:	SPL-2030 with Liner for Split Injection Mode
Detector:	(1) (2) BID-2030, (3) BID-2030, FID-2030
	(Column length Inserted to BID: 70 mm, FID:69 mm)
Column:	MICROPACKED ST 2 m × 1 mm I.D. (P/N: MP-01)
	(250 m × 0.5 mm I.D., df =10 µm for flow calculation)
Inj. Temp.:	100 °C
Inj. Mode:	(1) Split (1:4), (2) (3) Splitless*1
Sampling Time:	(2) (3) 1 min
Carrier Gas:	He, constant column flow (9 mL/min)
Purge Flow:	0 mL/min
Column Temp.:	35 °C (2 min) → (5 °C/min) → 60 °C → (40 °C/min)
	→ 200 °C → (25 °C/min) → 250 °C → (15 °C/min)
	→ 275 °C (3 min)
BID Temp.:	280 °C
Discharge Gas:	He, 50 mL/min
FID Temp.:	(3) 280 °C
Makeup Gas:	(3) He, 24 mL/min
H_2 Flow:	(3) 32 mL/min
Air Flow:	(3) 200 mL/min

*1 A liner for splitless can also be used, but measurements here were performed with a liner for split (P/N: 227-35007-01).

Table 2 Differences of Measurement Conditions of (1) - (3)

	Detector	Injection Mode
(1)	BID	Split
(2)	BID	Splitless
(3)	BID + FID	Splitless

■ Analysis of GHGs in the Atmosphere

(1) Split Injection with BID

The atmosphere includes approximately 410 ppm of CO_2, 1.8 ppm of CH_4, and 0.32 ppm of N_2O. The measurement conditions in Table 1 were used to analyze the atmosphere, and Fig. 1 shows the chromatogram obtained by (1). CH_4, CO_2, and N_2O were detected and separated. CH_4 is adjacent to krypton (Kr), whose concentration in the atmosphere is about 1.14 ppm, but they were separated. The resolution of CH_4 and Kr was 0.95.

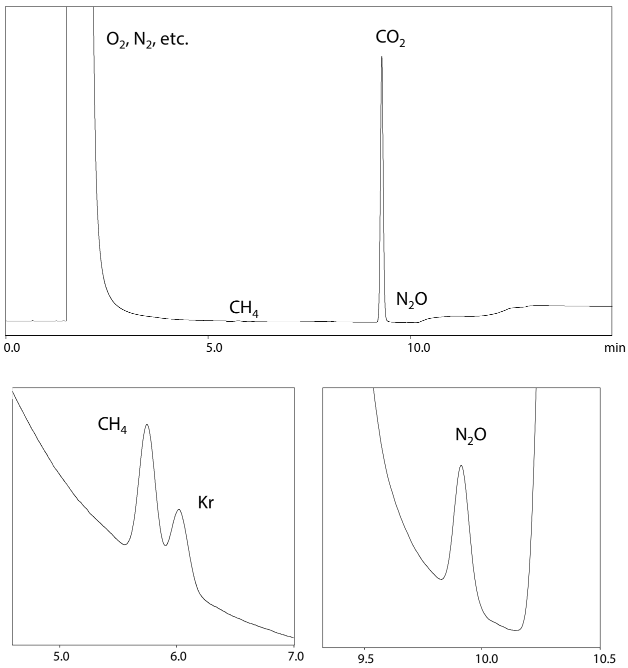

Fig. 1 Chromatograms of the Atmosphere Measurement
Upper: Whole Chromatogram, Lower: Enlarged Chromatogram
(CO_2: Approx. 410 ppm, CH_4: Approx. 1.8 ppm, N_2O: Approx. 0.32 ppm)

(2) Splitless Injection with BID

To detect N_2O with higher sensitivity, the amount of sample injected was increased by splitless injection mode. Fig. 2 shows the chromatograms of (1) split and (2) splitless injections. CH_4, CO_2, and N_2O were detected also in splitless mode and the areas of CH_4 and N_2O in (2) were larger than in (1). The resolution between CH_4 and Kr was reduced to 0.76 due to the O_2 and N_2 baseline and Kr peak.

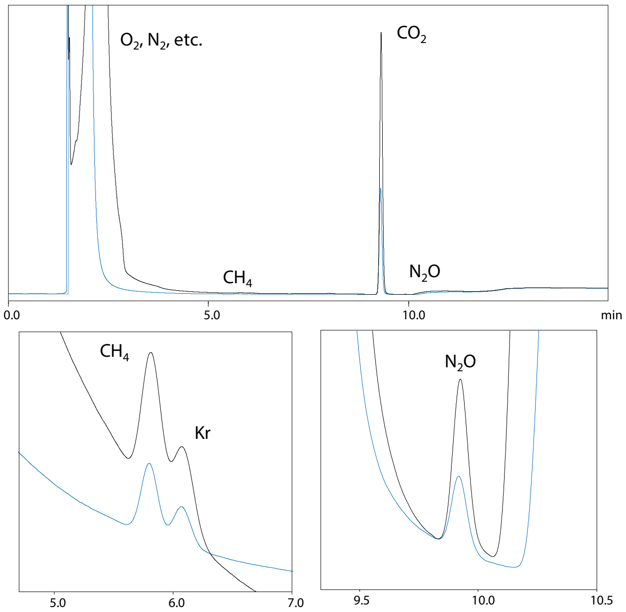

Fig. 2 Chromatograms of the Atmosphere Measurement
Upper: Whole Chromatogram, Lower: Enlarged Chromatogram
Black: (2) Splitless, Blue: (1) Split

