Application Note
Environmental

High-Precision Determination of Four Greenhouse Gases in the Atmosphere Using the Agilent 8890 GC

Authors

Xinglong Fu
Agilent Technologies
(China) Co. Ltd

Yuanshan Du, Jie Zhang, and
Youjuan Zhang
Agilent Technologies
(Shanghai) Co. Ltd

Abstract

High-precision greenhouse gas monitoring enables accurate quantification of carbon emissions, verification of emission reduction effectiveness, and provides scientific support for climate policies. The core technical requirements include achieving ppb-level detection limits and simultaneous analysis of multiple components. This application note demonstrates how the Agilent 8890 GC system with a multivalve, multicolumn configuration is optimized to achieve high-precision monitoring of four key greenhouse gases in the atmosphere, thereby providing reliable and user-friendly analytical solutions for environmental monitoring stations at all levels.

Introduction

Currently, China is actively implementing dual-control measures on total energy consumption and intensity. The Ministry of Ecology and Environment issued "The 14th Five-Year Plan for Ecological and Environmental Monitoring", which specifically highlights the advancement of technologies for direct measurement of carbon emissions. It calls for organizing pilot projects in multiple key industries and enterprises to monitor greenhouse gas emissions such as carbon dioxide and methane, establishing greenhouse gas monitoring networks in key cities, and upgrading the greenhouse gas monitoring capabilities of national atmospheric background stations. As a result, conducting greenhouse gas monitoring within the environmental protection stations of provinces and cities has become a critical task.

Methane (CH_4), carbon dioxide (CO_2), nitrous oxide (N_2O), and sulfur hexafluoride (SF_6) are the main analytical targets of China's greenhouse gas monitoring network. These gases originate from different emission sources, and their concentration levels vary by up to six orders of magnitude (for example, the concentration of CH_4 in ambient air is approximately 1 to 2 ppm, while the concentration of SF_6 ranges from 9 to 15 ppt). Accurate monitoring of these four types of gases requires high-sensitivity detection methods. In terms of monitoring precision, the GB/T 31705-2015[1] standard specifies that monitoring methods must achieve quantitative precision (n = 10) better than 0.05% for CO_2 and 0.1% for CH_4 when analyzing standard samples with concentrations close to actual greenhouse gas levels. For the other two gases, N_2O and SF_6, which are not covered by the GB/T 31705-2015 method, the National Environmental Monitoring Center requires monitoring repeatability to be better than 0.1% for N_2O and 0.5% for SF_6.

The high-precision greenhouse gas monitoring solution primarily utilizes online equipment based on cavity ring-down spectroscopy (CRDS) technology. CRDS measurement precision varies slightly for different greenhouse gases, but is generally better than 0.05%. However, CRDS technology is not suitable for measuring SF_6. In practical applications, it must be combined with other technologies specifically designed for SF_6 measurement to complete the monitoring of the four target compounds. The use of different analytical techniques increases the requirements for operator experience and skills, and the integration of different analytical platforms raises the cost. Developing a solution based on a widely used analytical technique or a verified platform that delivers reliable and high-precision analysis is crucial for establishing a greenhouse gas monitoring network. Gas chromatography (GC) is one of the important candidate platforms for this purpose.

The use of GC for detecting greenhouse gases has a long history. The conventional methods used gas sampling valve for injection, TCD and FID for sequential detection of CO_2 and CH_4, or combining a methanizer with an FID to detect CO_2 and CH_4 in one analytical channel and detecting N_2O on ECD in another analytical channel.[2] The analytical precision for CO_2, CH_4, and N_2O achieved with such configurations typically ranges from 0.2% to 0.5%, but it is difficult to obtain precision better than 0.1%, which does not meet the current requirements for greenhouse gas monitoring accuracy and precision. Moreover, the traditional methods rarely report analytical precision for SF_6 at ppt concentration levels.

To monitor trace levels of CO_2, CH_4, N_2O, and ultratrace levels of SF_6 on the same GC system with high-precision results, it is necessary to optimize multiple factors included in sample injection, separation, and detection. Furthermore, the system configuration must be flexible enough to allow expansion for future analytical needs, such as incorporating trace CO analysis in air.

