Analyze Permanent Gases and Light Hydrocarbons with Agilent J&W Particle Trap Columns

Application Note

Energy and Chemicals

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Abstract

Agilent J&W PoraBOND Q PT and CP-Molsieve 5Å PT particle trap columns were evaluated by analyzing permanent gases and light C1-C2 hydrocarbons with GC/TCD, configured with two valves using helium and argon as carrier gases, respectively. The CP-Molsieve 5Å PT column was used to separate Ar, O_2, H_2, N_2, CH_4, and CO. Excellent resolution, especially for Ar and O_2, was achieved. The combination of a PoraBOND Q PT column and isolation valve was used for the separation of CO_2 and light hydrocarbons. RSD for peak area obtained from 250 replicate analyses of a standard gas mix was below 0.5%, and no signal spikes related to particle shedding were observed using helium as carrier gas. PLOT PT columns also exhibit good repeatability and stability when using argon as carrier gas, which can greatly improve hydrogen sensitivity.

Agilent J&W PLOT PT column with integrated dual-ended particle trap technology can protect isolation valves from particles that can shed from the PLOT column, and offer increased stability and reliability for valve-switching analysis.

Agilent Technologies

Introduction

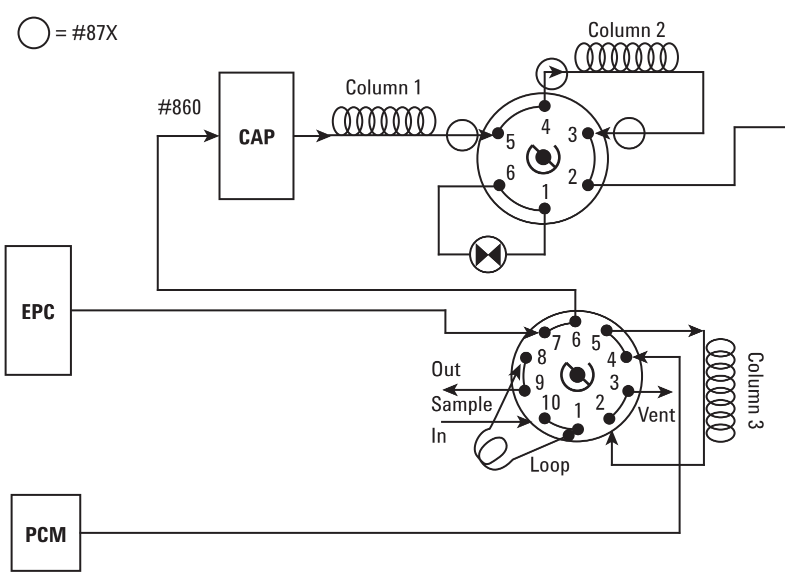
Analysis of permanent gases and light hydrocarbons has been widely applied in the petrochemical, chemical and energy industries. Permanent gases such as H_2, O_2, Ar, N_2, CH_4, CO, and CO_2 are the common target compounds in refinery gases, natural gas, petroleum gas, purified gas, water gas, stack gas, and so on. Understanding the concentration of these components can be important to control manufacturing processes and production quality.

Normally, packed columns and porous layer open tubular (PLOT) capillary columns are used to analyze permanent gases and light hydrocarbons [1,2]. PLOT columns have the disadvantage that the stationary phase layer is not mechanically stable, and so the shedding of particles can plug or even damage column switching valves, and cause detector contamination. Connecting particle trap devices to the columns still presents a potential risk of leakage or blockage at the connectors.

Agilent J&W PLOT PT columns include integrated particle traps on both ends of the column to offer greater stability than conventional PLOT and packed columns [3,4]. This application demonstrates the performance of Agilent J&W PoraBOND Q PT and CP-Molsieve 5Å PT columns for the analysis of permanent gases and C1-C2 light hydrocarbons using an Agilent GC/TCD equipped with two valves. Typically, nitrogen or argon is used as carrier gas for the determination of hydrogen and helium. Hydrogen or helium carrier is used for the detection of all other permanent gases. In this work, the PoraBOND Q PT and CP-Molsieve 5Å PT columns were evaluated by analyzing permanent gases and light hydrocarbons using helium and argon as carrier gases, respectively. In line with common methods, isothermal and temperature-programmed approaches were used for testing.

