Analysis of Permanent Gases and Methane with the Agilent 6820 Gas Chromatograph

Application

Petrochemical

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Abstract

The analysis of permanent gases using the Agilent 6820 equipped with a single filament Thermal Conductivity Detector is described. For these applications, the Agilent 6820 gas chromatography system was configured with a gas sampling valve, isolation valve, and purged-packed inlet. Agilent Cerity for Chemical QA/QC was used to control the 6820 GC and to provide data acquisition and date analysis. HP-PLOT Q and HP-Molsieve 5A columns were used for separation of permanent gases including carbon monoxide, carbon dioxide, oxygen, nitrogen, hydrogen, and methane. Carbon dioxide, oxygen, nitrogen, and methane were analyzed at the level of 10 ppm. In this application note, benefits of the Agilent 6820 Thermal Conductivity Detector are also discussed.

Introduction

Permanent gas analysis finds wide application in the fields of petrochemical, chemical, and energy industries. Permanent gases such as carbon monoxide, CO_2, O_2, N_2, and methane are common in refinery gases, natural gas, fuel cell gases, and many other industrial processes. Understanding the concentration of these components can be important for controlling manufacturing processes and production quality. For example, impurities such as carbon monoxide and CO_2 in polymer grade propylene and ethylene are deleterious to certain catalysts.

Several methods for permanent gas analysis based on packed columns are standardized. For example, the American Society for Testing and Materials (ASTM) D2504 covers the determination of H_2, N_2, O_2, and carbon monoxide at the parts-per-million (ppm) (v/v) level in C_2 and lighter hydrocarbon products [1]. ASTM D1946 analyzes permanent gases, methane, ethane, and ethylene [2]. The Chinese domestic standard method GB/T3394 determines carbon monoxide and CO_2 in polymer grade ethylene and propylene using a nickel catalyst accessory and Flame Ionization Detector (FID) [3]. This application offers a highly flexible system assembled with three porous layer open tubular (PLOT) capillary columns and rotary valves for analysis of permanent gases and light hydrocarbons. Compared to packed columns, PLOT columns offer many advantages including separation power, temperature range, stability, low bleed, and the ability to achieve lower detection limits.

Experimental

Experiments were performed on the Agilent 6820 GC equipped with a purged packed inlet and single filament Thermal Conductivity Detector (TCD). The valving diagram for the configuration used is presented in Figure 1, which shows two analysis systems. System 2 is used for analyzing hydrocarbons (spit/splitless inlet and FID) and is discussed in a separate application note. System 1 is used for analyzing permanent gases. This application is based on a 10-port valve (Valve 1) for gas sampling and backflush of the precolumn to the detector. Two HP-PLOT Q columns are associated with the 10-port valve. A 6-port column isolation valve (Valve 2), with adjustable restrictor, is used to switch the Molesieve 5A column in and out of the carrier stream. Valve 2 is switched to the OFF position to allow unresolved peaks containing air, carbon monoxide, and methane to enter the Molesieve 5A PLOT as they elute from the PLOT Q column. Once these components are in the Molesieve 5A column, it is isolated (Valve 2=ON). After heavier components and CO_2 elute from the PLOT column and are detected, Valve 2 is turned OFF to elute the trapped components to the single filament TCD through the 5A PLOT. The purged packed inlet is interfaced directly to the valve to provide a source of carrier gas.

