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GC/TCD Analysis of A Natural Gas Sample on A Single HP-PLOT Q Column

Application Note
228-387

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Abstract

An Agilent 6890 series gas chromatograph (GC) equipped with a TCD (thermal conductivity detector) was used with and HP-PLOT Q capillary column for the analysis of a natural gas sample. Over 70 sequential runs showed good separation for a wide variety of analytes with good method reproducibility.

Introduction

Natural gas is an important energy source and widely used as a starting material for many chemical processes. It contains mainly methane and different levels of other hydrocarbons and fixed gases such as nitrogen, helium, and carbon dioxide. Hydrocarbons heavier than C7 are usually present at ppm levels. Hydrogen sulfide and other sulfur compounds may be present, either naturally or as added odorants. Additional components may include polar compounds, such as low levels of water, and small amounts of methanol and/or glycol which may have been added for processing purposes [1,2]. Natural gases from different sources usually have the same composition but different concentration levels.

In GC analyses, the variety of components in natural gas requires the separation of both polar/non-polar compounds. Multi-dimensional GC is often required since no single column can separate this wide variety of natural gas constituents. Nor can a single detector detect all compounds satisfactorily. Specifically, the separation of fixed gases and water from hydrocarbons is very difficult to obtain on most wall-coated open-tubular (WCOT) columns; and TCD has a limited sensitivity for trace level compounds and odorant compounds.

Multi-dimensional GC coupled with switching valves requires the use of several different types of PLOT columns [2-4]. The HP-PLOT Al_2O_3 column [3-4] is often used for hydrocarbon separations and the determination of BTUs. The HP-PLOT MoleSieve column is used for the separation of fixed gases such as oxygen, nitrogen and helium, and even argon, [3-4] from methane. And the separation of polar and active compound—such as water, CO_2, and odorants—is obtained using a porous polymer PLOT column, mostly Q type [3].

All three columns are connected by one or more multiple port valves and the complete separation is obtained by time switching eluents to each column and detector. Backflushing hydrocarbon compounds heavier than C_7 is necessary in most cases. Clearly the column interchange and connection as well as the valve and time switching make this a difficult technique to use for routine analyses.

The ideal approach would be one-dimensional GC. Natural gas analysis using two parallel connected PLOT columns has been done with the successful separation of hydrocarbons and oxygen and nitrogen [4]. However, this method is limited because the separation of polar compounds from hydrocarbons cannot be

achieved on these two kinds of PLOT columns. Additionally, water, CO_2, and odorants deactivate Al_2O_3 and molesieve PLOT column coatings. Therefore, these interactions cause shifting of retention times thereby affecting the repeatability, reliability, and accuracy of the natural gas analysis.

Porous polymer, Q-type PLOT columns combine the separation features of the Al_2O_3 PLOT and molesieve PLOT columns when separating features of the Al_2O_3 PLOT and molesieve PLOT columns when separating alkanes and fixed gases. The PLOT-Q coating overcomes the reproducibility problem caused by polar compounds deactivating Al_2O_3 and molesieve absorbent coatings in natural gas samples.

Additionally, PLOT-Q columns can separate CO_2, water, and odorants from an alkanes matrix. Thus, the analysis of natural gas on PLOT-Q columns will satisfy most the separation requirements from BTUs through hydrocarbon components and polar compound determinations.

However, there are also some problems associated with the use of PLOT-Q columns for natural gas analysis. Fixed gas (such as air, CO, and noble gases) cannot be separated on PLOT-Q columns at above ambient temperatures. The upper temperature limits are usually low (250°C) for most commercial PLOT-Q columns.

For some commercial PLOT-Q columns, loose particle binding in the coating, high column bleed, and the limited resolution of nitrogen/air from methane are major problems restricting their usefulness in natural gas analyses. Loose particle binding in the coating causes baseline spiking when the sampling valve is operated or fast temperature ramping is used.

High column bleed makes these columns useful only at temperatures below 250°C and this situation prolongs the analysis time for hydrocarbons heavier than C_7 and/or requires backflushing of the hydrocarbons. The limited resolution of nitrogen/air from methane requires low starting temperatures (@ 40°C) which increases analysis time and affects the accuracy of the analysis. Since a fraction of the nitrogen, carbon dioxide, and methane peaks overlap, the concentration of methane will be incorrectly quantified.

New HP PLOT-Q columns overcome some of these problems making them suitable for natural gas analyses. This application note examines a simple GC/TCD mehtod for the analysis of natural gas using a new HP porous polymer, Q-type, PLOT column. The resolution of nitrogen and carbon dioxide from methane on different commercially available PLOT columns is compared and reproducibility and reliability are evaluated.

Experimental

Gas chromatography analysis of a natural gas sample was done using an Agilent 6890 series gas chromatograph (GC) with electronic pneumatics control (EPC) and a Thermal Conductivity Detector (TCD). For conventional gas analysis, a six-port valve with an 0.25 cc sampling loop was used to introduce natural gas sample onto the HP-PLOT Q column in split mode (split ratio 18:1). The GC parameters are listed in **Table 1**.

A natural gas sample supplied by Scott Specialty Gases, Inc, (Plumsteadville, PA) was used and the original compounds and concentrations are listed in **Table 2**. This sample was modified by adding methanol, water, and hydrogen sulfide. During analysis, the possible leaking of some air in the sampling loop may also have caused some change in concentrations.
Analyses were run using an HP-PLOT Q porous polymer column (part number 19095P-QO4) with two other brands (X and Y) of Q-type PLOT columns used for resolution comparisons. All columns were conditioned at 250°C overnight per manufacturer recommendation to reduce column bleed.

Table 2. Natural Gas Sample

Compound	Concentration (v/v%)
Nitrogen	2.500
Methane	88.660
Carbon Dioxide	3.000
Ethane	3.520
Propane	1.050
iso-Butane	0.400
n-Butane	0.400
neo-Pentane	0.100
iso-Pentane	0.150
n-Pentane	0.150
Hexane	0.050
Heptane	0.020

Table 1. GC Experimental Conditions

GC	6890 GC with EPC
Columns	0.53 mm x 30 m PLOT-Q columns
Carrier	Helium 8.6 ml/min @ 60°C, Constant flow mode
Oven	60°C (2 min) 30°C/min to 240°C (1 min)
Injection	Split mode, 250°C, 0.25 cc sampling loope
Split flow	150 ml/min
Valve	Valco 6-port valve, 0.25 cc sampling loop
Detector	TCD
Reference flow	Helium, 30 ml/min
Auxilary gas flow	Helium, 3 ml/min

Results and Discussions

HP-PLOT Q type columns are coated with porous polymer particles made of divinylbenzene and ethylvinylbenzene and can separate hydrocarbons up to C_{14} as well as some polar compounds. Their upper isothermal and programming temperature limits are 270°C and 290°C, respectively.

The separation of the constitutents in the natural gas sample was done using a porous polymer HP-PLOT Q column as shown in **Figure 1**. The analysis time for this run was 9 minutes. Hydrogen sulfide, water, and methanol were well-separated from ethane, propane and iso-butane. Although baseline spiking is commonly associated with this analysis for some commercially available columns, no baseline spiking was observed with the HP-PLOT Q column, indicating that the stationary phase of this PLOT column provides excellent immobilization that can withstand: fast oven temperature ramping (30°C/min), a pressure pulse generated from valve actuation, and carrier gas pressure ramping at constant flow mode. Resultant column bleed was very low.