Materials and Methods

The experiments were performed on an Agilent 7890A gas chromatograph equipped with a thermal conductivity detector (TCD). The valve diagram and column configurations are shown in Figure 1. This application is based on a 10-port valve (valve 1) for gas sampling and back flushing heavier components; normally, components heavier than ethylene are back flushed to vent. A packed column, HayeSep Q (Column 3) associated with the 10-port valve, was used as a pre-column for this application. A 10-m porous polymer Q column, such as 10 m × 0.53 mm PoraBOND Q PT, can also be used as a pre-column and can provide easier operation and is more widely available for this analysis. Two PLOT columns are needed for the separation: (1) a CP-Molsieve 5Å PT column for permanent gases such as H_2, CO, Ar, O_2, N_2, and CH_4 and (2) a PoraBOND Q PT column for the heavier gases, CO_2 and C_2 hydrocarbons. A 6-port column-isolation valve (valve 2), with adjustable restrictor, was used to switch the CP-Molsieve 5Å PT column in and out of the carrier stream.



Column 1: Agilent J&W PoroBOND Q PT, 30 m × 0.53 mm, 10 µm, (p/n CP7354PT)

Column 2: Agilent J&W CP-Molsieve 5A PT, 50 m × 0.53 mm, 50 µm, (p/n CP7539PT)

Column 3: Agilent J&W HayeSep Q, 80/100, 3 ft m × 1/8, UltiMetal (p/n G3591-81020)

Figure 1. Valve diagram.

Conditions 1

Columns:	See Columns and conditions
Carrier:	Helium, constant flow, 10 mL/min
Inlet:	Split/splitless inlet, 150 °C, split ratio 10:1
Oven (isothermal method):	40 °C
Oven (temperature programmed method):	40 °C for 7.8 min, at 40 °C/min to 120 °C, 120 °C for 5 min
Valve box temperature:	100 °C
PCM flow:	10 mL/min
Detector:	TCD, 200 °C, reference gas 30 mL/min, makeup gas 5 mL/min
Sample loop:	1 mL
Time events:	
Event	Time (min)
Valve 1 ON	0.01
Valve 1 OFF	1.4
Valve 2 ON	2.4
Valve 2 OFF	4.6
TCD negative polarity ON	6.0
TCD negative polarity OFF	6.4

Conditions 2

Columns:	See Columns and conditions
Carrier:	Argon, constant flow, 10 mL/min
Inlet:	Split/splitless inlet, 150 °C, split ratio 10:1
Oven (isothermal method):	70 °C
Oven (temperature programmed method):	70 °C for 7.4 min, at 40 °C /min to 120 °C, 120 °C for 8 min
Valve box temperature:	100 °C
PCM flow:	10 mL/min
Detector:	TCD, 200 °C, TCD negative polarity ON, reference gas: 30 mL/min, makeup gas: 5 mL/min
Sample loop:	1 mL
Time events:	
Event	Time (min)
Valve 1 ON	0.01
Valve 1 OFF	1.5
Valve 2 ON	2.75
Valve 2 OFF	4.15

Columns and conditions

Column	Agilent J&W	Dimensions	Part number
1	PoraBOND Q PT	25 m × 0.53 mm, 10 µm with 2 particle traps	CP7354PT
2	CP-Molsieve 5Å PT	50 m × 0.53 mm, 50 µm with 2 particle traps	CP7539PT
3	HayeSep Q 80/100 mesh	3 ft × 1/8 inch, 2 mm, UltiMetal	(G3591-81020

Agilent supplies

BTO Non-stick 11 mm septa, 50/pk	(p/n 5183-4757)
Ultra Inert Liner, universal	(p/n 5190-2295)
Universal column nut	(p/n 5181-8830)
Internal nut	(p/n G2855-20530)
Flexible Metal ferrule, 0.53 mm id	(p/n G3188-27506)
Micrometering valve for flow balancing gas flows of 2 to 50 mL/min	(p/n 0101-0633)
Tube assembly, inert, 1/16 inch × 50 cm, 0.020 inch id	(p/n G1580-60062)

A fixed standard mix gas, supplied by Messer Gas Products Co., Ltd.(Wujiang), was used. The components and concentrations are listed in Table 1.