(3) Splitless Injection with Series BID-FID

(2) Splitless analysis with BID improved the sensitivity, but it is difficult to analyze CH_4 with high accuracy because the resolution of CH_4 is reduced by the O_2 and N_2 baseline and Kr peak. Therefore, FID, which is not sensitive to these components, was connected in series after BID.

The atmosphere was analyzed in splitless mode by BID-FID series connection and the chromatogram is shown in Fig. 3. CH_4 was detected by FID after the detection by BID, with a slight delay in retention time (RT). Using BID, which is sensitive to Kr, the RTs of CH_4 and Kr were close and it was necessary to separate them. On the other hand, FID, which is not sensitive to Kr, allowed for selective analysis of CH_4 without being affected by Kr. By this method, the three GHGs were simultaneously analyzed with high sensitivity.

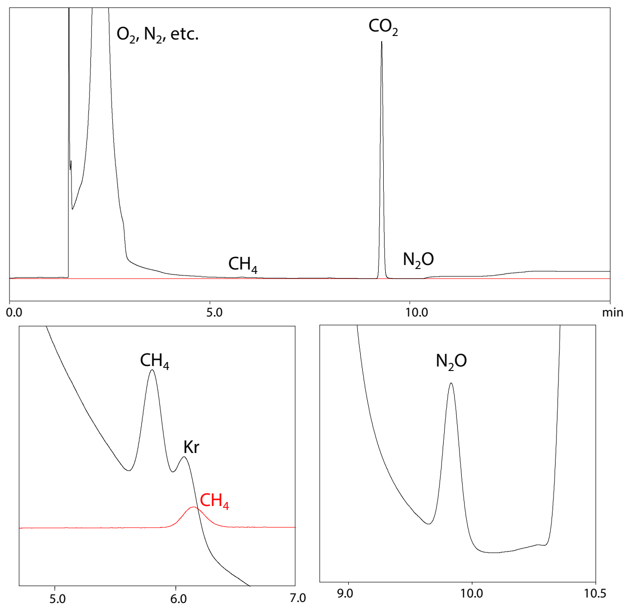

Fig. 3 Chromatograms of the Atmosphere Measurement
Upper: Whole Chromatogram, Lower: Enlarged Chromatogram
Black: BID, Red: FID

■ How to Connect BID and FID

In (3) BID-FID analysis, the BID vent on the back of the GC and FID were connected with a metal column in addition to the system of (2) splitless with BID analysis. Fig. 4 shows the image of the BID vent (VENT2) connected to the FID with a metal column. The length of metal column inserted into the BID vent was approximately 10 mm as shown in Fig. 5. A graphite ferrule and a nut were used to attach the adaptor to the metal column. The list of parts used, and the assembly image are shown in Table 3 and Fig. 5, respectively.

Fig. 4 BID Vent Connected to FID with Metal Column

Table 3 List of Parts Used in BID-FID Series Connection

	Parts	P/N	Notes
A	Silicone O-ring, for SUS Column	201-35184-00	50 PC
B	Nipple Adapter GN-CAP	221-32508-00	-
C	Washer, WG	201-30050-84	10 PC
D	Nut, GF	201-30006-00	-
E	Ferrule Cap Assm 0.8	221-32126-08	10 PC Same as when connecting GC column to SPL
F	Injection Port Column Nut	221-16325-01	Same as when connecting GC column to SPL
G	Ultra ALLOY Deactivated Tube 5 m × 0.53 mm I.D.	UADTM-5W	Cut to approx. 1 m Substitutable with 0.5 mm I.D. metal tube

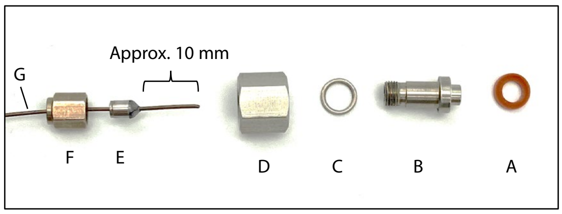

Fig. 5 Assembly Image of Metal Column Connection to BID Vent

■Calibration Curves

CH_4, CO_2, and N_2O in nitrogen (N_2) were diluted with N_2 and the analyses for calibration curves were performed by (1) split with BID and (3) split with BID-FID. The ranges of the calibration curves were CH_4: 1-100 ppm, CO_2: 10-1000 ppm, and N_2O: 0.1-10 ppm. Fig. 6 shows the calibration curve in BID analysis and Fig. 7 in FID analysis. For each component, good linearities were obtained in the analysis of (1) and (3).