Limited resolution of nitrogen and carbon dixoide from methane is obtained using most commercial PLOT-Q columns. To evaluate the resolution of the new HP-PLOT Q column (**Figure 1**), an HP-PLOT Q column and two other brands of PLOT-Q columns (brand X brand Y) were compared. All columns were 0.53 mm internal diameter. The natural gas sample size was 0.25 cc with a split ratio of 18:1. Peak resolutions (R_S) were calculated based on the formulae in (1) and the results listed in **Table 3**.

$$R_s\,(A/B) = \frac{2^*\,(t_b - t_a)}{1.7^*\,(W_{a(1/2)} + W_{b(1/2)})}$$

- Where t_a and t_b are the retention times of peaks A and B

Table 3. Resolution Comparisons (Sample and size, natural gas, 0.25 cc)

Resolution R_S	HP-PLOT Q	Brand X	Brand Y
R_S (N_2-Air/Methane, 40°C)	2.560	2.380	1.760
R_S (N_2-Air/Methane, 60°C)	1.760	1.600	1.340
R_S (CO_2/Methane, 40°C)	11.200	8.100	10.100
R_S (CO_2/Methane, 60°C)	7.200	5.100	5.300

- $W_{a(1/2)}$ and $W_{b(1/2)}$ are their peak widths at half height, respectively.

Peak resolution for N_2-air/methane using the HP-PLOT Q column was greater than 1.5 which is the conventional requirement for base line separation, even at a 60°C initial oven temperature. The resolution of carbon dioxide from methane at 60°C on the HP-PLOT Q column is 40% higher than the same resolution on the other two brands of PLOT-Q columns tested. This separation capability of the HP-PLOT Q column also can sufficiently resolve nitrogen and carbon dioxide from methane, even if the methane peak is tailing due to sample overload. The starting temperature of 60°C also results in a 30% reduction in GC cycle time.

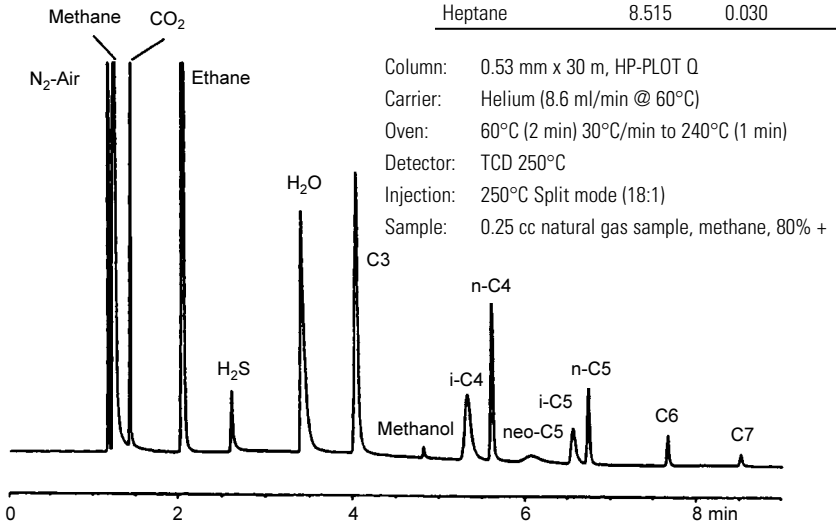
One of the concerns associated with using PLOT columns for natural gas analysis is reproducibility. It is well known that — when using alumina PLOT and molesieve PLOT columns — the retention times for hydrocarbons shift due to deactivation of column absorbants from sample components such as water and CO_2 during repeated runs. Retention time shifting makes the sample timing switch more difficult and sometimes incorrect. To investigate this problem, 70 sequential runs were performed over three days. **Tables 4** and **5** list the relative standard deviations (RSDs) for the retention time averages as well as the peak ratios.

Table 4 shows that the change in retention time is very small for most components. The largest variation, up to 0.6%, was observed for water. This indicates that column performance

Table 4. Sequential Runs of Natural Gas: Retention Time (min)

Compound	Average	RSD%
Nitrogen	1.165	0.190
Methane	1.220	0.490
Carbon Dioxide	1.429	0.200
Ethane	2.036	0.220
Water	3.413	0.560
Propane	4.027	0.130
i-Butane	5.313	0.060
n-Butane	5.600	0.060
i-Pentane	6.563	0.040
n-Pentane	6.740	0.030
Hexane	7.671	0.030
Heptane	8.515	0.030

Figure 1. Separation of Natural Gas



will not be affected by water. **Table 5** shows some larger variations in methane and heptane peak areas.

The larger variation in peak area ratio in comparison to those for retention time can be caused by two factors. First, sample size changed due to sample loop leakage with a resultant change in water amount. Second, the integration of peak areas for methane and heptane was not very accurate. The methane peak is relatively sharp but tailing, which affects the baseline determination for the integral peak area, while the heptane peak is very small. Tight control of the sample size should minimize the variation in the peak area ratios.

The chromatograms obtained at the beginning and the end of the sequential runs are shown in **Figure 2.** This figure demonstrates that the retention time, elution order and peak shape do not change after repeat runs.

For safety reasons, the analysis of natural gas containing mercaptans (added to natural gas as odorants) was not carried out in this experiment. However, **Figure 3** shows the GC separation of four kinds of mercaptans, carbonyl sulfide and hydrogen sulfide, starting from 60°C. They are well separated and resolved. Their elution positions still fall in between those for ethane and i-butane using the same conditions as those listed in **Table 1**.

Although backflushing heavier compounds in natural gas analysis is very common for all PLOT columns, this technique may not be needed for HP-PLOT Q columns. **Figure 4** shows this possibility, where heavier alkanes up to C_{14} were eluted on HP-PLOT Q column at 300°C, at such a high temperature, the column maintained relatively low bleed.

Conclusion

Natural gas analysis by GC/TCD operation on a single porous polymer HP-PLOT Q column gives satisfactory separation using a very simple GC/TCD configuration and operation. The reproducibility of the analysis is very good. Backflush may not be needed for hydrocarbons up to C_{14}, which can be eluted at 300°C temperatures.

Table 5. Sequential Runs of Natural Gas: Peak Area Ratio

Ratio	Average	RSD%
Methane/Ethane	10.280	5.899
CO_2/Ethane	0.846	1.867
Propane/Ethane	0.359	2.800
Heptane/Ethane	0.011	12.712