This work demonstrates how the 8890 GC achieves high-precision analysis of four key greenhouse gases by optimizing the injection volume, controlling injection reproducibility, and utilizing multichannel separation and high-sensitivity detectors to ensure the system runs stably in long-term operation.

Experimental

Reagents and samples

The carrier gas and the detector gases were purchased from Dalian Special Gases Co., Ltd. Six mixed gas standard samples were obtained from the National Institute of Metrology, China. The standard gases use air as the balance gas, and their composition information is shown in Table 1. Samples 1 to 5 were used to establish the calibration curve, while sample 6 was used for system repeatability evaluation.

Table 1. Standard gases composition and concentration information.

Compound	Concentration (mol/mol)					
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
Methane (CH_4) × 10^{-6}	1.3	1.9	2.4	2.9	3.4	2.9
Carbon Dioxide (CO_2) × 10^{-6}	350	400	450	500	550	295
Nitrous Oxide (N_2O) × 10^{-9}	300	350	400	450	500	450
Sulfur Hexafluoride (SF_6) × 10^{-12}	10	15	20	25	40	24

Instrumental

The 8890 GC is configured as a three-channel/multivalve/multicolumn system, enabling independent analysis of four greenhouse gases—CH_4, CO_2, N_2O, and SF_6—within 8 minutes using a single injection. The target compounds are analyzed in separate channels, reducing chromatographic peak broadening and thereby improving sensitivity and repeatability.

For CO_2 analysis, a methanizer is used to convert CO_2 to CH_4, which is then detected by FID. The system eliminates the need for dehydration through backflushing and venting operation via switching valves, preventing interference from moisture and oxygen in the air and extending the lifespan of the methanizer.

For N_2O and SF_6 analysis, the ECD with hidden anode design is used for high-sensitivity detection and strong anti-contaminant capability.

The CH_4 analysis is conducted on a single column with a dedicated large injection loop, significantly enhancing detection sensitivity and repeatability, achieving a detection limit for methane as low as single-digit ppb levels.

The system configuration and schematic flow path is shown in Figure 1 and Table 2.

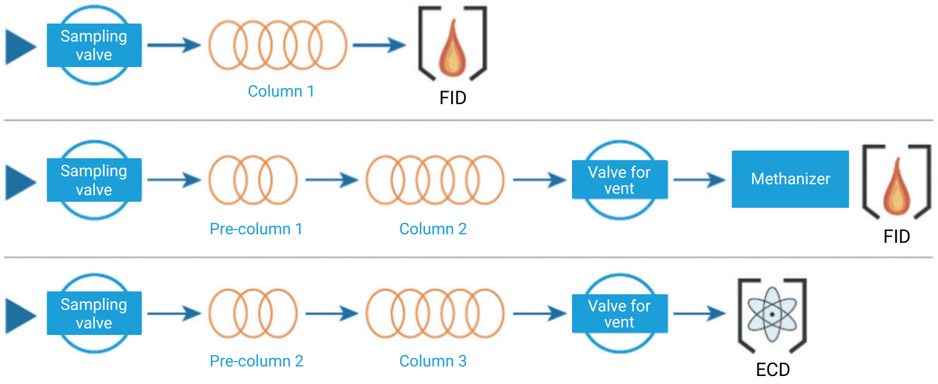

Figure 1. A schematic illustration of the system flow path.

Table 2. Analytical conditions on the Agilent 8890 GC for greenhouse gas analysis.

	CH_4 Channel (FID)	CO_2 Channel (FID)	N_2O/SF_6 Channel (ECD)
Column Type	Packed columns of varied length, HayeSep type		
Column Flow Rate (mL/min)	~30 to 40	~20 to 30	~20 to 30
Carrier Gas	Nitrogen		
Oven Temperature (°C)	60		
Valve Box Temperature (°C)	60		
Sample Flow Rate (mL/min)	30		
Detector Temperature (°C)	300	300	350
Hydrogen Flow Rate (mL/min)	30	48	–
Air Flow Rate (mL/min)	400	400	–
Makeup Gas (N_2) Flow Rate (mL/min)	–	–	2

Results and discussion

Chromatograms of standard gases

Standard gas samples are introduced into the sample loop under a controlled flow rate. When analyzing the air samples, air is collected into a positive-pressure sampling container via an external positive-pressure sampling device, then connected to the sample loop. Choice of sample loop size must consider the concentration levels of the target analytes. An appropriate volume is required to ensure a sufficiently high response at the detector while maintaining adequate compound resolution on the same analytical channel.