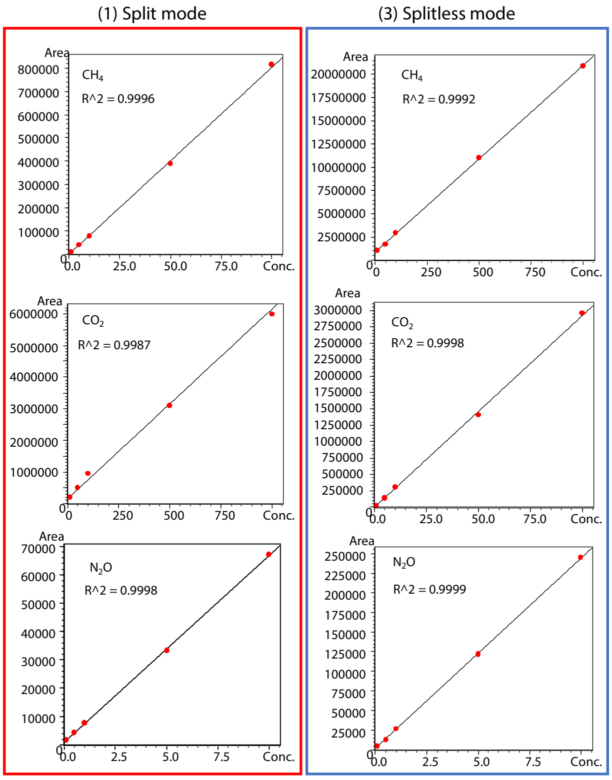

Fig. 6 Calibration Curves of BID Analysis
Left: (1) Split, Right: (3) Splitless
(CH_4: 1, 5, 10, 50, 100 ppm, CO_2: 10, 50, 100, 500, 1000 ppm,
N_2O: 0.1, 0.5, 1, 5,10 ppm)

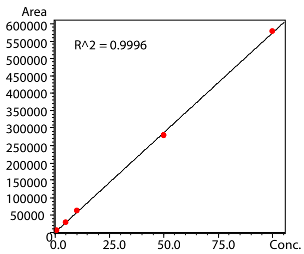

Fig. 7 Calibration Curve of FID Analysis
(3) Splitless with BID-FID (CH_4:1, 5, 10, 50, 100 ppm)

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■ Quantitation of the Atmosphere Analysis

The quantification values of the atmosphere analysis using the calibration curves above are shown in Table 4. The values were almost same as the theoretical values both in (1) split with BID and (3) splitless with BID-FID connection. For CH_4, the value in (3) FID analysis, which was not affected by the O_2 and N_2 baseline and Kr, was the closest to the theoretical value.

Five consecutive analyses of the atmosphere were performed and the reproducibilities are shown in Table 5, and the S/N values in Table 6. Good reproducibilities were obtained, and the S/N values were more than 10 in both analyses.

Table 4 Quantification Values of Each Component of the Atmosphere (ppm)

	CH_4	CO_2	N_2O
(1)	2.07	427	0.31
(3) BID	2.23	443	0.31
(3) FID	1.91	–	–

Table 5 Reproducibility (%RSD) of Each Component of the Atmosphere (n = 5)

	CH_4	CO_2	N_2O
(1)	1.34	0.28	0.95
(3) BID	0.69	0.23	1.37
(3) FID	0.42	–	–

Table 6 S/N of Each Component of the Atmosphere

	CH_4	CO_2	N_2O
(1)	64	21438	20
(3) BID	94	40864	36
(3) FID	58	–	–

■ Conclusion

The three major greenhouse gases, CH_4, CO_2, and N_2O were analyzed with gas chromatograph Nexis GC-2030. For N_2O analysis with higher sensitivity, analysis in splitless mode was useful. Besides, to use BID and FID in series and detect the targets simultaneously, all the components, CH_4, CO_2, and N_2O were analyzed at the same time with high sensitivity without being affecting by O_2 and N_2 baseline and Kr.

The analysis of the standard gases revealed the good linearity of the calibration curves, for which the quantification values of CH_4, CO_2, and N_2O in the atmosphere were close to the theoretical values.

All the analyses in this article can be performed with a simple configuration and ECD is not required for N_2O analysis. Table 7 shows the characteristics and the cautions for each analysis. Please refer to the analysis conditions in accordance with the target components and their concentrations.

Table 7 Characteristics and Cautions of Each Analysis in this Article

	Characteristics	Cautions
(1)	Simultaneous analysis of three GHGs only with BID	–
(2)	Highly sensitive analysis of N_2O only with BID	CH_4 is adjacent to Kr
(3)	Simultaneous and highly sensitive analysis of three GHGs	BID-FID series connection is required

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01-00363-EN First Edition: Jul. 2022