

Application News

Simultaneous Analysis of Greenhouse Gases Using Nitrogen Carrier Gas

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User Benefits

- ◆ The main greenhouse gases CO₂, CH₄, and N₂O can be simultaneously analyzed.
- ◆ The Jetanizer™ can detect CO₂ with a flame ionization detector and perform analysis with a simple equipment configuration.
- ◆ Reasonable and accessible N₂ can be used as the carrier gas.

Introduction

There is a global desire to combat global warming by reducing levels of greenhouse gases. Hence, many fields of industry and science are pursuing research and development aimed at achieving carbon neutrality, a state of net zero greenhouse gas emissions.

The main greenhouse gases are carbon dioxide (CO₂), methane (CH₄), and dinitrogen monoxide (N₂O). Because CO₂, CH₄, and N₂O are present at very different concentrations in the atmosphere, a thermal conductivity detector (TCD), a flame ionization detector (FID), and an electron capture detector (ECD) are needed to measure levels of all three greenhouse gases in the atmosphere simultaneously. The Jetanizer™ can detect CO₂ with an FID, thus enabling the simultaneous analysis of greenhouse gases with a simpler equipment configuration. More information on the performance of the Jetanizer can be found in Application News 01-00599. This article describes using a Jetanizer-FID and ECD to perform a simultaneous analysis of CO₂, CH₄, and N₂O.

Equipment Configuration and Analytical Conditions

First, the FID nozzle was replaced with a Jetanizer. The capillary adapter on the lower part of the injection port was replaced with a two-way branched capillary adapter,*¹ and two columns were connected to the adapter. The insertion lengths of the columns were 51 and 61 mm. Gas samples were introduced using the MGS-2030 gas sampler, and samples were divided and introduced to both columns through the lower part of the injection port and detected by the Jetanizer-FID and the ECD. A plumbing diagram of the system is shown in Fig. 1, and the analytical conditions are shown in Table 1.

*¹ Requires an INJ2-way branch unit (S221-75231-41).

The unit consists of a two-way branched adapter (a multi-column hanger and two INJ nuts).