CH_4 and CO_2 in ambient air are present at 10^{-6} mol/mol concentration levels, with the concentration of CH_4 being two orders of magnitude lower than that of CO_2. To enhance the response for methane, the injection volume for CH_4 must be increased. However, large-volume injections of hundreds of ppm CO_2 are not favorable for the methanizer. Therefore, CO_2 and CH_4 are analyzed in two separate channels with different injection volumes, which balance the method sensitivity with the system robustness and long-term stability.

For N_2O/SF_6 analysis, although their concentration difference in ambient air exceeds three orders of magnitude, SF_6 has strong electronegativity and a high response factor on the µECD detector. As a result, both compounds can be analyzed in the same analytical channel using the same sample loop and detector, achieving excellent signal-to-noise ratios and good separation for the two analytes.

The chromatogram of the gas sample 1 is shown in Figure 2.

For sample loop-based injections, it is important to note that the actual injection volume of the gas sample may experience slight variations due to fluctuations in atmospheric conditions (pressure and temperature). For routine analysis (where precision at the single-digit percentage level is sufficient), these minor variations have negligible impact on results precision. However, for the high-precision analysis as required in this application, maintaining a stable laboratory environment (minimal variations in ambient temperature and pressure) is essential for obtaining the highly accurate and precise measurement.

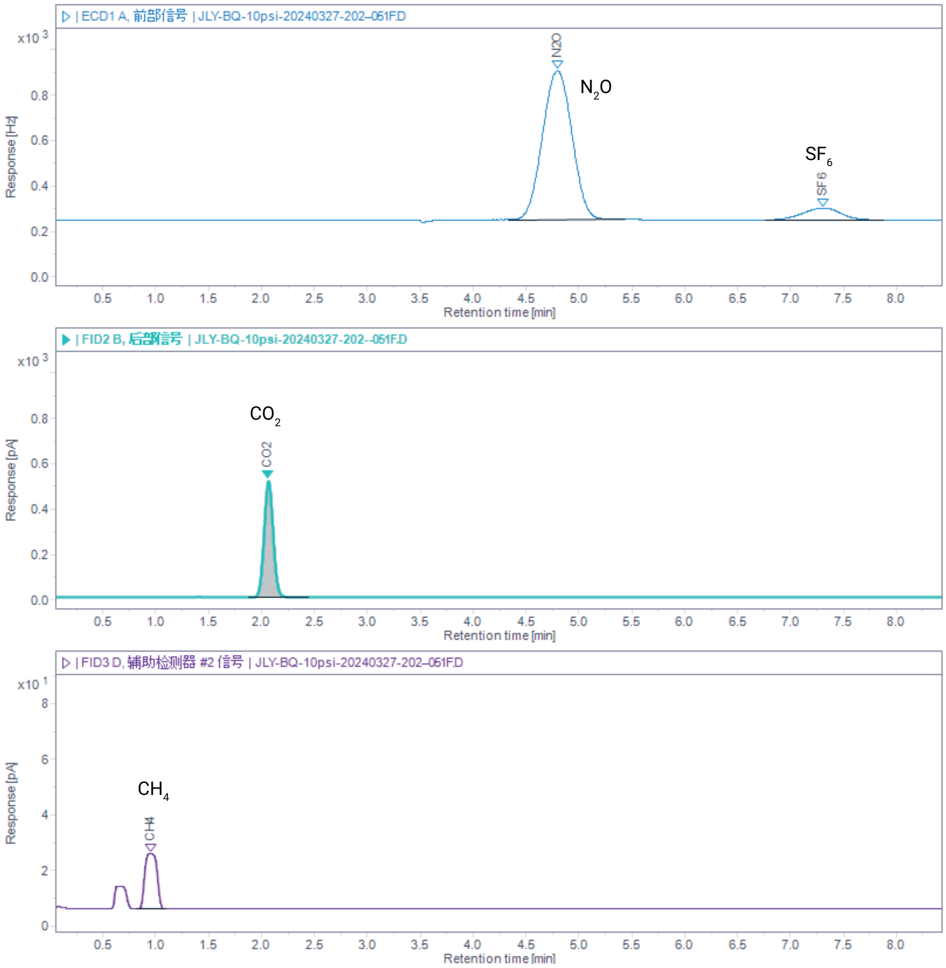

Figure 2. Chromatogram of gas sample 1.

