Application Note

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Analysis of Trace Permanent Gases and Greenhouse Gases Using Agilent 5977C GC/MSD and HES

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Abstract

This application note presents a solution for the determination of 10 trace permanent gases and greenhouse gases using the Agilent 5977C GC/MSD with high-efficiency source (HES). The solution demonstrates exceptional sensitivity with detection limits down to the ppb level, as well as excellent repeatability and linearity. It is suitable for carbon dioxide (CO_2) reduction gas detection, greenhouse gas analysis, and permanent gas impurity analysis in hydrogen (H_2) for vehicular fuel applications.

Introduction

At the United Nations General Assembly on 22 September 2020, the Chinese government pledged to achieve carbon peak by 2030 and achieve carbon neutrality by 2060. Driven by the goal of "carbon peaking and carbon neutrality", related industries have not only accelerated industrial chain restructuring but also significantly increased investment in scientific research. For example, in the field of green energy development and utilization, China has prioritized support for the H_2 energy and H_2 fuel cell industries. In scientific research, studies on the green conversion of CO_2 are advancing vigorously, while the environmental protection sector is systematically implementing greenhouse gas monitoring programs. These industries and fields are involved in the analysis of permanent gases and greenhouse gases, including the analysis of CO_2 reduction gases and impurity analysis in H_2 for vehicular fuel applications.

GC with valve switching techniques has long been the gold-standard methodology for analyzing such gases. Agilent has developed a series of GC solutions tailored for CO_2 reduction product detection, greenhouse gas analysis, and gas impurity profiling in H_2 for vehicular fuel applications. These solutions provide robust analytical support for researchers and testing laboratories. However, in studies of isotopic tracer products from CO_2 reduction and the conversion rates of reduction reactions, the isotopically labeled and nonlabeled compounds cannot be separated using conventional columns. Consequently, high-sensitivity GC/MS becomes the preferred choice to address these analytical challenges.

This study developed an analytical protocol for simultaneous detection of multiple gases through a single injection using the 5977C GC/MSD equipped with an HES.

Experimental

Reagents and samples

The standard gas mixture used in this experiment was purchased from Air Liquide, and its composition is listed in Table 1. The gas mixture was subsequently diluted using the Agilent dynamic dilution system to evaluate the system's analytical performance, including dynamic range and detection limits.

Table 1. Composition of the standard gas mixture used in the experiment.

Number	Name	Concentration (ppm, v/v)	Gas Type
1	Hydrogen (H_2)	4.95	Permanent
2	Oxygen (O_2)	5.02	Permanent
3	Nitrogen (N_2)	5.03	Permanent
4	Argon (Ar)	4.97	Permanent
5	Methane (CH_4)	4.96	Permanent/greenhouse
6	Carbon monoxide (CO)	5.00	Permanent
7	Carbon dioxide (CO_2)	5.01	Greenhouse
8	Nitrous oxide (N_2O)	5.04	Greenhouse
9	Ethylene (C_2H_4)	4.96	Common chemical
10	Sulfur hexafluoride (SF_6)	4.97	Greenhouse
11	Helium (He)	Balance gas	Permanent

Instrumentation

The Agilent 8890 GC and 5977C GC/MSD equipped with HES and dual columns (as shown in the schematic in Figure 1) were used. The system's valve switching technology enabled two separation modes, namely single-column mode and dual-column mode.

GC and MS conditions are displayed in Tables 2 and 3, respectively.

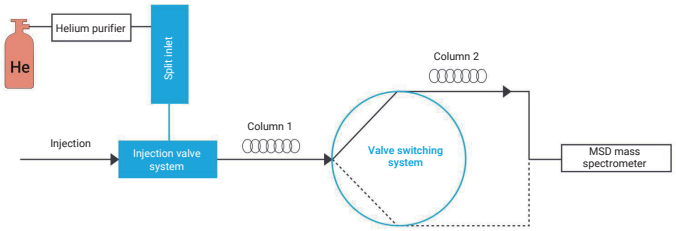

Figure 1. Schematic of instrument system

Table 2. GC conditions.

Parameter	Value
Instrument	Agilent 8890 GC
Valve Oven Temperature	50 °C
Inlet Temperature	100 °C
Carrier Gas	High-purity helium (purity 99.9995%)
Analytical Column	Column 1: Agilent J&W Pora-BOND Q, 25 m × 0.25 mm × 3 µm (p/n CP7348PT) Column 2: Agilent J&W CP-Molsieve 5 Å, 25 m × 0.25 mm × 30 µm (p/n CP7533) Note: Both are PLOT columns with integrated particle traps
Column Flow	Constant flow, 1.2 mL/min
Column Oven Ramp Program	Dual-column mode: 40 °C for 4.5 min, then 50 °C/min to 110 °C and 110 °C for 6 min Single-column mode: 35 °C for 10 min
Transfer Line Temperature	230 °C

Table 3. MS conditions.