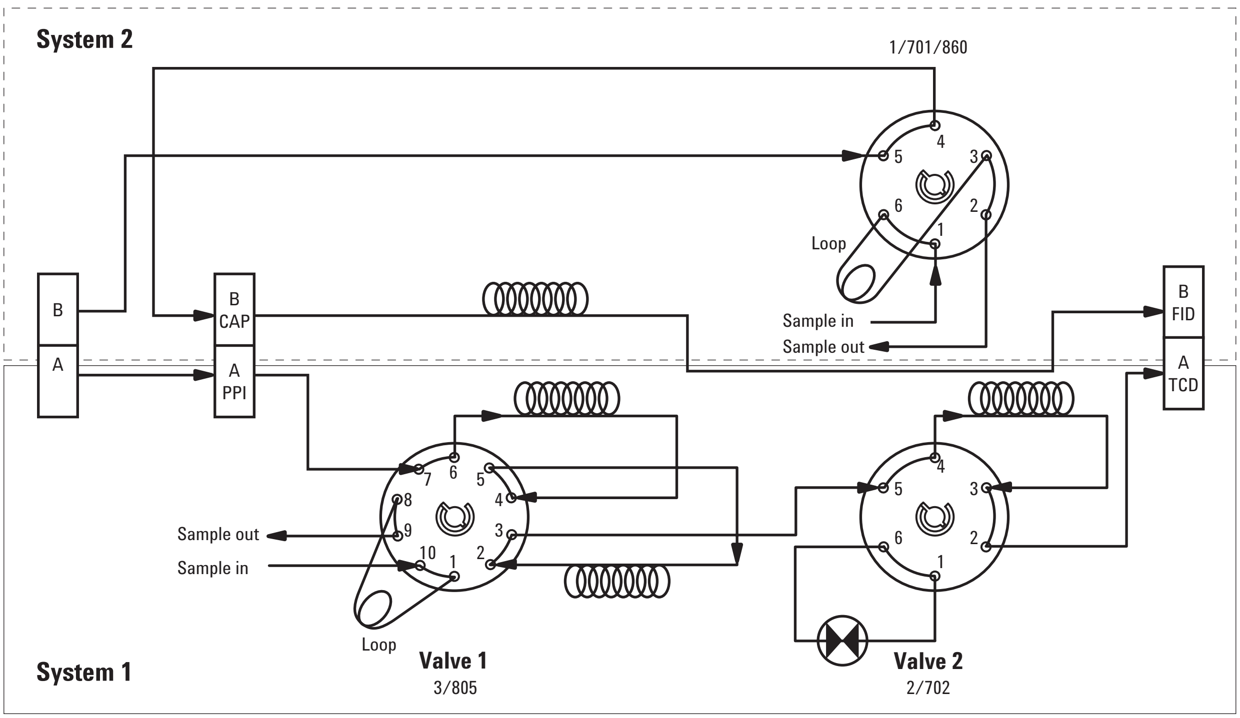

Figure 1. Valve diagram.

The analysis was performed by separating the gas sample into a two-column system. An HP-PLOT Q 15 m × 0.53 mm × 40 µm was used to separate hydrocarbons in the gas sample. An HP PLOT Molesieve 5A 30 m × 0.53 mm × 50 µm was used to separate O_2, N_2, carbon monoxide, and methane. An additional column, the HP PLOT Q 30 m × 0.53 mm × 40 µm, was used as the precolumn in a blackflush to detector configuration. The GC parameters are listed in Table 1.

Table 1. Gas Chromatographic Conditions: System 1

GC	Agilent 6820 Gas Chromatograph
Data system	Agilent NDS Cerity for QA/QC
Purged packed Inlet	50 °C
Valve temperature	80 °C
Sample loop	0.25 mL
Column flow (H_2)	4.8 mL/min
Column	HP-PLOT Q 15 m × 0.53 mm × 40 µm (p/n: 19095P-Q03)
	HP-PLOT Q 30 m × 0.53 mm × 40 µm (p/n: 19095P-Q04)
	HP PLOT Molesieve 5A 30 m × 0.53 mm × 50 µm (p/n: 19095P-MSO)
Oven	50 °C Isothermal
Detector	TCD, 180 °C
Reference	40 mL/min
Make up	10 mL/min

Special fused silica adapters and bulkhead fittings were used in this application to connect the megabore columns to the 1/16-inch tubing from the valves. These provide a reliable, airtight, low internal volume connection system for optimal chromatography. This connection is also important for ppm level gas applications. The fused silica adapter was used to help to decrease the leak risk from the column connection and to provide a zero dead volume connection of a capillary column to a valve. This adapter includes: a polyamide ferrule (p/n 0100-1512), counter-bored nut (p/n 0100-1511), polyamide liner (p/n 0100-1513 for 0.53 mm column), and a clear slotted tube (p/n 18900-20850). Figure 2 illustrates the parts used to attach the column to the bulkhead fitting in the oven.