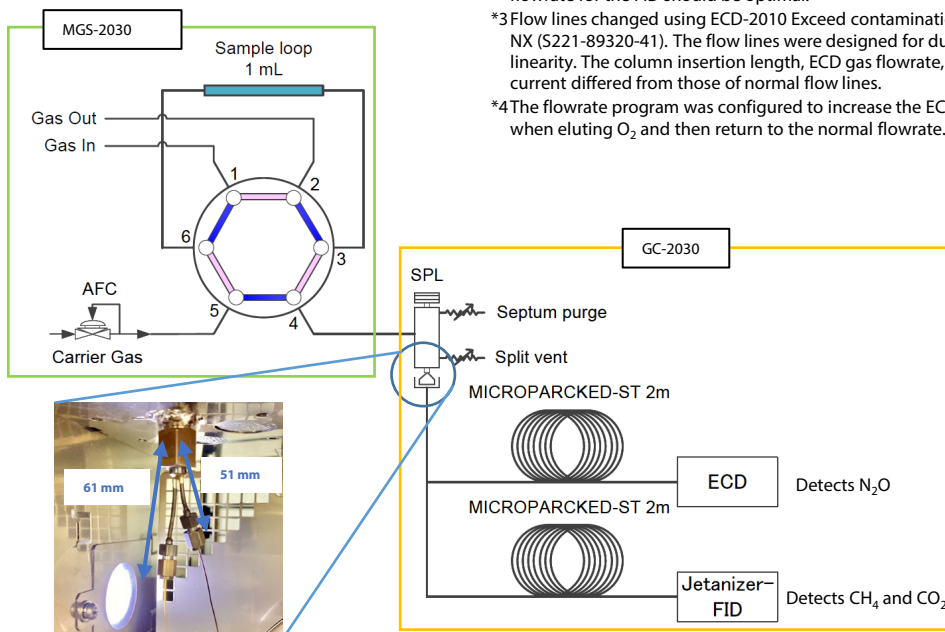


Fig. 1 Plumbing Diagram of System

Table 1 Analytical Conditions

Model:	Nexis GC-2030
Gas Sampler:	MGS-2030 + 1 mL Loop
Inj. Temp.:	100 °C
Inj. Mode:	Split
Split Ratio:	1:9
Carrier Gas:	N ₂ , fixed column flowrate mode (5 mL/min)
Purge Flow:	0 mL/min
Column:	MICROPACKED-ST 2 m × 1 mm I.D. 2 columns (250 m × 0.50 mm I.D., df = 10 μm entered to calculate flowrates) (Column insertion lengths on injection port side: 51 mm, 61 mm)
Column Temp.:	50 °C (2 min) → 40 °C/min → 200 °C → 25 °C/min → 250 °C → 15 °C/min → 275 °C (5 min)
Detector:	FID+Jetanizer* ² (Column insertion length: 45 mm) ECD-2010 Exceed* ³ (Column insertion length: 32 mm)
ECD Temp.:	340 °C
ECD Gas:	Ar + 5 %CH ₄
ECD Gas Prog.* ⁴ :	30 mL/min (0 min) → 400 mL/min ² → 200 mL/min (2 min) → -400 mL/min ² → 30 mL/min (11.57 min)
ECD Current:	1 nA
FID Temp.:	400 °C
Makeup Gas:	N ₂ , 20 mL/min
H ₂ Flow:	32 mL/min
Air Flow:	250 mL/min

*²A normal FID can only be used when analyzing just CH₄ and not CO₂. The parameters for the column insertion length, detector temperature, and gas flowrate for the FID should be optimal.

*³Flow lines changed using ECD-2010 Exceed contamination prevention kit NX (S221-89320-41). The flow lines were designed for durability and linearity. The column insertion length, ECD gas flowrate, and electric current differed from those of normal flow lines.

*⁴The flowrate program was configured to increase the ECD gas flowrate when eluting O₂ and then return to the normal flowrate.

■ Confirming Linearity

Calibration curves were prepared by diluting CH₄, CO₂, and N₂O with N₂. The calibration curve ranges were 1-100 ppm for CH₄, 10-1000 ppm for CO₂, and 0.05-2.5 for N₂O. The calibration curves for each compound are shown in Figs. 2 and 3. Good linearity was obtained with all three compounds.

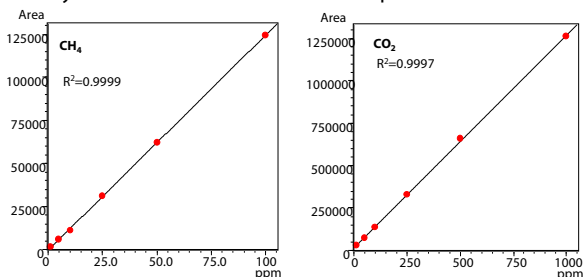


Fig. 2 Jetanizer-FID Calibration Curves

CH₄: 1, 5, 10, 25, 50, 100 ppm CO₂: 10, 50, 100, 250, 500, 1000 ppm

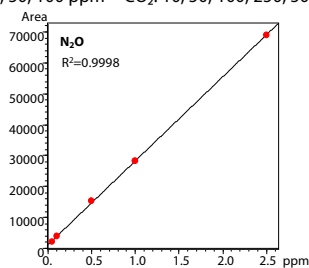


Fig. 3 ECD Calibration Curve

N₂O: 0.05, 0.1, 0.5, 1, 2.5 ppm

■ Quantitative Analysis of Atmosphere and Repeatability

Samples of atmosphere were analyzed five times consecutively. The resulting chromatograms are shown in Fig. 4, and the levels in the atmosphere, which were determined using the calibration curves and the peak area repeatability, are shown in Table 2. The peak area repeatability was good for all three compounds.

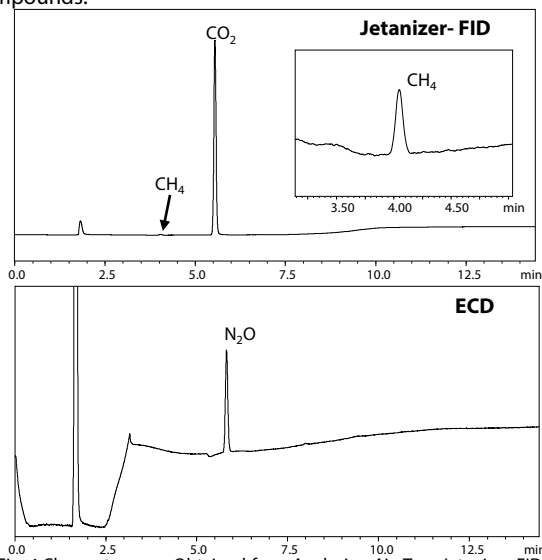


Fig. 4 Chromatograms Obtained from Analyzing Air: Top: Jetanizer-FID, Bottom: ECD