Parameter	Value
Instrument	Agilent 5977C GC/MSD with HES
Ion Source Temperature	230 °C
Quadrupole Temperature	150 °C
Ionization Energy	70 eV (low ionization energy for H_2 detection to minimize interference from He)
Acquisition Mode	SIM mode, *m/z*: H_2 (2); O_2 (16, 32); N_2 (14, 28); Ar (40); CH_4 (15, 16); CO (12, 28); C_2H_4 (27, 28); CO_2 (12, 44); N_2O (30, 44); SF_6 (89, 127)
Gain Factor	0.5

Results and Discussion

Dual-column mode

Separation of 10 gases, including permanent and greenhouse gases

In dual-column mode, all target gases except O_2 and Ar could be chromatographically separated. Particularly noteworthy were CO and N_2, as the *m/z* 28 ion was the most abundant fragment ion for both gases. In dual-column mode, these two gases were fully separated, and the *m/z* 28 ion could serve as the quantitative ion for both gases, achieving excellent sensitivity. Although O_2 and Ar coeluted, their distinct fragment ions enabled unambiguous differentiation based on the MS results. Figure 2 shows the total ion chromatograms of nine target gases (O_2, N_2, Ar, CH_4, CO, C_2H_4, CO_2, N_2O, and SF_6, excluding H_2) obtained under conventional 70 eV ionization energy conditions.

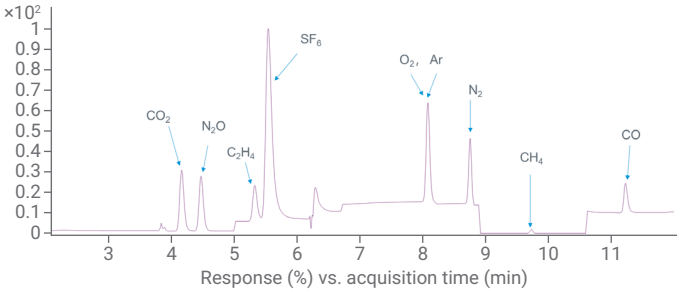

Figure 2. Total ion chromatograms of nine target gases (excluding H_2) at a concentration of 5 ppm (v/v) under conventional 70 eV ionization conditions.

For H_2, detection was conducted under low ionization energy conditions. These conditions could also be used to detect the other nine gases, but the sensitivity was lower compared to the conventional 70 eV ionization energy conditions. Figure 3 illustrates the total ion chromatograms of all 10 target gases (including H_2) under low ionization energy conditions, while Figure 4 displays their extracted ion chromatograms under the same conditions.

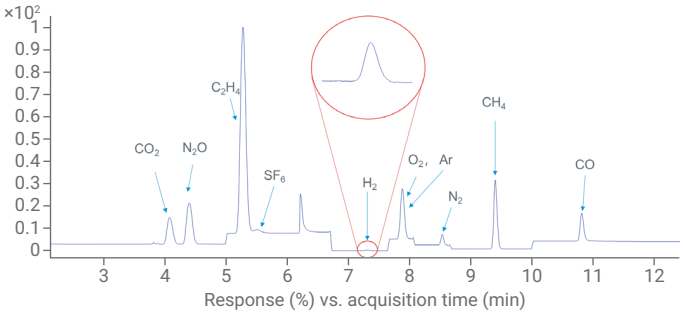

Figure 3. Total ion chromatograms of all 10 target gases (including H_2) at a concentration of 5 ppm (v/v) under low ionization energy conditions.

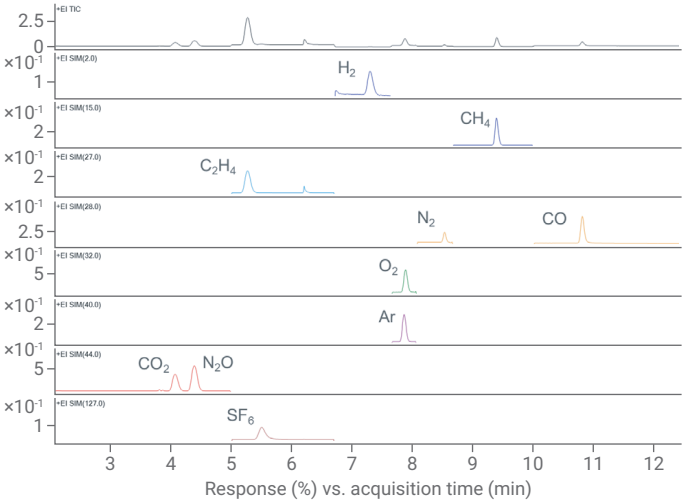

Figure 4. Extracted ion chromatograms of all 10 target gases (including H_2) at a concentration of 5 ppm (v/v) under low ionization energy conditions.

Repeatability and detection limits in dual-column mode

Analytical repeatability and detection limits under conventional 70 eV ionization energy conditions

The analytical repeatability and sensitivity were investigated under 70 eV ionization energy conditions. The standard gas mixture was diluted to 25 ppb using a dynamic dilutor, followed by eight consecutive injections. Analytical repeatability was evaluated using the relative standard deviation (RSD%) of the peak area, and the method detection limit (MDL) was calculated using the following formula:

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

Where t(n – 1, 0.99) represents the t-value at a 99% confidence level with n − 1 degrees of freedom, and n is the number of replicates.