Table 1. Standard gas mix

No.	Component	Concentration	CAS NO.
1	O_2	0.5%	7782-44-7
2	CO_2	3.0%	00124-38-9
3	C_2H_4	2.0%	74-85-1
4	C_2H_6	4.0%	74-84-0
5	CH_4	10.0%	74-82-8
6	H_2	15.0%	133-74-0
7	CO	1.0%	630-08-0
8	Ar	1.0%	7440-37-1
9	N_2	Balance	7782-44-7

Results and Discussion

Helium carrier gas

Resolution

Performing the analysis isothermally at 40 °C, the standard gas mixture was analyzed using Conditions 1. A 6-port column isolation valve (valve 2) was switched off to allow unresolved peaks containing H_2, Ar, O_2, N_2, carbon monoxide, and methane to enter the CP-Molsieve 5Å PT column as they eluted from the PoraBOND Q PT column. Once these compounds were in the CP-Molsieve 5Å PT column, it was isolated (valve 2 on). After CO_2 and heaver compounds eluted from the PoraBOND Q PT column and were detected, valve 2 was turned off to elute the trapped components to the TCD through the CP-Molsieve 5Å PT column. As shown in Figure 2, baseline separation was achieved for all compounds. The PoraBOND Q PT column was excellent for the separation of CO_2 and hydrocarbons (C_2H_4 and C_2H_6). The 50 m × 0.53 mm, 50 µm CP-Molsieve 5Å PT column exhibited high retention for permanent gases. In particular, excellent resolution of argon and oxygen was obtained at oven temperatures of 40 °C, because separation of these two compounds is quite challenging at room temperature, especially using multivalve and multicolumn systems.

Helium carrier gas provided the desired sensitivity for most gases except hydrogen. Hydrogen was detected as a negative peak because hydrogen has a small difference in thermal conductivity compared to helium. By setting the TCD polarity as shown in the time events table, the hydrogen signal could be reversed from a negative peak to a positive one, as shown in the chromatogram.

Permanent gases and C_2 hydrocarbons were separated by the PoraBOND Q PT column and CP-Molsieve 5Å PT column in approximately 31 minutes at oven temperatures of 40 °C. Run time can be decreased greatly with a higher oven temperature. For example, run time is about 22 minutes if performing the analysis isothermally at 50 °C, but with a compromise to peak resolution of Ar and O_2 which reduced from 1.5 to 1.2.

Using a GC oven temperature program is another option for fast analysis. As illustrated in Figure 3, excellent resolution for all components and short analysis time were achieved.