Figure 2. Sequential Runs of Natural Gas

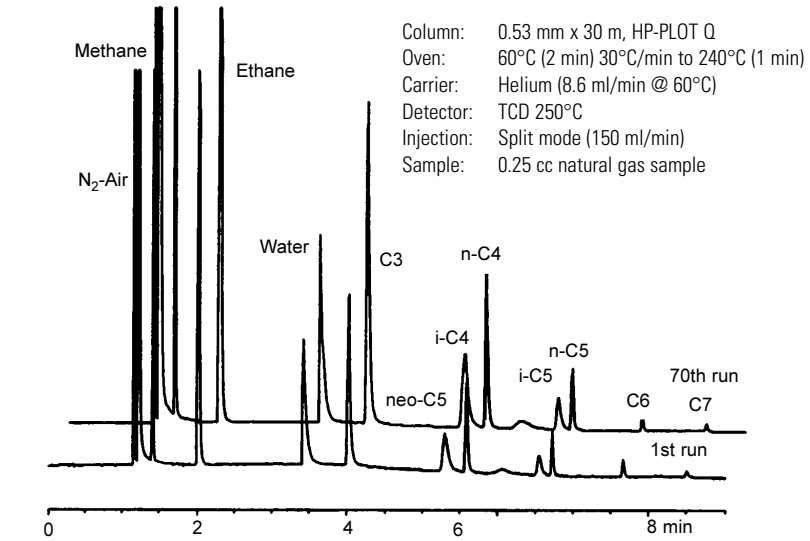


Figure 3. Sulfur Compound Separation

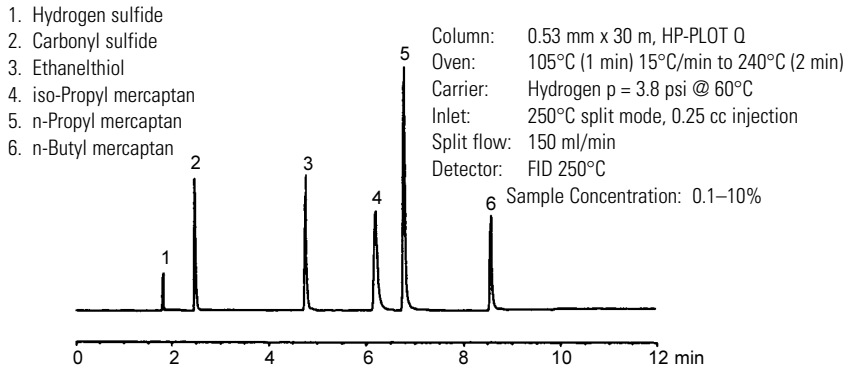
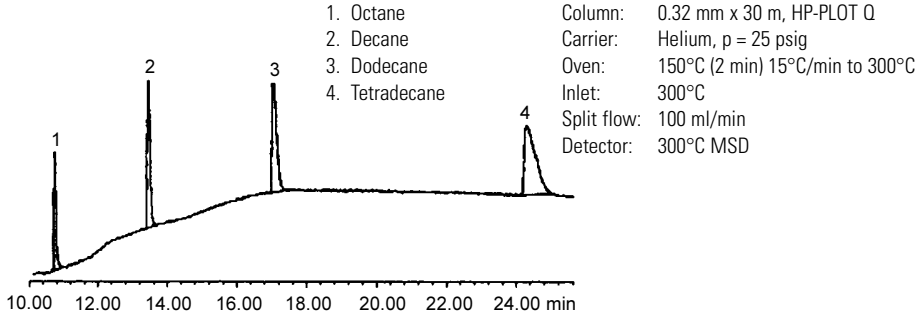


Figure 4. Elution of C8 to C14 on HP-PLOT Q column



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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.

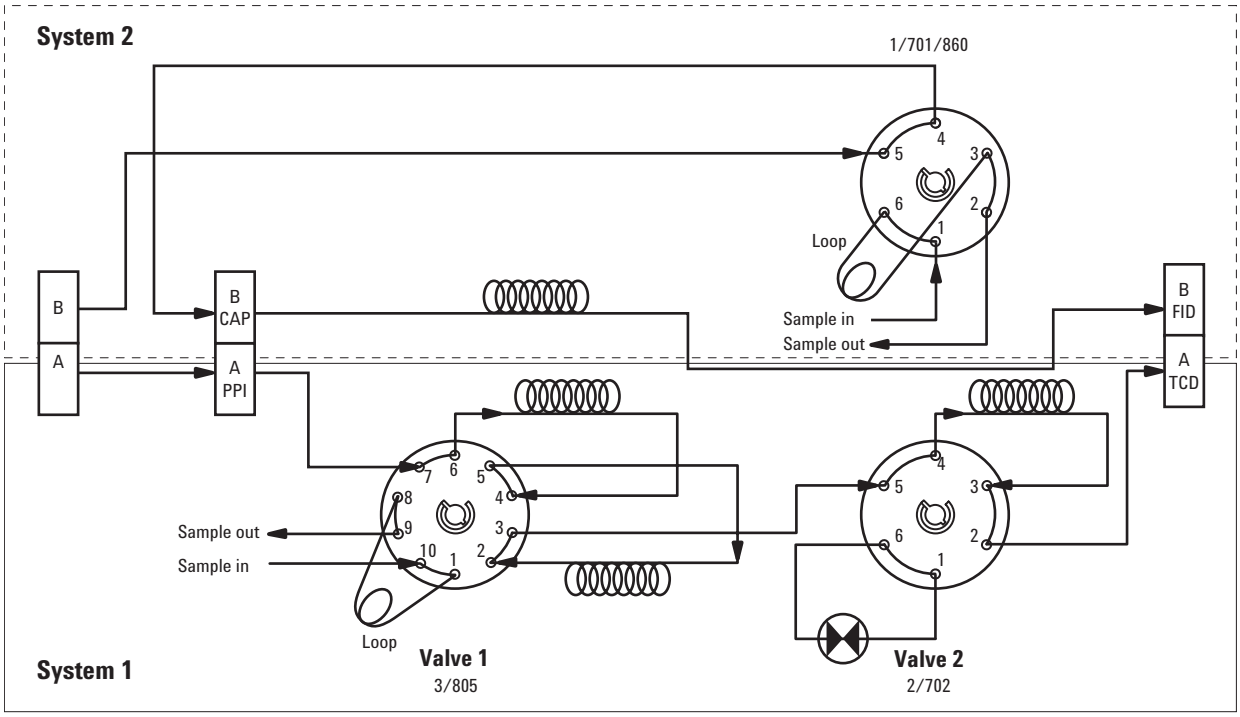

Figure 1. Valve diagram.

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.

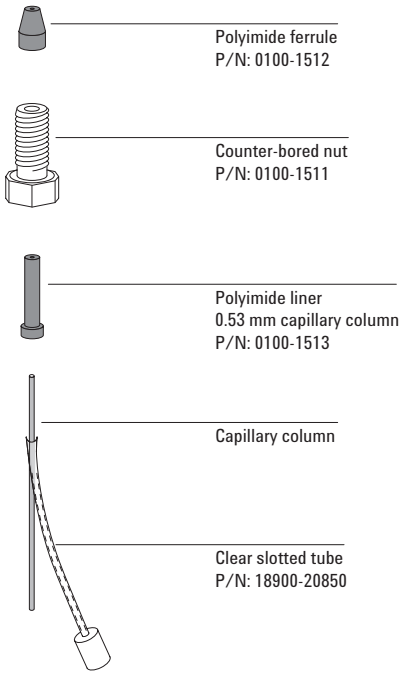

Figure 2. Installing capillary columns using fused silica adapters.

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.

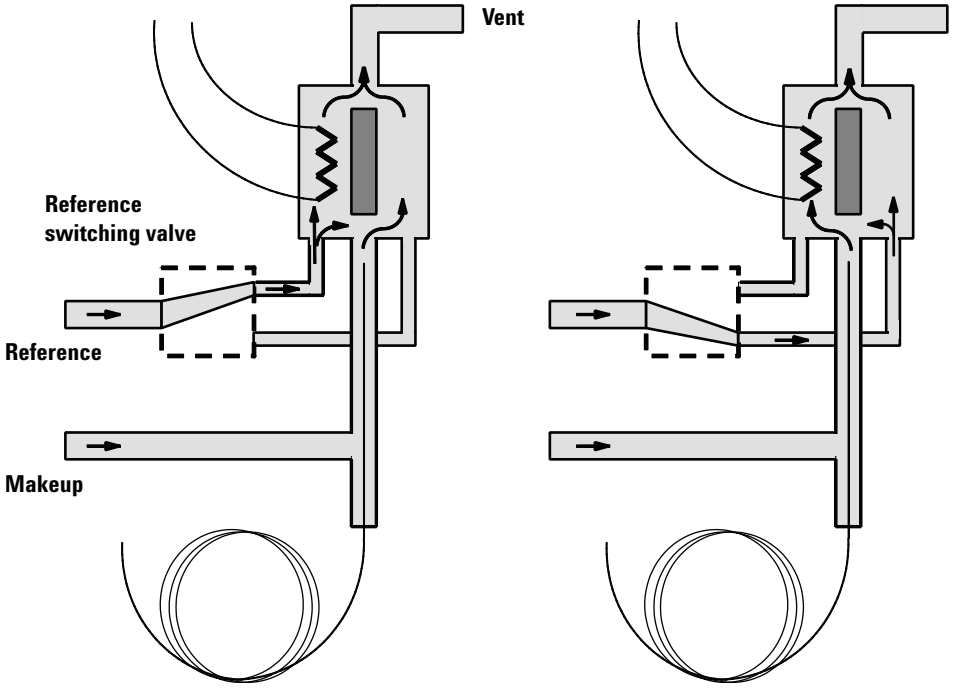

Figure 3. Pneumatic diagram of the Agilent single-filament TCD.