Some of these results are shown in Table 4. As shown in Table 4, the peak area RSDs (%) of six target gases, including CO_2, N_2O, C_2H_4, SF_6, CH_4, and CO, ranged from 0.7 to 4.9%, and their corresponding MDLs were all below 4.1 ppb. N_2, O_2, and Ar could not be diluted to the target concentration due to issues such as air infiltration and valve leakage during the dilution process, thus their MDLs were not determined. However, based on the response ratios of O_2, N_2, and Ar relative to other gases in the standard gas mixture, it can be inferred that their MDLs would likely be at the ppb level. For precise quantification of these three gases at ppb levels, a purged valve oven is recommended to eliminate air contamination during valve switching.

Figure 5 shows the overlaid chromatograms of six target gases (CO_2, N_2O, C_2H_4, SF_6, CH_4, and CO) from eight consecutive injections of the standard gas mixture at a concentration of 25 ppb (v/v) under conventional 70 eV ionization conditions. As shown in the figure, the repeatability was excellent for these six compounds, with near-perfect overlap of the overlaid chromatograms. Figure 6 shows the extracted ion chromatograms and signal-to-noise (S/N) ratio results for CO_2, N_2O, C_2H_4, SF_6, CH_4, and CO at a concentration of 10 ppb (v/v). The results demonstrate that favorable S/N ratios were maintained even at a concentration as low as 10 ppb, highlighting the exceptional sensitivity of the system.

Table 4. Repeatability and detection limits of selected target gases.

Target Gas	CO_2			N_2O			C_2H_4		
Sample name	Peak Area	RSD (%)	MDL (ppb, v/v)	Peak Area	RSD (%)	MDL (ppb, v/v)	Peak Area	RSD (%)	MDL (ppb, v/v)
STD 25 ppb-1	838	2.5	2.2	140	2.5	2.0	128	3.3	2.1
STD 25 ppb-2	842			136			123		
STD 25 ppb-3	853			139			125		
STD 25 ppb-4	830			133			120		
STD 25 ppb-5	815			135			118		
STD 25 ppb-6	802			138			119		
STD 25 ppb-7	802			130			117		
STD 25 ppb-8	803			139			119		
Target Gas	**SF_6**			**CH_4**			**CO**		
Sample name	**Peak Area**	**RSD (%)**	**MDL (ppb, v/v)**	**Peak Area**	**RSD (%)**	**MDL (ppb, v/v)**	**Peak Area**	**RSD (%)**	**MDL (ppb, v/v)**
STD 25 ppb-1	3105	0.7	0.63	29	1.5	1.2	395	4.9	4.1
STD 25 ppb-2	3091			29			383		
STD 25 ppb-3	3127			29			391		
STD 25 ppb-4	3096			29			352		
STD 25 ppb-5	3067			29			386		
STD 25 ppb-6	3080			28			345		
STD 25 ppb-7	3053			28			385		
STD 25 ppb-8	3094			28			378		