Table 2 Amount of Each Compound Measured in Air (ppm) and Peak Area Repeatability (%RSD, n = 5)

	CH ₄	CO ₂	N ₂ O
Quantified amount (ppm)	2.2	413	0.36
Peak area repeatability (%RSD)	1.1	0.38	0.55

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Jetanizer is a trademark or registered trademark of Activated Research Company in the US and other countries.

■ Assessing Long-Term Stability of ECD

Measuring N₂O with an ECD normally requires using Ar+5 % CH₄ as the ECD gas and a pre-cut of O₂. Since this analytical method introduces O₂ to the ECD, the stability of the ECD during the extended introduction of air was assessed to compare with using Ar+5 % CH₄ and N₂ as the ECD gas. An HS-20 headspace sampler was used for consecutive analysis, air was used for vial pressurization,^{*5} and analysis was performed on atmosphere sealed in vials. The area value reproducibility and sensitivity variation were evaluated by continuously analyzing N₂O in the atmosphere at every 100 mL air introduction volume. Table 3 shows N₂O peak area repeatability of measurements taken every 100 mL of introduced air. Good repeatability with all %RSD results below 0.5 was obtained using Ar+5 % CH₄ as the ECD gas, while almost all %RSD results were above 5 % when N₂ was used as the ECD gas. Fig. 5 shows the change in peak area ratio with the peak area measured by the first analysis as 1. There was almost no variation in sensitivity and measurements were stable when Ar+5 % CH₄ was used as the ECD gas. However, the peak area decreased after introducing 100 mL of air when N₂ was used as the ECD gas. These results show that Ar+5 % CH₄ must be used as the ECD gas to obtain stable measurements with good repeatability.

*5 He or N₂ is normally used as the vial pressurization gas.

Table 3 N₂O Peak Area Repeatability (%RSD) Every 100 mL of Introduced Air

Total Air Introduced (mL)	0	100	200	300	400	500	600	700	800	900	1000
Ar+5 %CH ₄ (%RSD)	0.40	0.25	0.29	0.20	0.42	0.45	0.46	0.41	0.40	0.40	0.43
N ₂ (%RSD)	2.29	5.29	6.42	5.15	7.38	6.10	5.48	6.38	5.13	6.25	4.96

Area Ratio

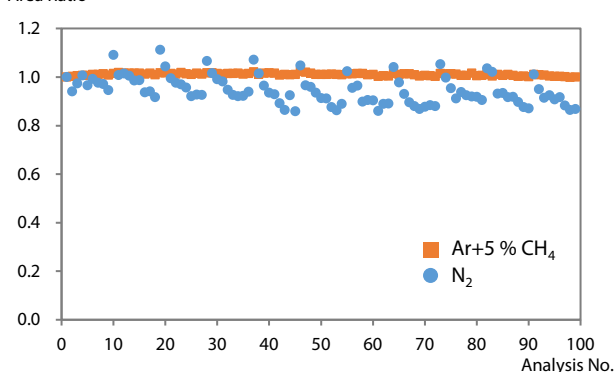


Fig. 5 Change in Peak Area Ratio Taking First Peak Area as 1

■ Conclusion

A Jetanizer-FID and ECD were successfully used to perform a simultaneous analysis of the main greenhouse gases CO₂, CH₄, and N₂O.

Analyzing standard gases confirmed good linearity, which enabled the quantitative analysis of atmospheric CO₂, CH₄, and N₂O. Furthermore, the long-term stability of the ECD was also confirmed.

The analytical method described in this article allows greenhouse gases to be measured using a simple equipment configuration that does not require helium gas.

< Related Application News Articles >

1. Assessment of Jetanizer™ and Quantitative Analysis of CO₂ and CH₄ in the Atmosphere: [Application News No. 01-00599-EN](#)



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