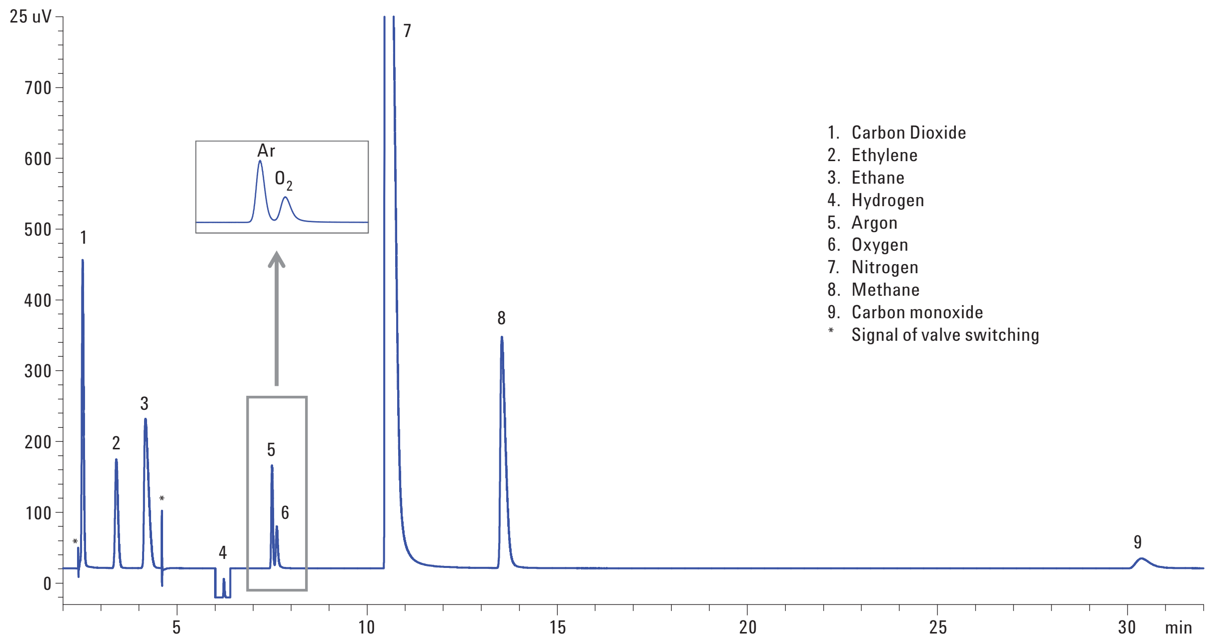


Figure 2. Chromatogram of standard gas mix, carrier gas helium, oven 40 °C.

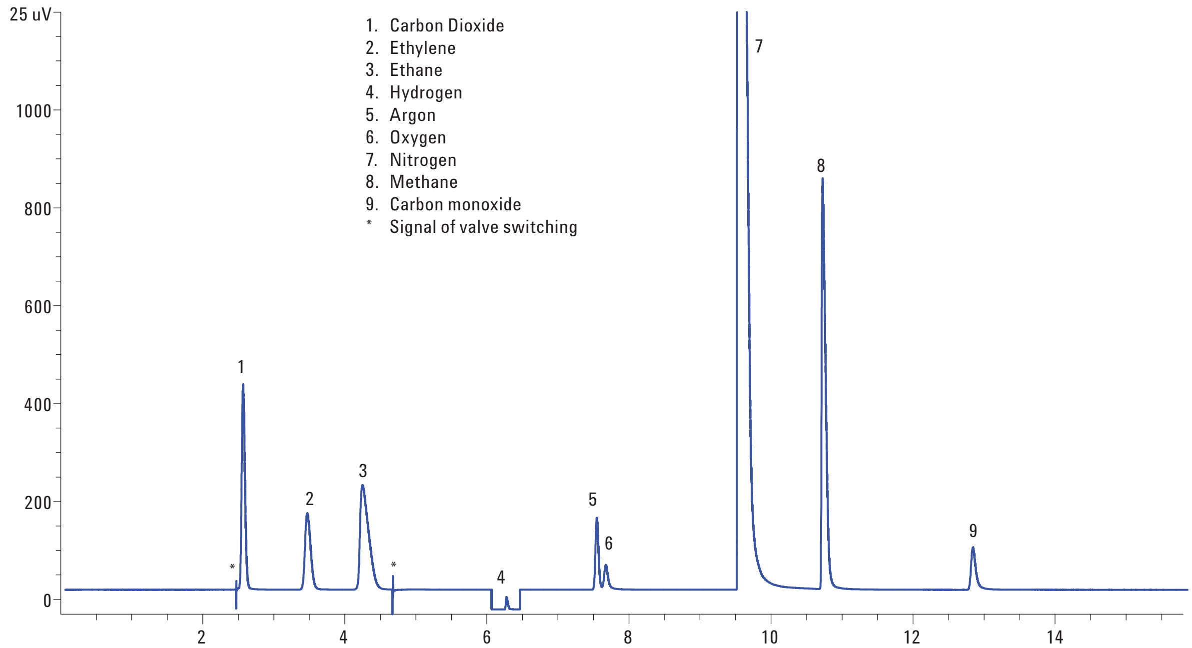


Figure 3. Chromatogram of standard gas mix, carrier gas: helium, oven 40 °C (7.8 minutes) to 120 °C at 40 °C/min, 120 °C (5 minutes).

Repeatability

To evaluate the performance of the PLOT PT columns, 250 injections were made of a standard mix gas over 5 days using Condition 1 (temperature programmed method) to demonstrate stability and repeatability. The results are given in Table 2 and Figure 4.