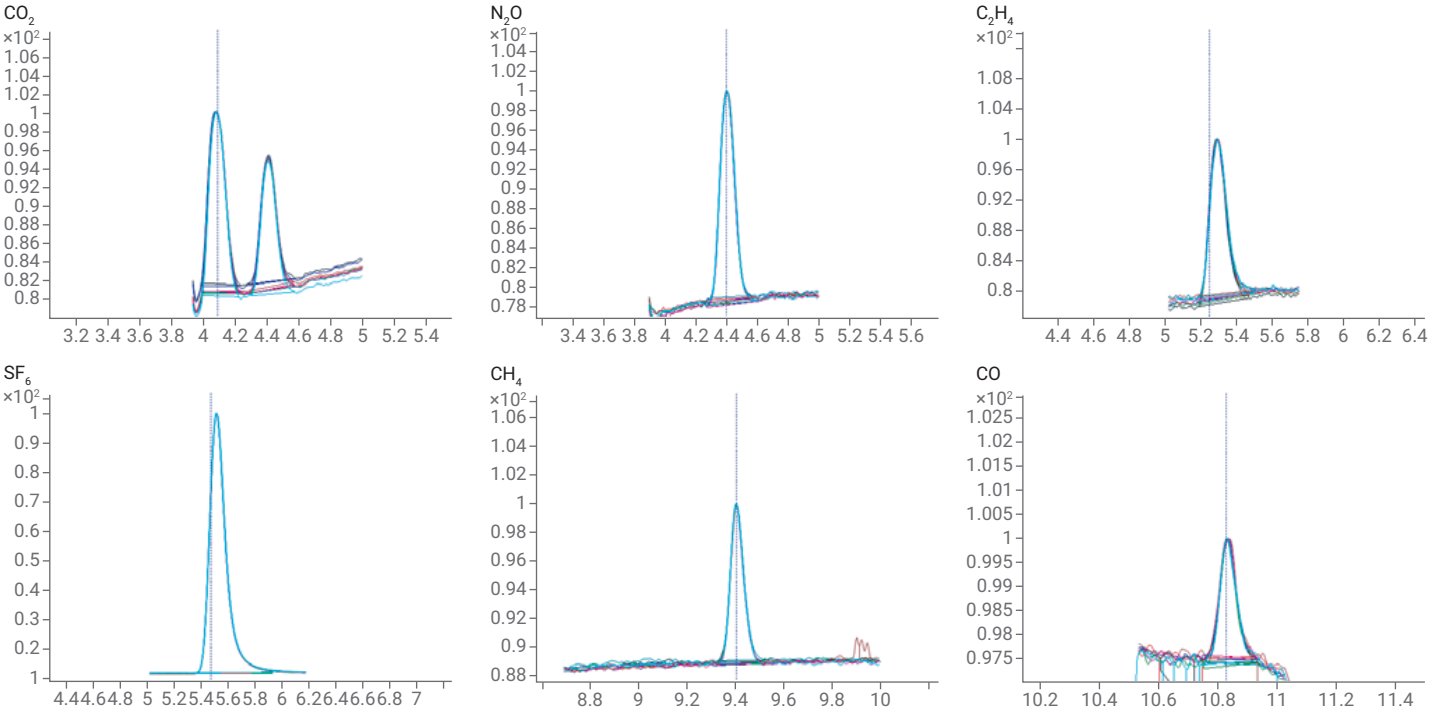

Figure 5. Overlaid chromatograms of selected target gases from eight consecutive injections of the standard gas mixture at a concentration of 25 ppb (v/v) under conventional 70 eV ionization conditions.

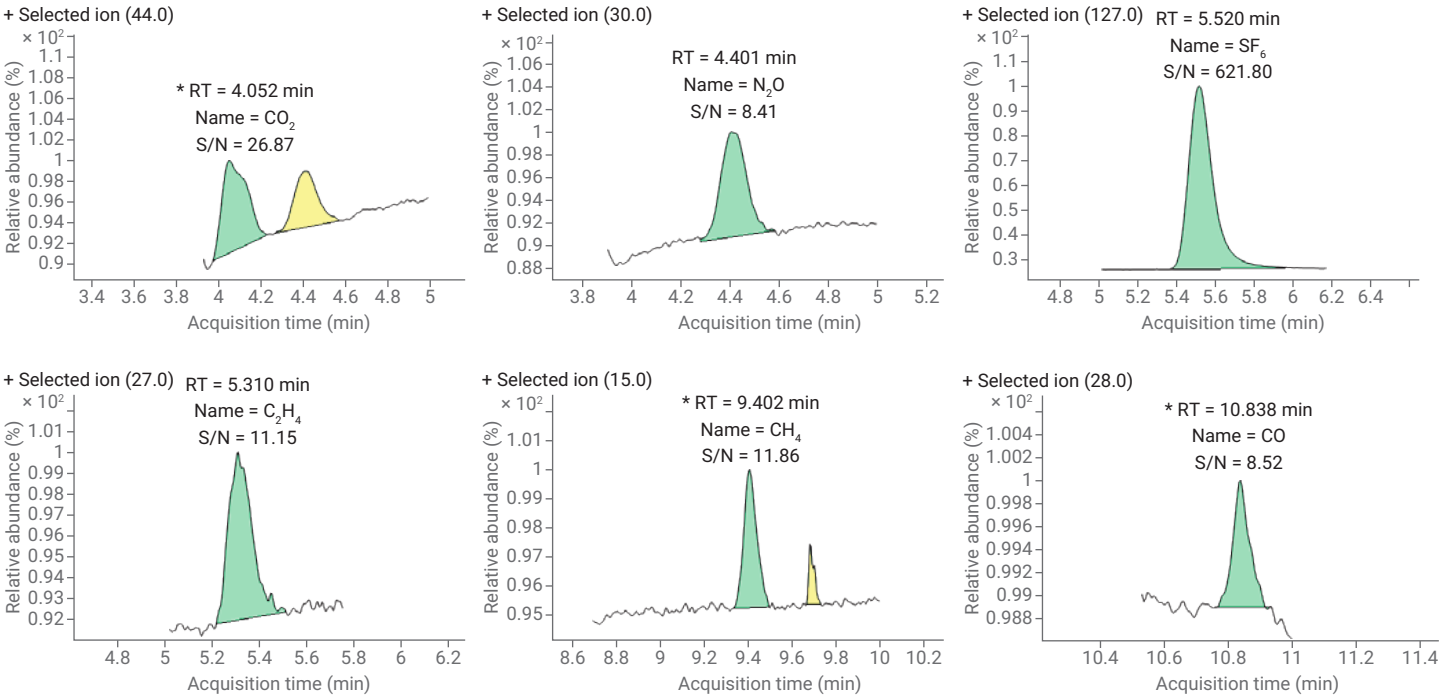

Figure 6. Extracted ion chromatograms and S/N ratios of selected target gases at a concentration of 10 ppb (v/v).