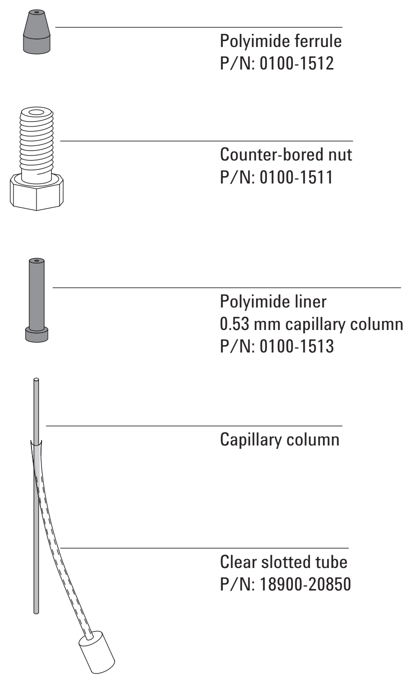

Figure 2. Installing capillary columns using fused silica adapters.

A fixed gas mix standard, supplied by Scott Specialty Gases Inc., was used in this application. This sample was dynamically blended or diluted to achieve concentrations down to 10 ppm per component [4]. The compounds and concentrations are listed in Table 2.

Table 2. Standard Mix Gas

Compound	Concentrations (ppm)
Carbon dioxide	100.6
Methane	100.8
Nitrogen	100.8
Oxygen	101.2

Agilent Cerity Networked Data System for Chemical QA/QC was used to control the 6820 GC and to provide data acquisition and reporting. Cerity was operated at a data acquisition rate of 5 Hz/0.04 min.

Results and Discussion

PLOT Columns

PLOT columns have an advantage of low bleed, which is important for trace analysis. A PLOT Molecular sieve 5A column exhibits a high retention for permanent gases. This makes permanent gas separations possible at starting oven temperatures of 50 °C. The PLOT Q column is excellent for the separation of CO_2 and hydrocarbons through C6, depending on the GC oven program used [5].

Agilent 6820 TCD

The TCD is a concentration sensitive detector. It is a simple, easy to use, low-cost detector suitable for the analysis of permanent gases, hydrocarbons, and many other gases. The single-filament flow-switching design eliminates the need for a reference column. This unique design alternately exposes the filament to column effluent and reference flows at a frequency of 10 Hz. Digital processing is used throughout. See Figure 3 for a cross-sectional diagram of the Agilent TCD.