Precision

In accordance with GB/T 31705-2015, standard gas sample 6 was injected consecutively 10 times (the overlaid chromatograms are shown in Figure 3), and the relative standard deviations (RSDs) of retention times and peak areas for all compounds were calculated (data listed in Table 3). The precision of peak areas for all compounds ranged between 0.02% and 0.5%, fully meeting the quantitative precision requirements of the national standard method and related laboratory for greenhouse gas analysis.

The high-precision test results are attributed to the excellent pneumatic control of the 8890 GC. After valve switching during the analysis, the system quickly stabilizes and maintains constant column flow rates, ensuring the detector delivers a stable baseline and consistent responses for target compounds. This results in highly reproducible chromatograms that are easy to integrate, enabling high-precision analysis of greenhouse gases.

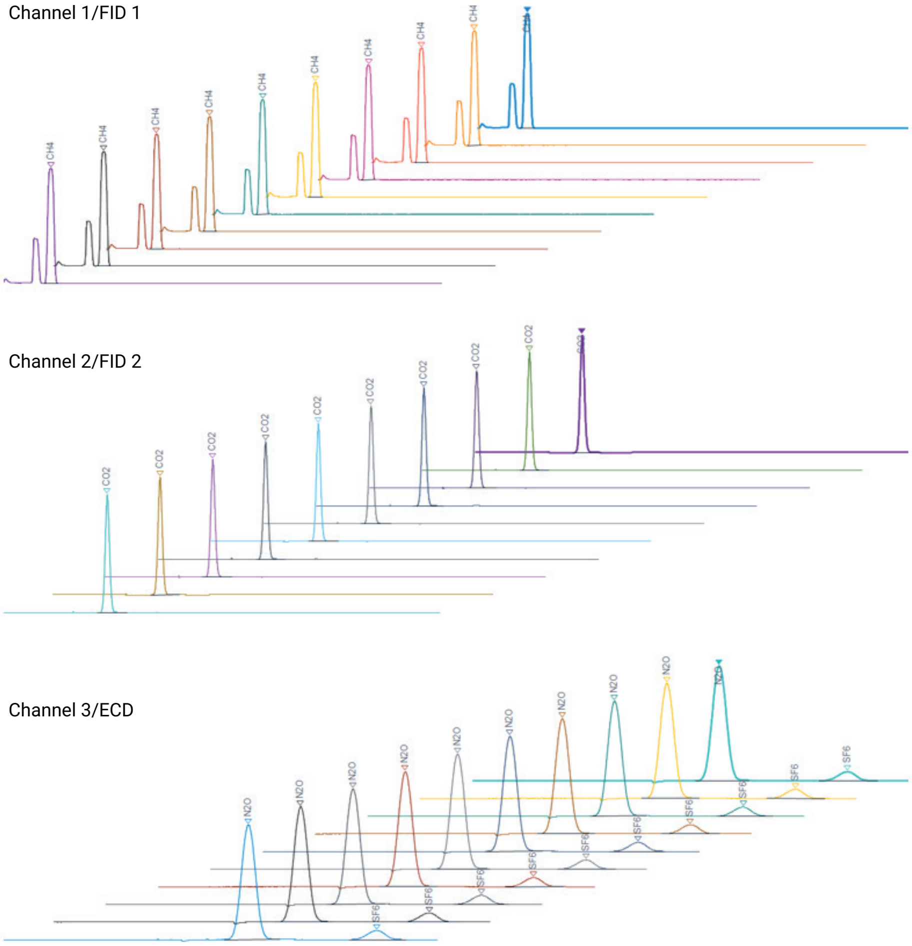

Figure 3. Chromatograms of standard gas sample 6 (n = 10).

Table 3. Area and RT precision of four analytes (n = 10).