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.

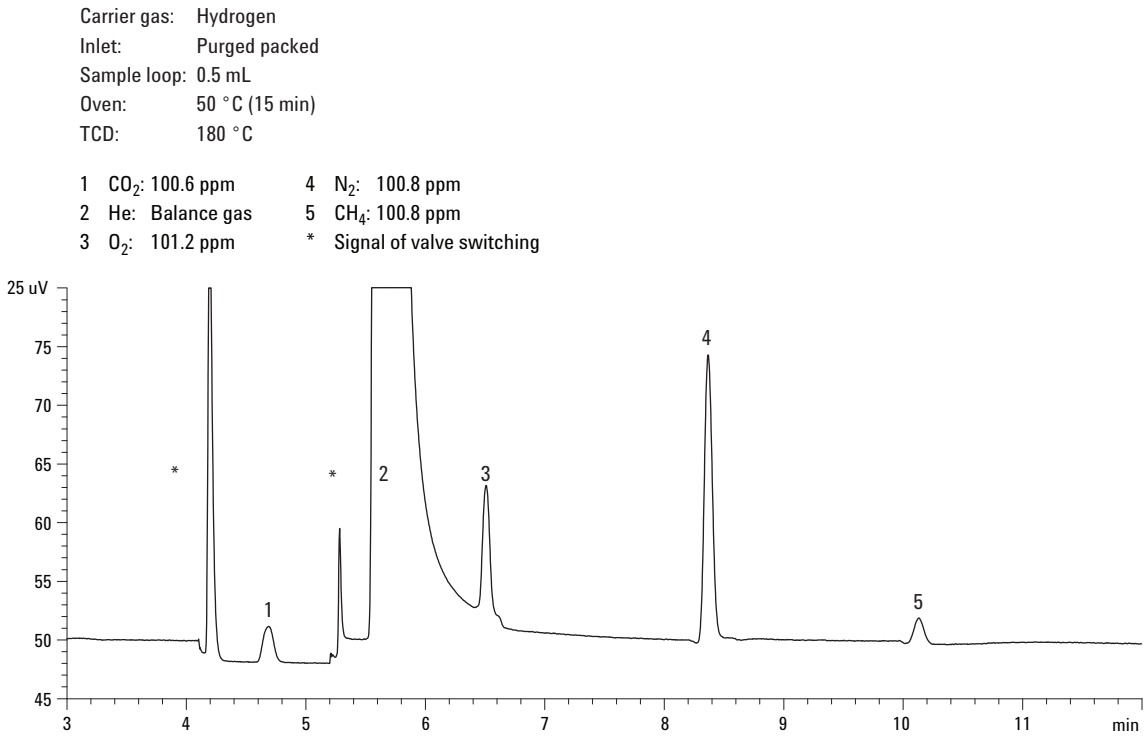

Figure 4. Chromatogram of 100 ppm permanent gas calibration standard, Carrier gas: Hydrogen.

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.

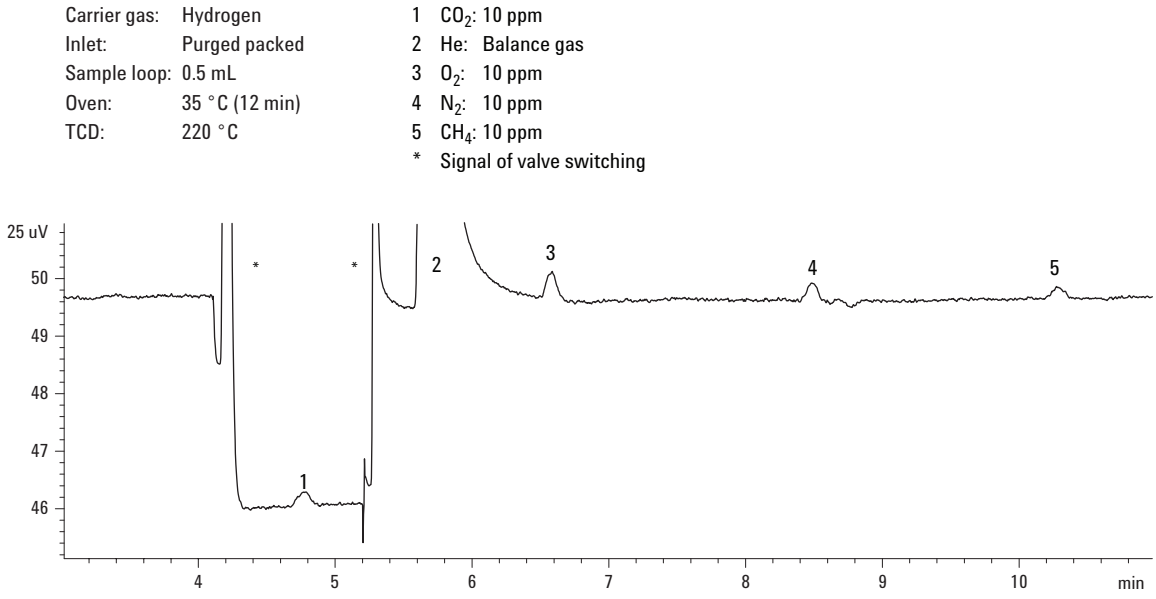

Figure 5. Ten ppm permanent gases by dynamic blending.

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.