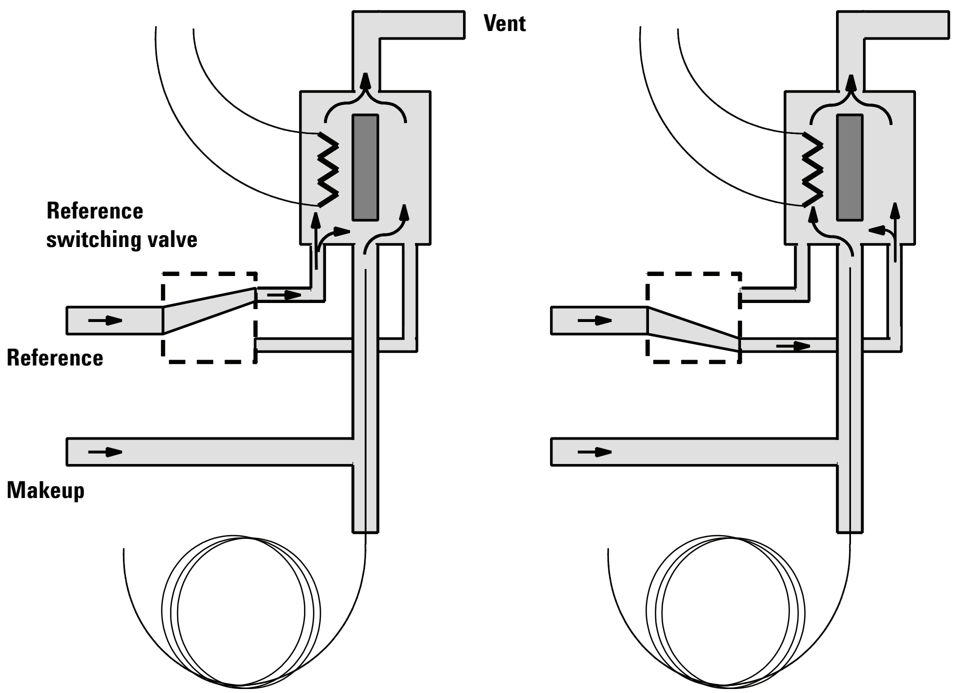

Figure 3. **Pneumatic diagram of the Agilent single-filament TCD.**

The most common TCD design is still based on the typical 4-element tungsten filament incorporated in a Wheatstone bridge design. This filament design requires dual channels (an analytical column and a blank column). The variation and column bleed in each channel can cause response changes, baseline noise, and drift. It is not an ideal approach for a capillary column application due to the large dead volume and the long time needed for stabilization. For low ppm level permanent gas applications such as N_2, carbon monoxide and CO_2, a dual-channel traditional TCD may not offer enough sensitivity and stability.

The Agilent single-filament TCD is optimized for use with capillary columns, improving the performance in sensitivity and stability. The cell volume is only 3.5 µL for fast response. The single-filament design eliminates the need to "match" the resistance or temperature coefficients of the filament, resulting in reduced noise and drift. These improved performance features contribute to chromatographic fidelity and sensitivity in many low-level gas analysis problems.

Low Level Permanent Gases

Figure 4 shows the chromatogram of a 100 ppm permanent gas mix. Hydrogen was used as the carrier gas and is a common choice for TCDs in China. CO_2, O_2, N_2, and methane gave a good response in this experiment. Because He is the balance gas in the standard sample (at a high concentration), O_2 separated on the tailing of the He peak.