	CH_4	CO_2	N_2O	SF_6
RT (min)	0.960	2.067	4.803	7.311
RT %RSD	0.146	0.004	0.018	0.077
Area	143.867 (pA×s)	3,587.574 (pA×s)	16,972.690 (Hz×s)	1,711.740 (Hz×s)
Area %RSD	0.055	0.011	0.048	0.321

Linearity

The system's linearity was evaluated using standard gases 1 to 5, with the concentration ranges of each compound covering their actual concentrations in ambient air. The external standard calibration curves for the four target compounds exhibited excellent linearity, with regression coefficients better than 0.999 (Figure 4). The outstanding linearity ensures the accuracy of quantitative results.

If the greenhouse gas concentrations in the atmosphere fluctuate minimally throughout the year, a single-point calibration method can be used to improve analytical efficiency and reduce operation costs. Specifically, if the standard gas concentration is very close to the actual sample concentration and falls within the linear range, the response factor for the target compound can be obtained using a single calibration gas. The target compound's response in the actual sample is then divided by the response factor to calculate the actual concentration of greenhouse gases in the atmosphere.

The single-point calibration method is employed based on the excellent linearity of the calibration curves validated during method verification. If the greenhouse gas concentrations in ambient air fluctuate significantly, quantitative analysis based on the full calibration curve will yield more accurate results.