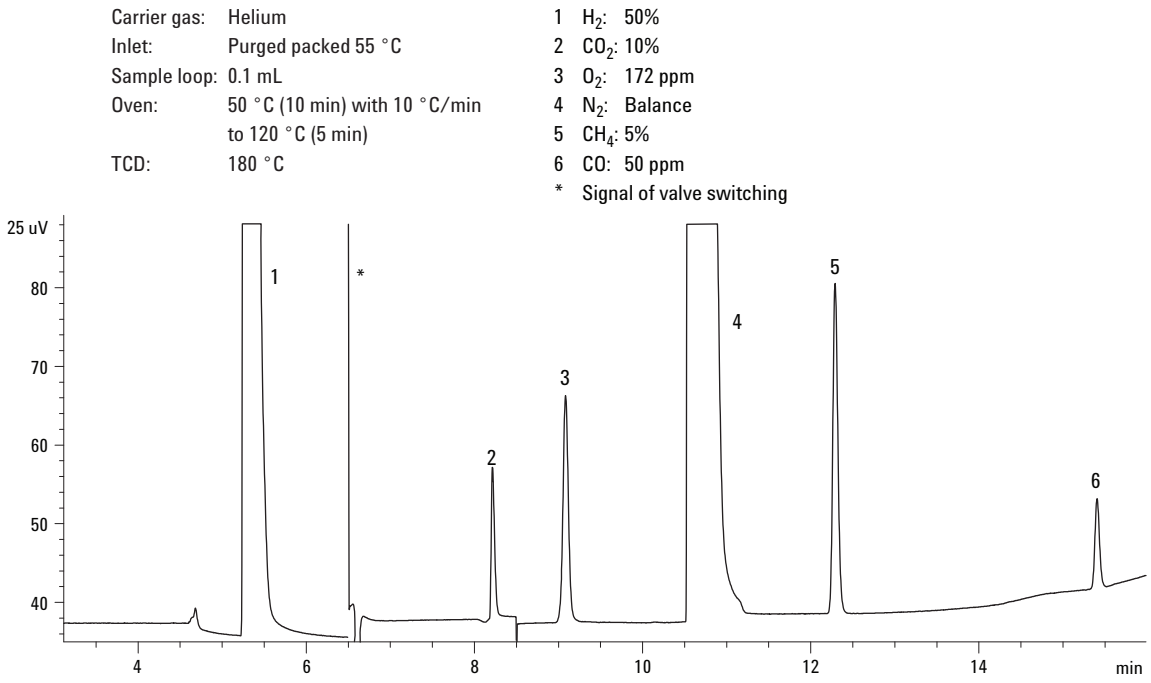

Figure 6. Chromatogram of fuel cell gas standard.

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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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.

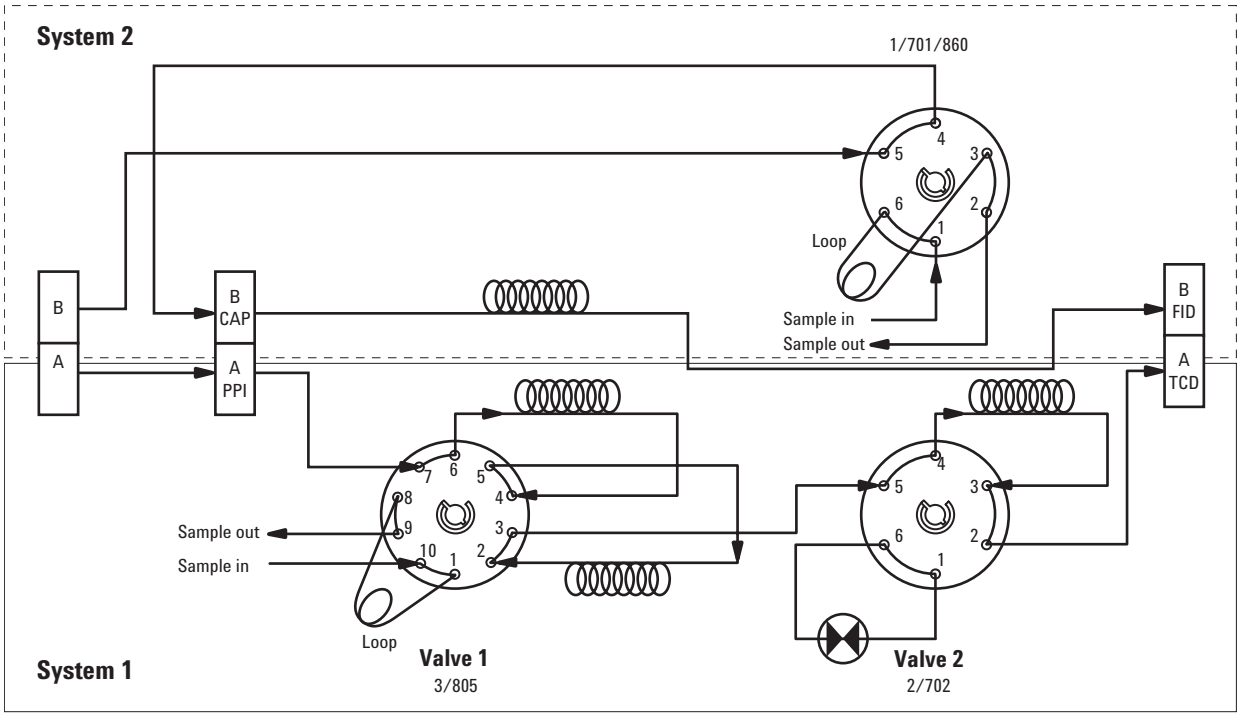

Figure 1. Valve diagram.

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.

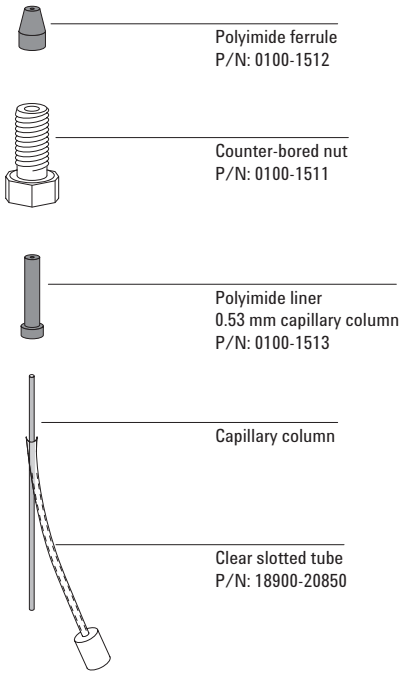

Figure 2. Installing capillary columns using fused silica adapters.

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.

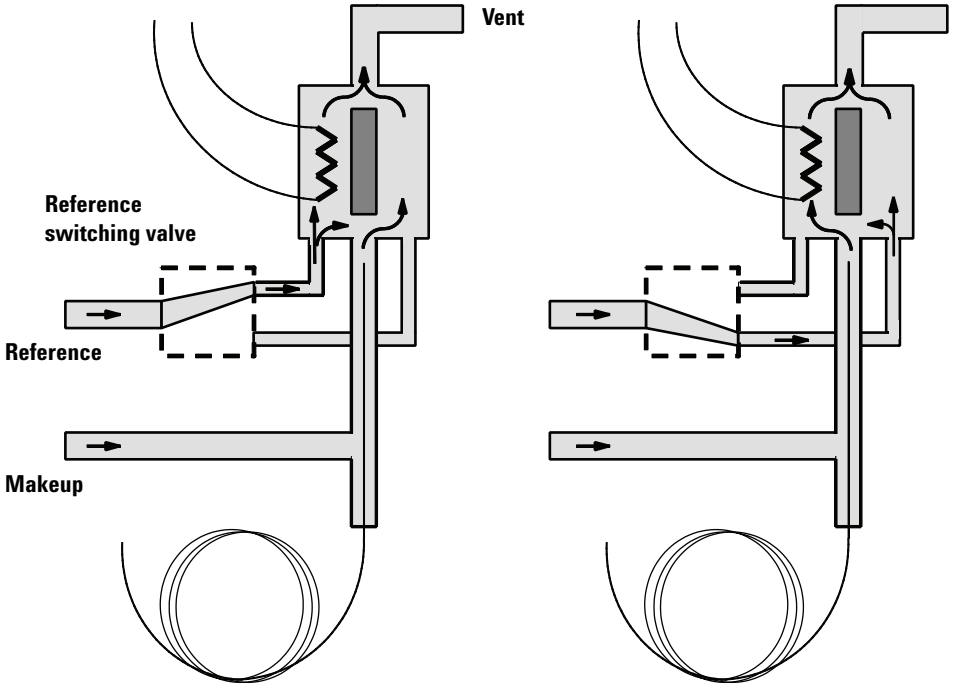

Figure 3. Pneumatic diagram of the Agilent single-filament TCD.