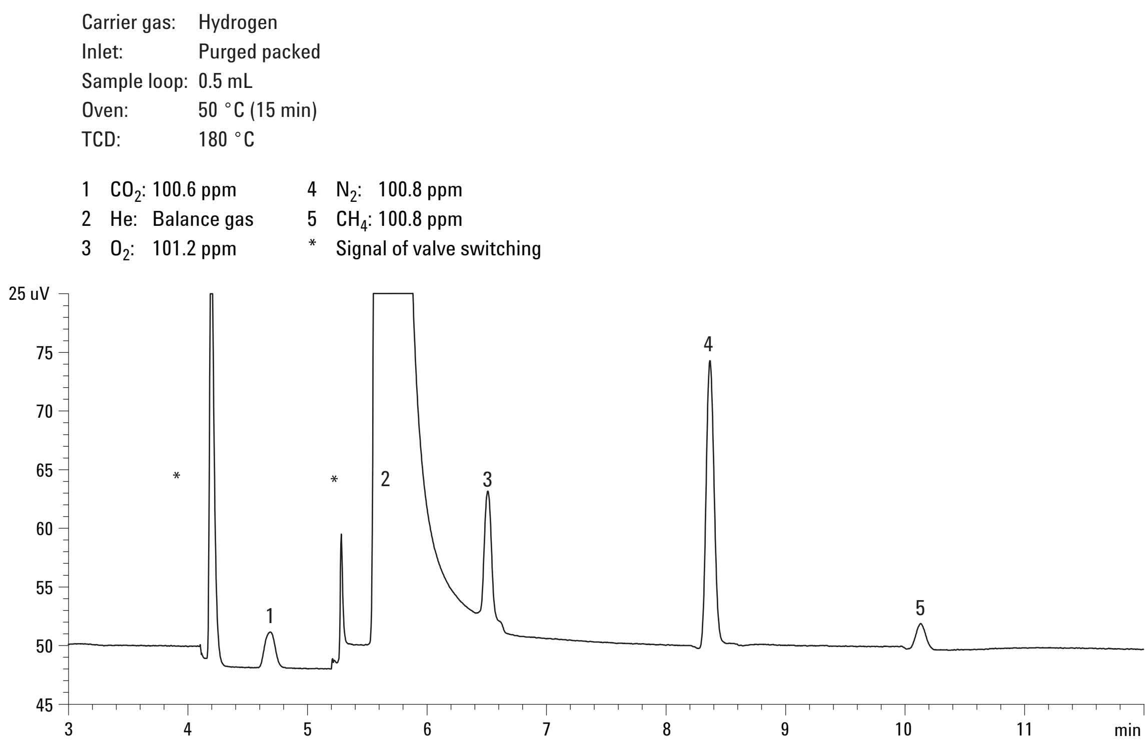

Figure 4. Chromatogram of 100 ppm permanent gas calibration standard, Carrier gas: Hydrogen.

Figure 5 shows the chromatogram of a permanent gas mix at 10 ppm. Dynamic blending was used to dilute the standard to the 10 ppm level. Chemical traps were used to efficiently condition carrier and diluent gas streams. An oxygen scrubber and second-level gas filter was used to remove other foreign material. This high level of contaminant removal is required when analyzing low level concentrations. A blank run was done to verify that the dilute gas was clean. The sample was diluted with H_2 from the 100 ppm level to 10 ppm. CO_2, O_2, N_2, and methane were easily detected at a good signal-to-noise ratio. The baseline was also very stable, making low-level analysis possible.

Carrier gas:	Hydrogen	1	CO_2: 10 ppm
Inlet:	Purged packed	2	He: Balance gas
Sample loop:	0.5 mL	3	O_2: 10 ppm
Oven:	35 °C (12 min)	4	N_2: 10 ppm
TCD:	220 °C	5	CH_4: 10 ppm
		*	Signal of valve switching

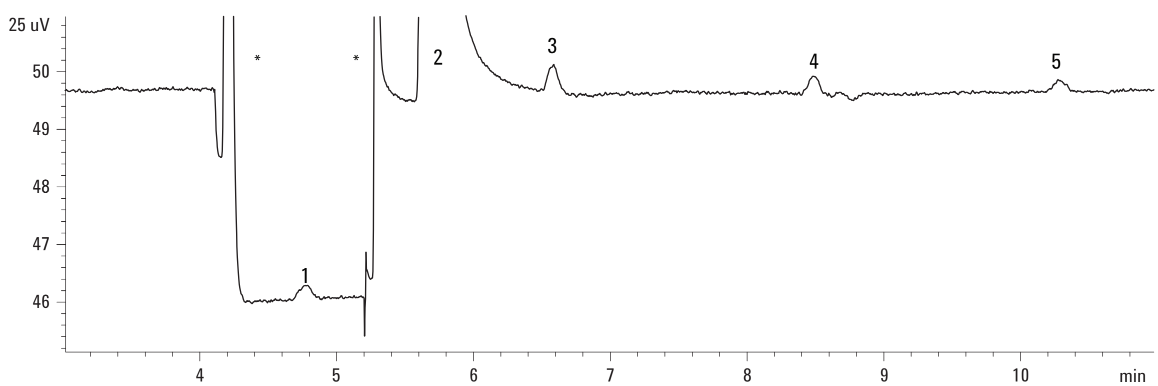

Figure 5. Ten ppm permanent gases by dynamic blending.