Analytical repeatability under low ionization energy conditions

Under conventional 70 eV ionization energy conditions, H_2 at ppm level or lower concentrations could not be detected due to the interference from helium as the carrier gas. By optimizing instrument parameters, we achieved reliable detection of H_2 and the other nine gases at ppm and sub-ppm levels under these low ionization energy conditions. Analytical reproducibility of the 10 target gases was further evaluated under low energy conditions. The standard gas mixture at a concentration of 5 ppm was injected consecutively eight times, and analytical repeatability was assessed by calculating the peak area RSD (%) for the 10 target gases. As shown in Table 5, the peak area RSD (%) for all 10 target gases ranged from 1.7 to 5.1%, demonstrating excellent reproducibility. Figure 7 shows an overlay of the total ion chromatograms obtained from eight consecutive injections of a 5 ppm (v/v) standard gas mixture under low ionization energy conditions. The figure demonstrates that all chromatographic peaks overlapped almost completely, reflecting the excellent repeatability of the system.

Table 5. Repeatability data for 10 gases at low ionization energy.

Target Gas	CO_2		N_2O		C_2H_4		SF_6		H_2		Ar		O_2		N_2		CH_4		CO	
Number	Peak Area	RSD (%)	Peak Area	RSD (%)	Peak Area	RSD (%)	Peak Area	RSD (%)	Peak Area	RSD (%)	Peak Area	RSD (%)	Peak Area	RSD (%)	Peak Area	RSD (%)	Peak Area	RSD (%)	Peak Area	RSD (%)
1	1958		3141		1059		389		45		808		1728		384		1314		1314	
2	1898		3060		1049		385		45		796		1756		390		1296		1296	
3	1880		3029		1030		376		44		785		1644		354		1284		1284	
4	1893	1.8	3026	2	1033	2	376	5.1	45	4.7	787	2.3	1727	2.9	390	4.8	1291	2.1	1291	1.7
5	1918		2996		1036		363		44		788		1644		358		1298		1298	
6	1976		2968		1048		333		48		828		1726		395		1309		1309	
7	1903		2974		1002		369		49		764		1638		360		1247		1247	
8	1938		2961		1003		349		48		786		1660		355		1273		1273	

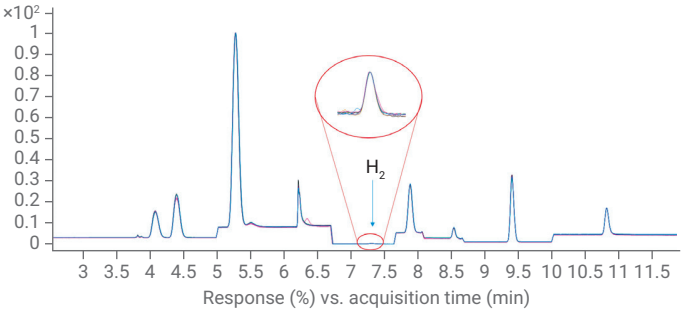

Figure 7. Overlay of total ion chromatograms obtained by eight consecutive injections of a 5 ppm (v/v) standard gas mixture under low ionization energy conditions.

Hydrogen detection limit under low ionization energy conditions

The standard gas mixture was diluted to 500 ppb and subsequently tested. The extracted ion chromatogram of H_2 is shown in Figure 8. As shown in the figure, the S/N ratio of H_2 was close to 3, indicating an MDL of approximately 500 ppb for H_2 under low ionization energy conditions. To specifically evaluate the reproducibility of H_2 analysis at this MDL concentration, a 500-ppb standard gas mixture was injected consecutively eight times to calculate the peak area RSD (%) of H_2. The resulting peak area RSD (%) was 6%, with near-perfect overlap of the overlaid chromatographic peaks (as shown in Figure 9), demonstrating excellent analytical repeatability.

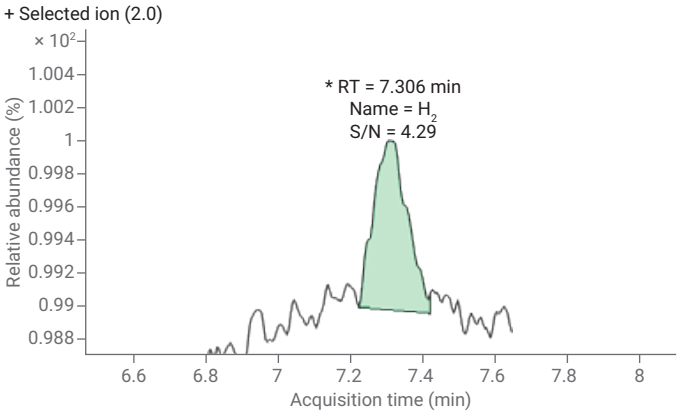

Figure 8. Extracted ion chromatogram of 500 ppb (v/v) H_2 under low ionization energy conditions.