Table 2. Repeatability data of standard gas mix

	Mean peak area ± SD (% RSD)				
Compound	**Day 1 N = 50**	**Day 2 N = 50**	**Day 3 N = 50**	**Day 4 N = 50**	**Day 5 N = 50**
CO_2	1382.56 ± 4.76 (0.34%)	1382.19 ± 4.24 (0.31%)	1381.91 ± 4.43 0.32%)	1380.98± 4.66 (0.34%)	1383.71 ± 3.95 (0.29%)
C_2H_4	852.48 ± 1.20 (0.14%)	851.97 ± 1.18 (0.14%)	851.14 ± 1.20 (0.14%)	850.55 ± 1.15 (0.14%)	853.09 ± 1.28 (0.15%)
C_2H_6	1792.29 ± 2.42 (0.14%)	1790.93 ± 3.16 (0.18%)	1789.55 ± 2.41 (0.13%)	1788.53 ± 2.60 (0.15%)	1793.89± 3.03 (0.17%)
H_2	46.80 ± 0.20 (0.43%)	46.81 ± 0.22 (0.48%)	46.77 ± 0.23 (0.48%)	46.67 ± 0.19 (0.40%)	46.46 ± 0.19 (0.40%)
Ar	432.63 ± 1.02 (0.24%)	432.24 ± 1.07 (0.25%)	432.00 ± 1.75 (0.40%)	431.33 ± 1.17 (0.27%)	432.84 ± 1.20 (0.28%)
O_2	186.63 ± 0.91 (0.49%)	186.85 ± 0.96 (0.51%)	186.57 ± 0.74 (0.40%)	186.40 ± 0.70 (0.37%)	187.17 ± 0.84 (0.45%)
N_2	24267.55 ± 60.69 (0.25%)	24240.60 ± 57.76 (0.24%)	24208.97 ± 68.62 (0.28%)	24204.36 ± 57.40 (0.24%)	24270.01 ±70.31 (0.29%)
CH_4	3167.02± 6.81 (0.22%)	3167.62± 8.10 (0.26%)	3163.54± 6.09 (0.19%)	3163.06± 7.97 (0.25%)	3172.06± 8.60 (0.25%)
CO	391.19± 1.50 (0.38%)	390.99± 1.41 (0.36%)	390.66± 1.57 (0.40%)	390.61± 1.53 (0.39%)	391.99± 1.68 (0.43%)

The average peak area for multiple injections of the standard gas mix showed low standard deviation (SD) and had relative standard deviations (RSD) below 0.5% over five consecutive days of analyses. As shown in Figure 4, good reproducibility of retention times can be achieved by using J&W PLOT PT columns. RSD obtained from 250 replicate analyses of standard gas mix was found to be below 0.06%. This showed that excellent repeatability (intra-day) and long-term precision (inter-day) was achieved using the J&W PLOT PT columns.

No signal spikes related to particle shedding were observed in the 250 injections of the standard mix gas, indicating that J&W PLOT PT columns with integrated dual-ended particle trap technology could prevent particle shedding, protect column switching valves, and offer increased stability and reliability for multicolumn-valve analysis.