Analysis of Fuel Cell Gases

Figure 6 shows the chromatogram of the fuel cell mix. The composition of the mix is typical of the gases that need to be measured during the development of fuel cell systems. Baseline separation is achieved for all the permanent gases and methane. Hydrogen is detected as a negative peak because helium is used as the carrier gas in order to achieve desirable sensitivity for most gases. By setting TCD polarity in the run table, the hydrogen signal can be reversed from a negative peak to a positive one, as shown in the chromatogram. Argon is a good carrier gas if hydrogen analysis over a wide concentration range is required.

Carrier gas:	Helium
Inlet:	Purged packed 55 °C
Sample loop:	0.1 mL
Oven:	50 °C (10 min) with 10 °C/min to 120 °C (5 min)
TCD:	180 °C

1 H_2: 50%
2 CO_2: 10%
3 O_2: 172 ppm
4 N_2: Balance
5 CH_4: 5%
6 CO: 50 ppm
* Signal of valve switching

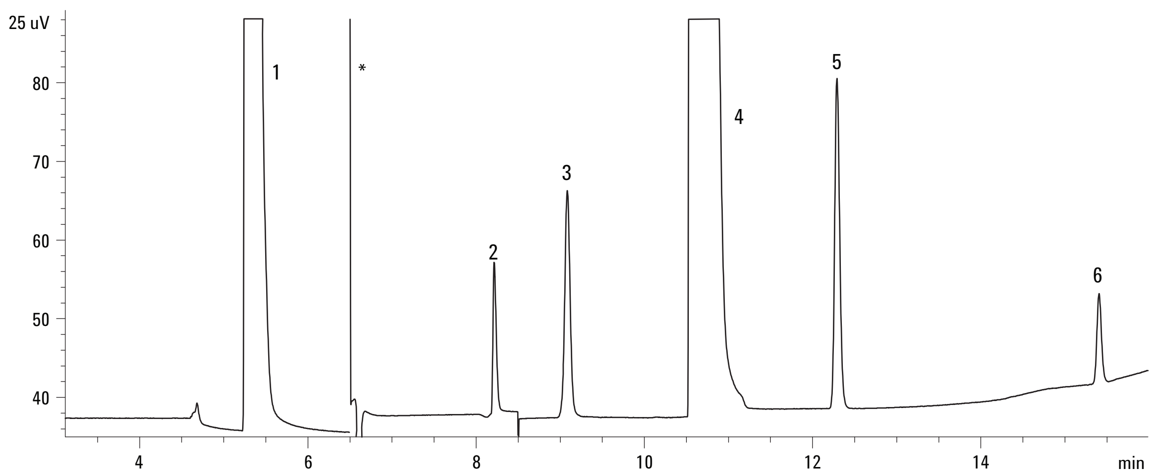

Figure 6. Chromatogram of fuel cell gas standard.

Conclusions

The Agilent 6820 Gas Chromatograph equipped with TCD detector and two valves was used to analyze permanent gases and methane. An HP-Molsieve 5A was used for the separation of O_2, N_2, carbon monoxide, H_2, and methane. The combination of an Agilent HP- PLOT Q column and isolation valve was used for the separation of CO_2 from the other gases. Higher hydrocarbons, such as ethane and propane, could also be separated and measured with the HP-PLOT Q. Of course, if only the permanent gases and methane need to be measured, the 10-port valve with PLOT Q columns would not be needed. The Agilent 6820 single filament TCD demonstrated excellent sensitivity; even 10 ppm permanent gases can be detected reliably. This system offers excellent flexibility. When light hydrocarbon analysis is required (C1 to C8), System 2 (see Figure 1) with alumina PLOT column and FID can be used. This system is suitable for a variety of applications in the petrochemical and energy industries, including natural and refinery gases, fuel cell gas, propylene, and ethylene.

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