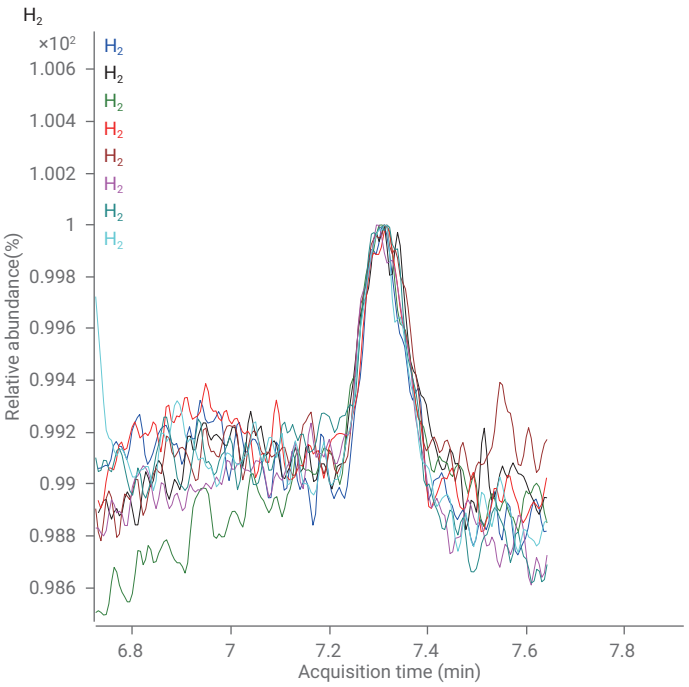

Figure 9. Overlaid chromatograms of H_2 from eight consecutive injections of a 500 ppb (v/v) standard gas mixture under low ionization energy conditions.

Linearity in dual-column mode

The 5-ppm standard gas mixture was diluted to target concentrations of 10, 12.5, 25, 50, 100, 125, 250, and 500 ppb, respectively. Then, each diluted standard gas mixture and the original undiluted mixture were measured under conventional 70 eV ionization energy conditions. The calibration curve was established by plotting concentration (X-axis) against peak area (Y-axis), with the regression curve forced through the origin. The results for six target gases (CO_2, N_2O, C_2H_4, SF_6, CH_4, and CO) are shown in Figure 10. As shown in the figure, the linear correlation coefficients (R^2) for all six target gases were greater than 0.9993 across the 10 to 5000 ppb concentration range, indicating excellent linearity of the method. However, N_2, O_2, and Ar were excluded from the linearity assessment due to hardware limitations, preventing their dilution to the target concentrations. Similarly, the linearity of H_2 was not investigated because its minimum detectable concentration under low ionization energy conditions was 0.5 ppm (v/v), which was outside the evaluated range.

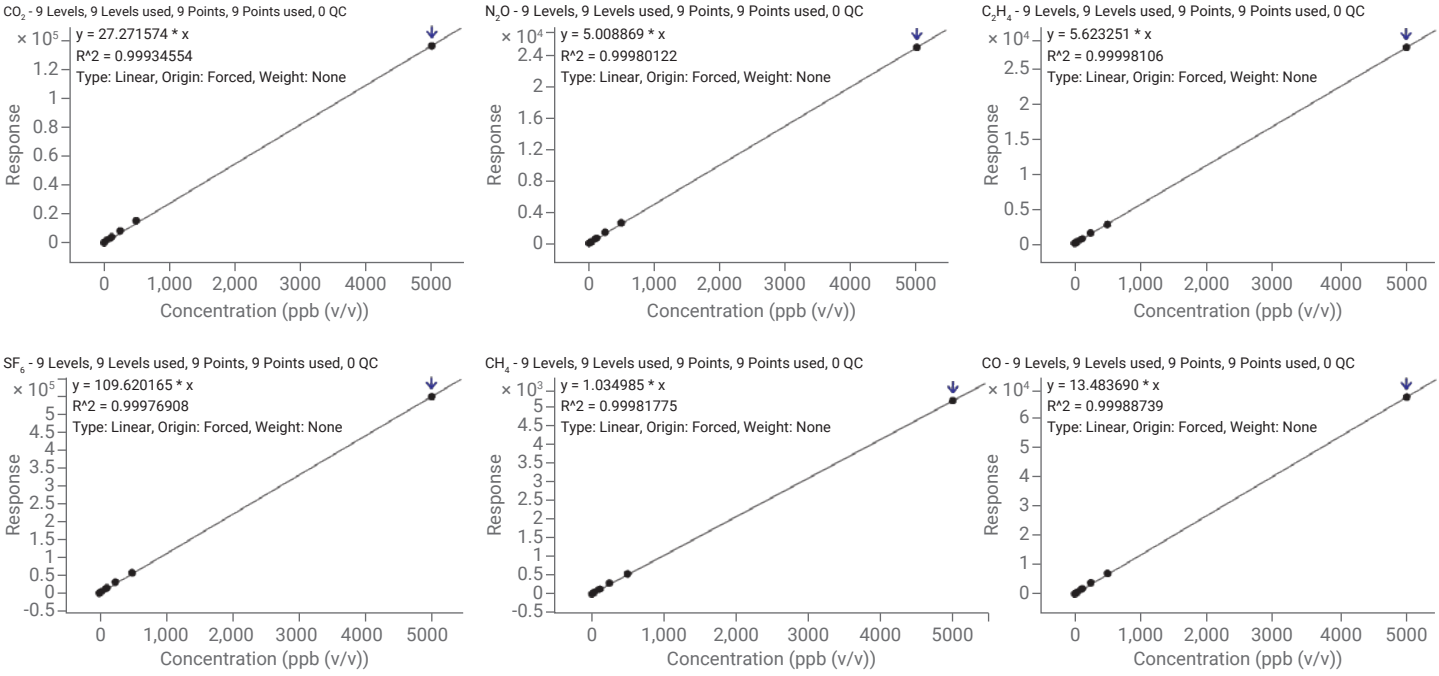

Figure 10. Calibration curves for some gases in the concentration range of 10 to 5000 ppb (v/v).