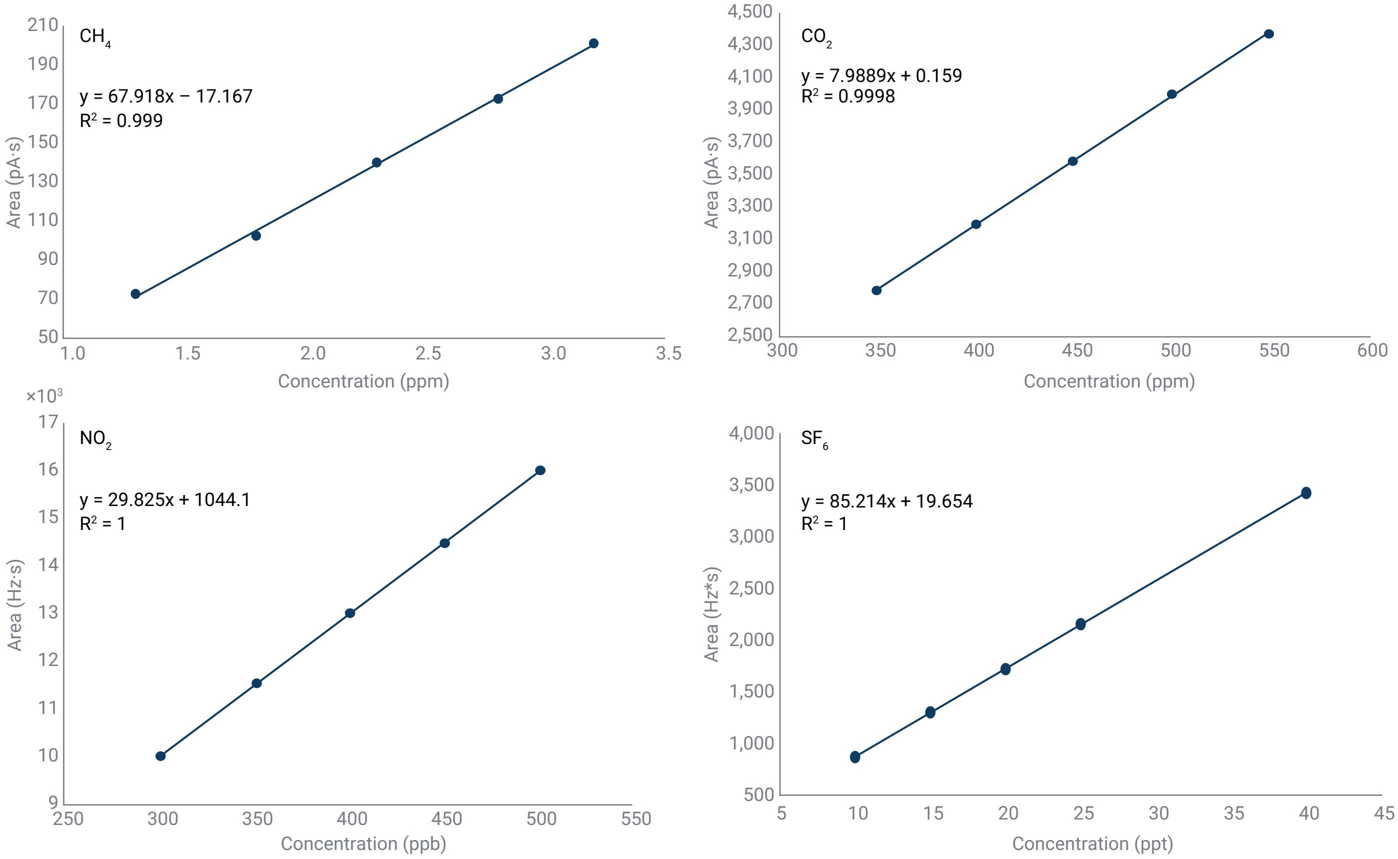

Figure 4. Linearity results for the four greenhouse gases, CH_4, CO_2, NO_2, and SF_6.

Method detection limit (MDL)

The MDL was evaluated according to the technical guideline for the development of environmental monitoring analytical method standards HJ168-2020.[3] The standard gas sample 1 was diluted to concentrations 3 to 10 times the detection limit of the target compounds. The diluted gas was then measured seven times to obtain the standard deviation of the measured concentrations. The MDL was calculated using Equation 1. Evaluation results across multiple 8890 GC platforms demonstrated that the MDL for methane was below 10 ppb, and the MDL for SF_6 was below 1 ppt. Table 4 lists the MDLs for four greenhouse gases obtained using one 8890 GC system. The exceptional MDLs ensure that greenhouse gases in the atmosphere can produce high responses on the 8890 GC system, enabling accurate quantification of target compounds and reliable monitoring of their concentration change trends.

Equation 1.

$$MDL = t(n - 1, 0.99) \times S$$

Where:

n = Number of measurements = 7

t = t-distribution value (one-sided) with degrees of freedom of n – 1 at a 99% confidence level; in this method, t = 3.143

S = Standard deviation of seven parallel measurements

Table 4. MDL of the four greenhouse gases.

Compounds	Average of Measured Concentration (mol/mol)	Standard Deviation (mol/mol)	MDL (mol/mol)
Methane	0.017×10^{-6}	0.0016×10^{-6}	0.0050×10^{-6}
Carbon Dioxide	2.80×10^{-6}	0.1905×10^{-6}	0.599×10^{-6}
Nitrous Oxide	2.75×10^{-9}	0.1595×10^{-9}	0.501×10^{-9}
Sulfur Hexafluoride	1.02×10^{-12}	0.0801×10^{-12}	0.252×10^{-12}

Conclusion

Based on its exceptional pneumatic control and valve-based flow path design, the multivalve/multicolumn Agilent 8890 GC system achieves high-sensitivity and high-precision measurements of four key greenhouse gases. This is accomplished through optimized and precise control of sample flow rate/volume, selection of premium analytical columns, and the use of highly stable and robust FID and ECD.

Standard gas samples of CO_2, CH_4, N_2O, and SF_6, with concentrations equivalent to atmospheric levels, were measured continuously 10 times. The measurement precision for these gases was better than 0.05%, 0.1%, 0.1%, and 0.5%, respectively, fully meeting the high-precision monitoring requirements of environmental monitoring stations at various levels for target greenhouse gases. Compared to other monitoring solutions, this approach is based on a stable and reliable gas chromatography platform that is technically easier to master and deploy. It represents a trusted solution developed by Agilent to assist in establishing a greenhouse gas monitoring network in China.

References

1. GB/T 31705-2015: In Situ Measurement of Background Atmospheric Carbon Dioxide and Methane Concentration by Gas Chromatographic (GC) System.
2. Wang, C. Simultaneous Analysis of Greenhouse Gases Using Gas Chromatography. *Agilent Technologies application brief*, publication number 5990-5129CHCN, **2010**.
3. HJ 168-2020: The Technical Guideline for the Development of Environmental Monitoring Analytical Method Standards.

www.agilent.com

DE-010305

Printed in the USA, October 28, 2025
5994-8744EN