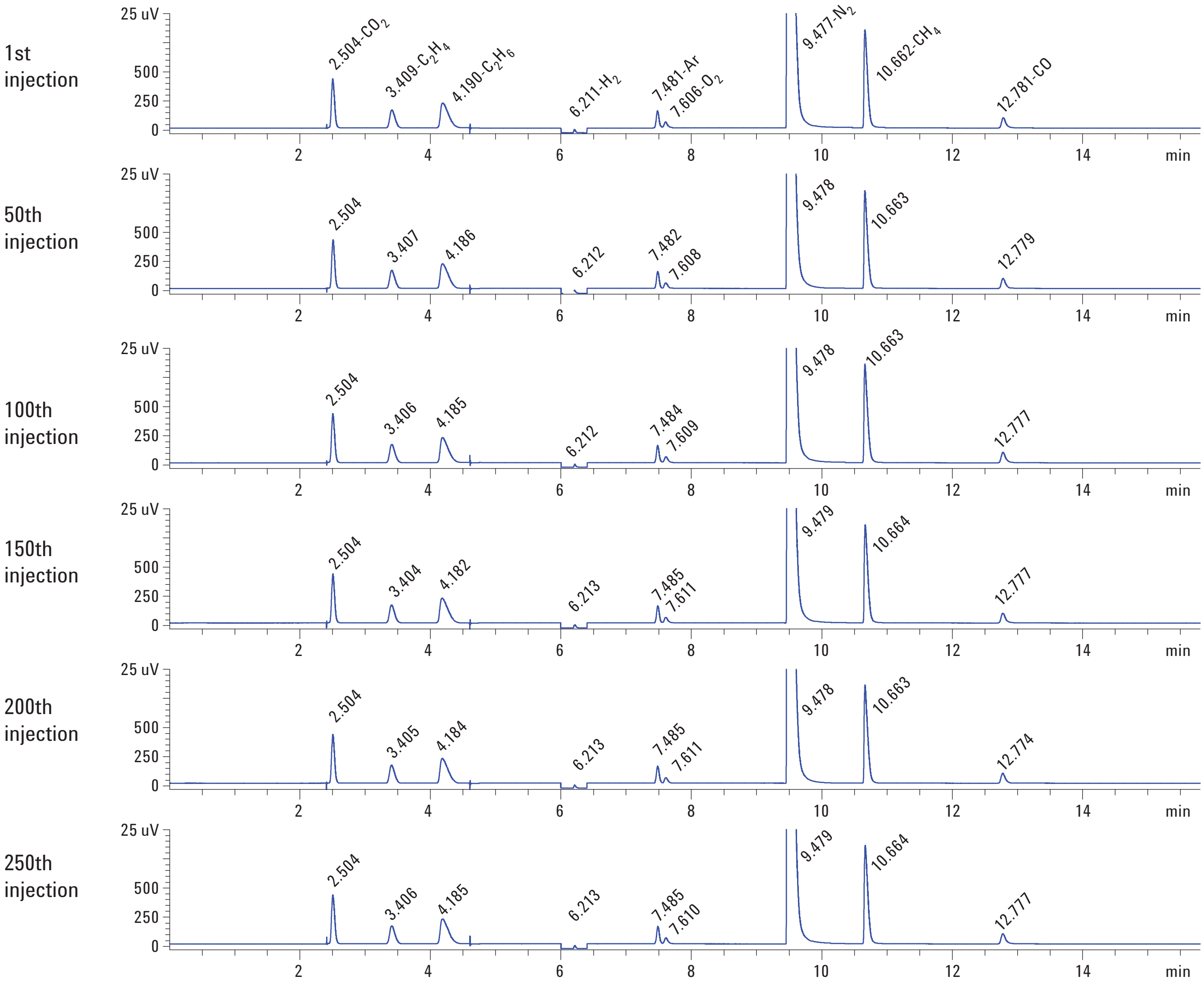


Figure 4. Chromatograms of a standard gas mix for different injections; carrier gas helium, oven 40 °C (7.8 minutes) to 120 °C at 40 °C/min, 120 °C (5 minutes).

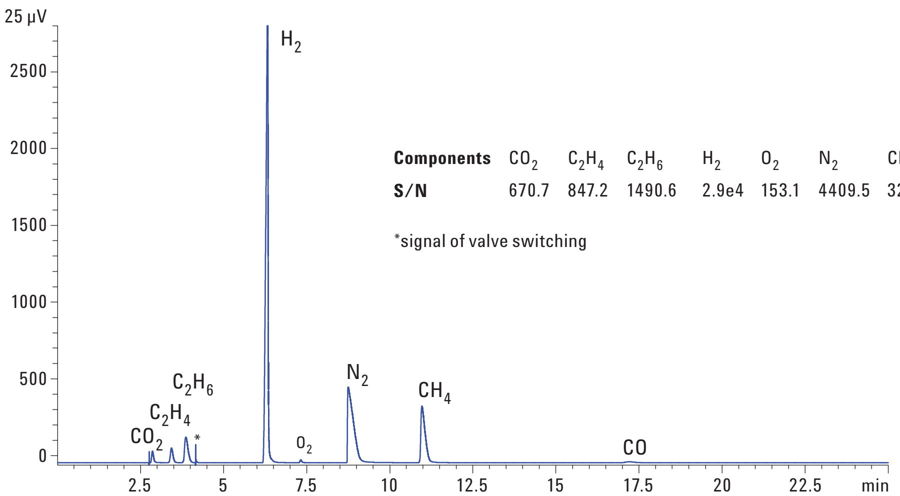
Argon carrier gas

As shown above, thermal conductivity detection with helium carrier gas can be used for permanent gases analysis such as Ar, O_2, N_2, CO, and CO_2. However, hydrogen has only a small difference in thermal conductivity compared to helium, making analysis of hydrogen by TCD using helium carrier gas difficult.