Single-column mode

Separation of 10 permanent gases and greenhouse gases in single-column mode

In single-column mode, a single PoraBOND Q column was used, and the analysis time was significantly shorter, achieving rapid separation within 7.5 minutes. However, in this mode, five target gases, including H_2, O_2, Ar, N_2, and CO, coeluted and had to be identified by their distinct fragment ions. Importantly, CO and N_2 coeluted in single-column mode, and the most abundant fragment ions of both were *m/z* 28, which could be distinguished by MS. Thus, lower-abundance fragment ions were selected to distinguish and quantify the two gases (*m/z* 14 for N_2 quantification and *m/z* 12 for CO quantification). Since fragment ions with lower abundance were used for the quantification of CO and N_2, the detection sensitivity was notably inferior to that achieved in dual-column mode. Figure 11 shows the total ion chromatograms of these nine target gases (excluding H_2) obtained in single-column mode under conventional 70 eV ionization energy conditions. Figure 12 shows the extracted ion chromatograms of these nine target gases (excluding H_2).

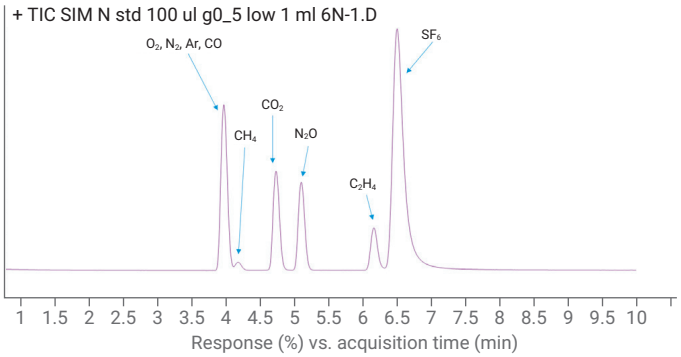

Figure 11. Total ion chromatograms of nine target gases (excluding H_2) at a concentration of 5 ppm (v/v) in single-column mode under conventional 70 eV ionization energy conditions.

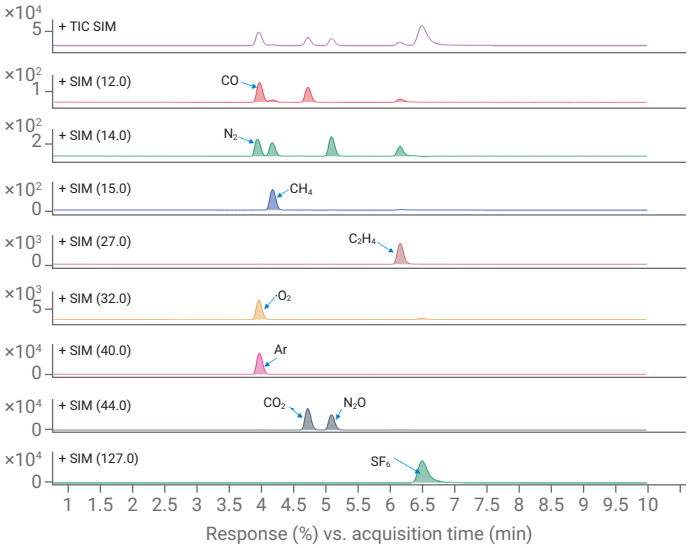

Figure 12. Extracted ion chromatograms of nine target gases (excluding H_2) at a concentration of 5 ppm (v/v).

Detection limit of carbon monoxide in single-column mode

In single-column mode under conventional 70 eV ionization energy conditions, the detection limits for these nine target gases (excluding H_2) were evaluated. The results showed that the detection limits of CH_4, CO_2, N_2O, C_2H_4, and SF_6 were consistent with those achieved in dual-column mode, which will not be reiterated here. N_2, O_2, and Ar could not be diluted to the target concentration due to air infiltration during the dilution process, so their detection limits were not determined. CO requires special consideration. In dual-column mode, CO was separated on a CP-Molsieve 5 Å PLOT column without coelution, and its most abundant ion (*m/z* 28) was used as the quantitative ion. However, in single-column mode, CO coeluted with N_2, and the less abundant fragment ion (*m/z* 12) was used as quantitative ion for CO. Therefore, the detection limit of CO in single-column mode was investigated and discussed separately. The detection results of CO at concentrations of 50 (v/v) and 100 ppb (v/v) are shown in Figures 13 and 14, respectively. Based on the S/N ratio results, it was inferred that the method detection limit of CO was approximately 50 ppb (v/v).