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.

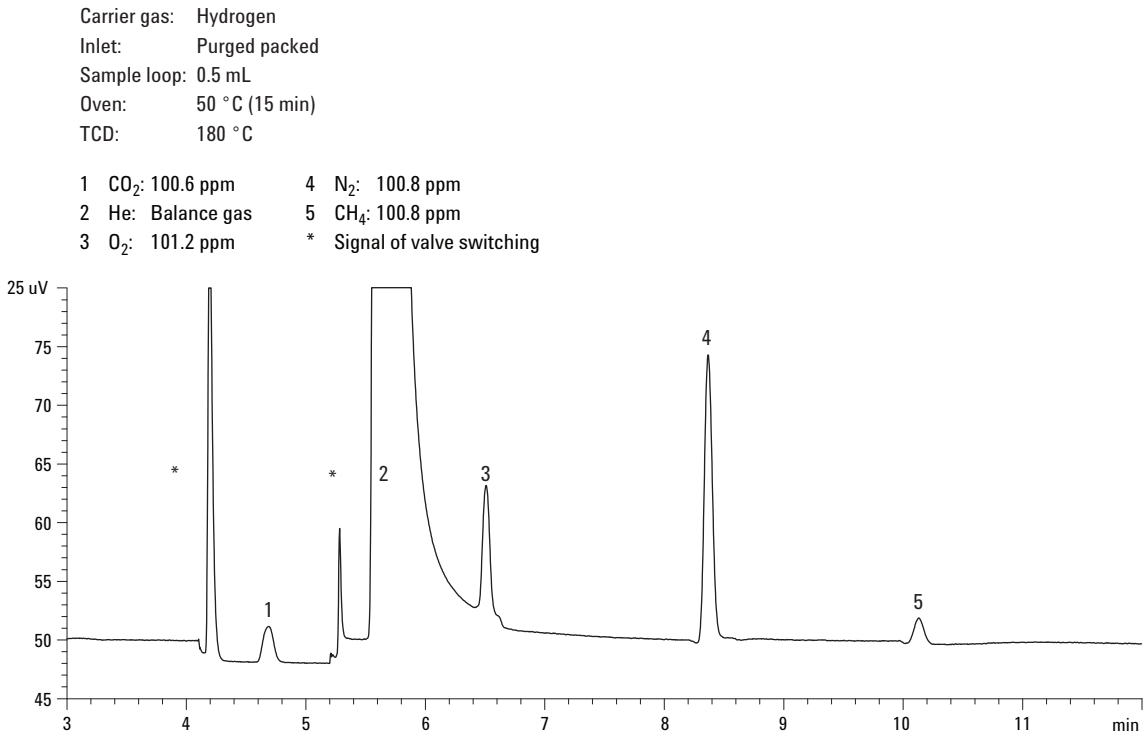

Figure 4. Chromatogram of 100 ppm permanent gas calibration standard, Carrier gas: Hydrogen.

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.

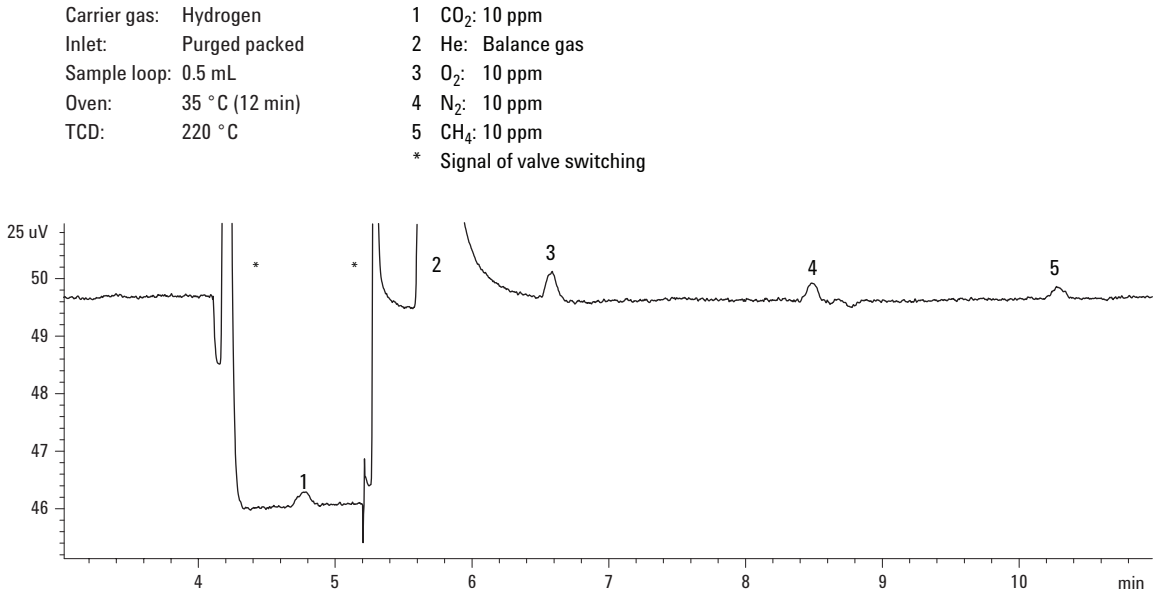

Figure 5. Ten ppm permanent gases by dynamic blending.

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.

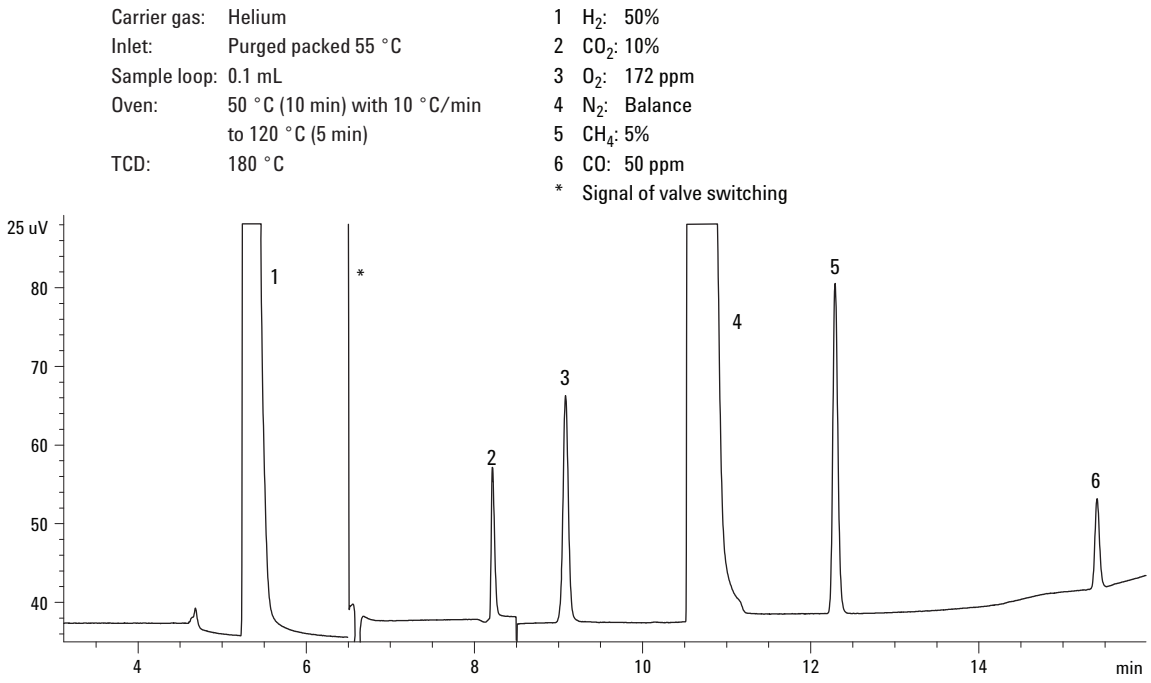

Figure 6. Chromatogram of fuel cell gas standard.