To achieve better response for hydrogen, TCD with nitrogen or argon as a carrier is typically required. Without considering the separation of argon and oxygen, the analysis can be performed isothermally at 70 °C, or at 70 °C as an initial oven temperature with short analysis and cycle times. As illustrated in Figures 5 and 6, argon was a good carrier gas that could greatly improve hydrogen sensitivity. Argon, however, will result in decreased sensitivity for the other permanent gases because argon's thermal conductivity is much closer to those of the measured analytes. Signal-to-noise (S/N) ratio based on a 1 mL loop and 10:1 split ratio in Figures 5 and 6 can also be used as a reference. A lower split ratio will give higher S/N ratio.

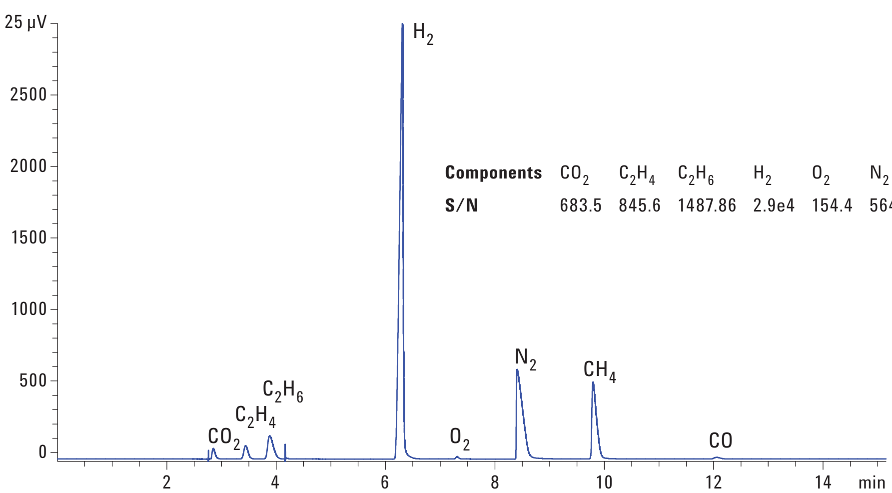
Argon provided the best detection of hydrogen, while still providing adequate detection of the other components of interest.

Due to unique stabilization technology, J&W PLOT PT columns exhibit excellent repeatability for 10 injections of a standard gas mix tested using Condition 2 (temperature programmed method). Relative standard deviations (RSD) were less than 1.9%. No signal spikes related to particle shedding were observed.



Components	CO_2	C_2H_4	C_2H_6	H_2	O_2	N_2	CH_4	CO
S/N	670.7	847.2	1490.6	2.9e4	153.1	4409.5	3291.4	43.8

Figure 5. Chromatogram of a standard gas mix, carrier gas argon, oven 70 °C.



Components	CO_2	C_2H_4	C_2H_6	H_2	O_2	N_2	CH_4	CO
S/N	683.5	845.6	1487.86	2.9e4	154.4	5643.3	4782.0	104.5

Figure 6. Chromatogram of a standard gas mix; carrier gas argon, oven 70 °C for 7.4 minutes, at 40 °C /min to 120 °C, 120 °C for 8 minutes.

Conclusions

Agilent J&W PoraBOND Q PT and CP-Molsieve 5Å PT columns were evaluated by analyzing permanent gases and light hydrocarbons by GC/ TCD equipped with two valves using helium and argon as carrier, respectively. Excellent repeatability, stability and resolution for the analyses were demonstrated. The results showed that Agilent J&W PLOT PT columns are the ideal choice for valve-switching applications.

References

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Printed in the USA
June 24, 2014
5991-4873EN

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