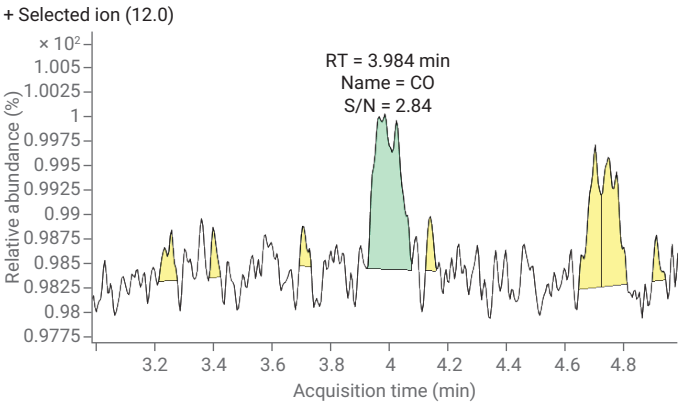

Figure 13. Detection result of CO at a concentration of 50 ppb (v/v) in single-column mode.

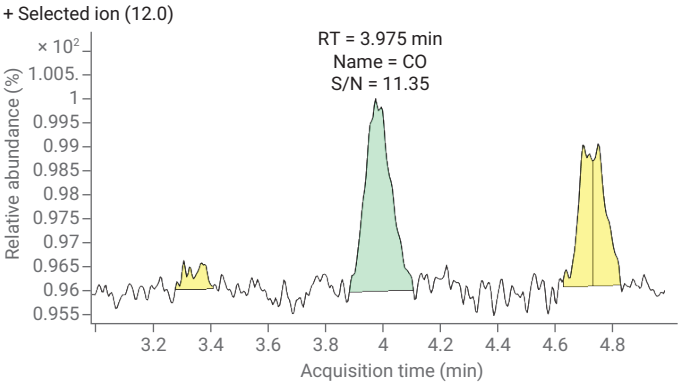

Figure 14. Detection result of CO at a concentration of 100 ppb (v/v) in single-column mode.

Linearity of carbon monoxide in single-column mode

The 5-ppm standard gas mixture was diluted to target concentrations of 50, 100, 125, 250, and 500 ppb, and then each diluted standard gas mixture and the original undiluted mixture (5 ppm) were measured in single-column mode under conventional 70 eV ionization energy conditions. The calibration curve was constructed by plotting concentration (X-axis) against peak area (Y-axis). The calibration curve for CO is shown in Figure 15. As shown in the figure, the linear correlation coefficients (R^2) were greater than 0.995 in the concentration ranges of 50 to 5000 ppb and 50 to 500 ppb, indicating excellent linearity of the method in both concentration ranges. Therefore, if H_2 detection is not required and the target CO concentration in the sample is above 50 ppb, dual-column mode is not necessary, and single-column mode is sufficient to meet analytical requirements.

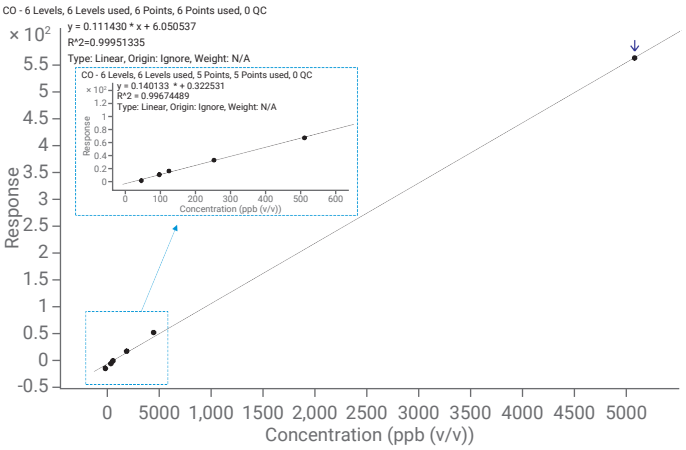

Figure 15. Calibration curves for CO in the concentration ranges of 50 to 5000 ppb (v/v) and 50 to 500 ppb (v/v) in single-column mode.

Conclusion

This application note presents a solution for the determination of 10 trace permanent gases and greenhouse gases using the Agilent 5977C GC/MSD with HES, achieving detection limits at the ppb level with excellent repeatability and linearity. The system employs a dual-column configuration, and its valve switching technology enables two modes, namely the single- and the dual-column modes. In single-column mode, nine target gases (excluding H_2) can be analyzed with high speed. In dual-column mode, all 10 target gases can be detected and chromatographically separated except for O_2 and Ar. The detection sensitivity for gases such as CO and N_2 is significantly improved, and the detection limits of certain gases can be below 10 ppb (v/v). For H_2 analysis, the detection limit reaches 500 ppb (v/v) under low ionization energy conditions. Furthermore, the analytical solution developed in this study supports customizable configurations tailored to specific user requirements. For example, an optional backflush module can be integrated to eliminate H_2O and heavy compounds. Additionally, the analysis scope can be expanded based on specific needs.

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