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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High-Pressure Liquid Injection Device for the Agilent 7890A and 6890 Series Gas Chromatographs

Application

Hydrocarbon Processing

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Abstract

In gas chromatography, sampling and representative analysis of highly volatile liquefied hydrocarbons with high precision and accuracy can be challenging. In the solution described here, a unique sample injection device based on a needle interface and liquid rotary valve has been designed for sampling light petroleum matrices with broad boiling point distributions. The 7890A GC-based system consists of a 4-port liquid valve, a deactivated removable needle, and auxiliary flow. The needle is directly installed on one port of the valve. This compact device is installed directly over the top of a split/splitless inlet. The unit is operated automatically just like a typical liquid autosampler; however, the needle is not withdrawn. Various pressurized liquid samples have been run on this device, such as liquefied natural gas (calibration standard), ethylene, propylene, and butadiene. Excellent repeatability is obtained with RSDs typically below 1% in quantitative analyses.

Introduction

There are several known techniques for injecting volatile liquefied hydrocarbons in gas chromatographs. The simplest tools are high-pressure syringes. However, the pressure limit is not high enough to analyze light hydrocarbons such as liquefied natural gas and ethylene. The traditional methods [1, 2] include the use of vaporizing regulators and rotary sampling valves. During sampling, discrimination of the analytes will take place for samples with wide boiling points due to condensing of heavy components and selective vaporization of light components in transfer lines. Recently, piston sampling valves were introduced and are commercially available [3]. These can suffer from discrimination and short service lifetimes at high vaporization temperatures or high sample pressures.

Combining the advantages of simple syringes and high-pressure rotary valves, a unique sample injection device has been designed. The system consists of a 4-port liquid sampling valve, a Siltek deactivated needle, and a split/splitless inlet. This compact device is installed directly over the GC inlet. This unit is operated just like a typical liquid autosampler; however, the needle is not withdrawn. The maximum limit of sample pressure is 5,000 psig. Various pressurized gas samples have been evaluated on this device such as liquefied natural gas (calibration standard), ethylene, propylene, and butadiene. Excellent repeatability is obtained with 0.47% to 1.09% RSD in quantitative analyses. Wide boiling point hydrocarbon samples (C5 to C40) have also been analyzed using this injector, with excellent quantitative results.

Experimental

Injection Device

The high-pressure liquid injection (HPLI) device consists of components as shown in Figure 1.

- **Valve:** Internal sample valve from Valco Instruments Co. Inc. 4-port equipped with a sample volume of 0.06 µL. Other rotor sizes are available from Valco Instruments Co. The valve works under 75 °C and 5,000 psi.
- **EPC:** An auxiliary flow from a 7890A Aux module is connected to port P. In sample analysis, the flow can be set at 50 mL/min to 200 mL/min. The higher auxiliary flow gives better peak shape.

The following components are recommended. These are not supplied in the option or accessory kit.

- **Filter:** To remove particles from samples, it is necessary to install a filter between the sample line and port S.
- **Restrictor:** To maintain sample pressure, a metering valve (Agilent PN 101-0355) is connected to the end of the sample exit line tubing. Restrictor is not included in option or accessory kit.

Guideline for choosing Aux flow source

7890AGC

G3471A Pneumatic Control Module (PCM) or

G3470A Aux EPC module

6890GC

G1570A Aux EPC or

G2317A PCM module

The PCM is the preferred source for both GCs.

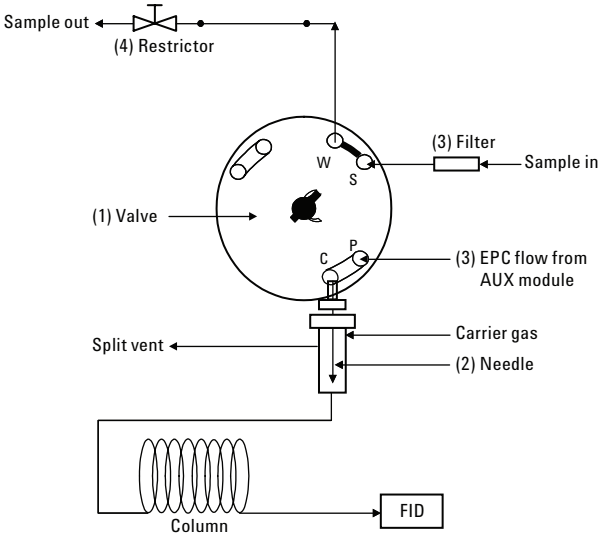


Figure 1. Flow diagram of the HPLI device.

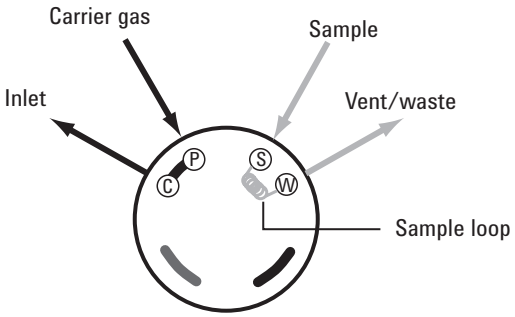
Samples for System Evaluation

- Liquefied natural gas: Calibration standard, 1,200 psi, with nC7-nC9 (0.102%–0.0503%)
- Liquefied ethylene: Purity 99.5, 1,200 psi
- Pressurized propylene: Grade C. P., purity 99.0%, 200 psi
- Pressurized propane + n-butane: 50.0%:50.0%, 200 psi
- Pressurized 1, 3-butadiene: Purity 99.5%, 180 psi
- n-Hexane + 1.0 % 2# BP standard (Agilent PN 5080-8768, nC5–nC18)
- nC5–nC40 D2887 1# BP standard (Agilent PN 5080-8716, diluted by CS_2)
- Glycols, including monoethylene glycol, diethylene glycol, and triethylene glycol
- C8 to C16 hydrocarbons at 100 ppm each

Operating Process

The valve is operated with an Agilent pneumatic air actuator. To load the sample, the valve is set at the OFF position (Figure 1). The sample is loaded from port S and vented to port W. The pneumatic and sample paths in load and inject positions are shown in Figure 2. To maintain the sample in the liquid phase and to avoid “bubbles” in the sample line, it is important to adjust resistance of the metering valve and check for possible leaks at the connections. To inject, the valve is switched to the

Load



Inject

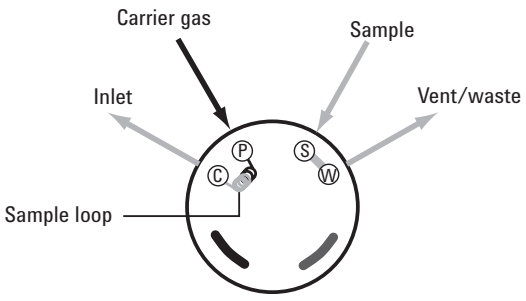


Figure 2. Pneumatic and sample paths in load and inject positions.

ON position. A 2- to 3-second injection time should be used.

The system should always be carefully checked for leaks before introduction of high-pressure hydrocarbons. Instrumental conditions and application-specific columns are shown in Table 1 and Table 2, respectively.

When the valve is actuated, a stream of carrier gas from the Aux EPC or PCM will enter the inlet and combine with the inlet carrier flow; the combined flow will vent through the split vent. Therefore, the actual split ratio will be higher than the value set from ChemStation. The actual split ratio can be calculated by measuring the split vent flow.

Figure 3. Agilent pneumatic air actuator/valve assembly installed on the 7890A.

Table 1. Instrumental Conditions

Gas chromatograph	Agilent 7890A
Injection source	HPLI device at near ambient temperature
Injection port	Split/splitless, 250 °C (350 °C for C5–C40)
Sample size	0.5-µL (0.2 µL for C5–C40) device supplied with 0.06-µL rotor
Carrier gas	Helium
Aux or PCM	150 mL/min (Helium)
FID	250 °C (350 °C for C5–C40) H_2, 35 mL/min Air, 400 mL/min

Table 2. Columns and Parameters

Samples	Columns	Column flow mL/min	Split ratio	Temperature program	Sample pressure psig
Natural gas	30 m × 0.53 mm × 0.5 µm DB-1 #125-1037	8	40:1	35 °C, 1 min 20 °C/min to 180 °C, 1 min	1200
Ethylene	50 m × 0.53 mm × 15 µm AL2O3 PLOT/KCL + 30 m × 0.53 mm × 5 µm DB-1, #19095P-K25 and #125-1035	8	20:1	35 °C, 2 min 4 °C/min to 160 °C, 3.8 min	1100
Propylene	50 m × 0.53 mm HP AL2O3 PLOT + 30 m × 0.53 mm × 5 µm DB-1	7	25:1	35 °C, 2 min 4 °C/min to 160 °C, 1.8 min	180
Propane + n-butane	30 m × 0.53 mm × 1.0 µm DB-1, #125-103J	5	50:1	35 °C	150
1,3-Butadiene	50 m × 0.53 mm AL2O3 PLOT/KCL	10	15:1	35 °C, 2 min 10 °C/min to 195 °C, 15 min	180
n-Hexane	30 m × 0.53 mm × 1.0 µm DB-1	5	50:1	45 °C	N/A
nC5-nC40	10 m × 0.53 mm × 0.88 µm HP-1, #19095Z-021	10	15:1	35 °C, 1 min 15 °C/min to 350 °C, 5 min	N/A
Glycols	30 m × 0.25 mm × 1.0 µm HP-1 ms	1.8	15:1	50 °C, 3 min 15 °C/min to 250 °C, 2 min	

Results and Discussion

Check for Carryover

A set of normal hydrocarbons was used to perform a basic check of the system, looking for good peak shape and lack of carryover.

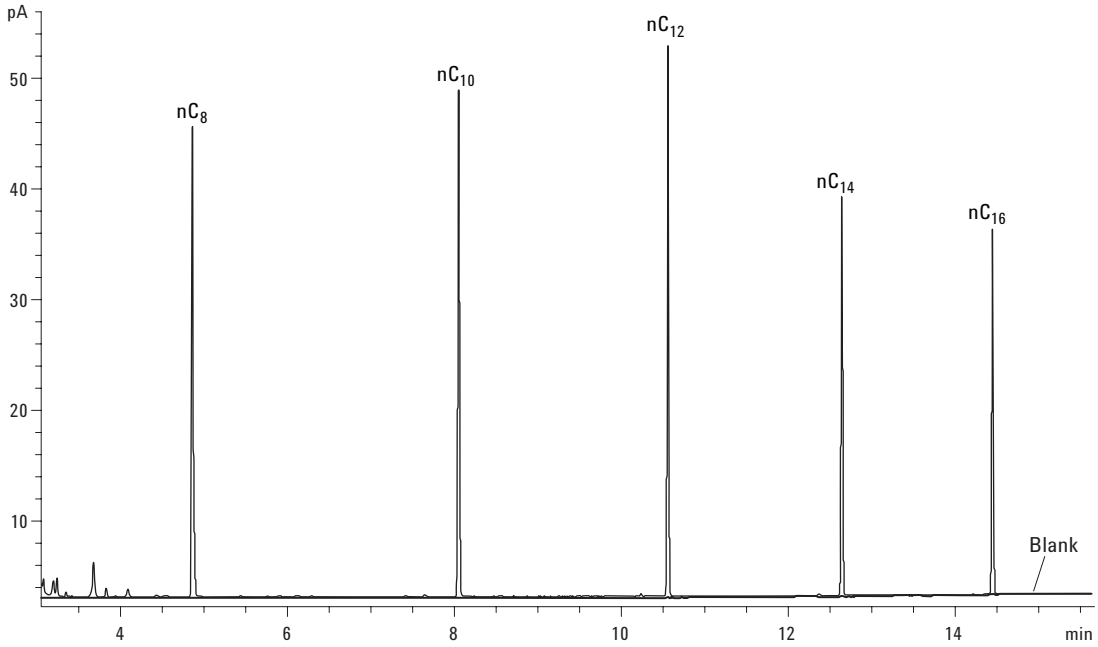


Figure 4. Overlay of standard versus blank (100 ppm each in cyclohexane).

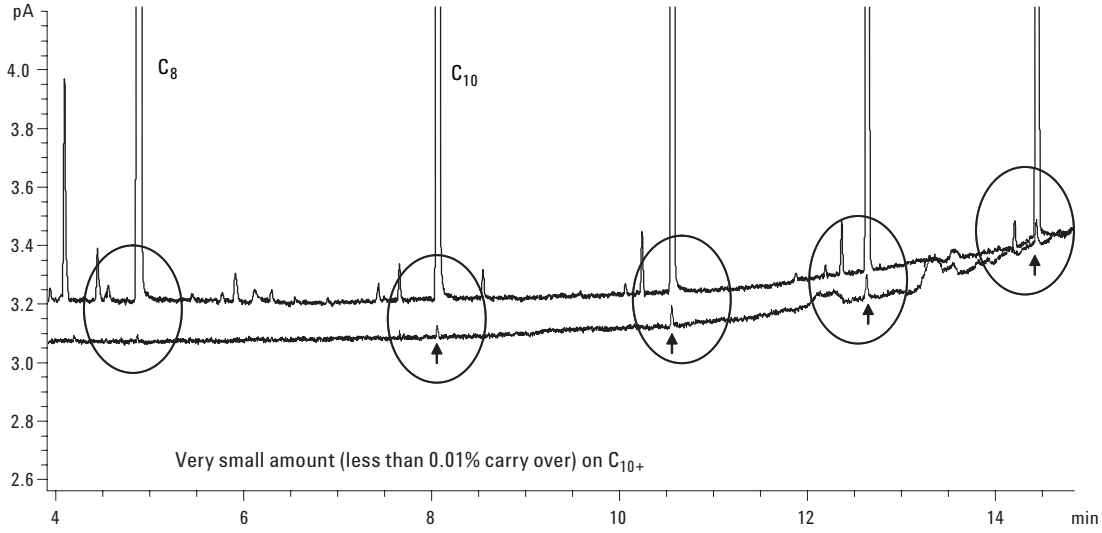


Figure 5. Carryover less than 0.01% on C_{10+}.

Sample Analysis

A series of glycols was used to model performance of the device for highly polar analytes. Minimal peak tailing is seen, due in part to the inertness of the needle interface. Also, carryover is very low.

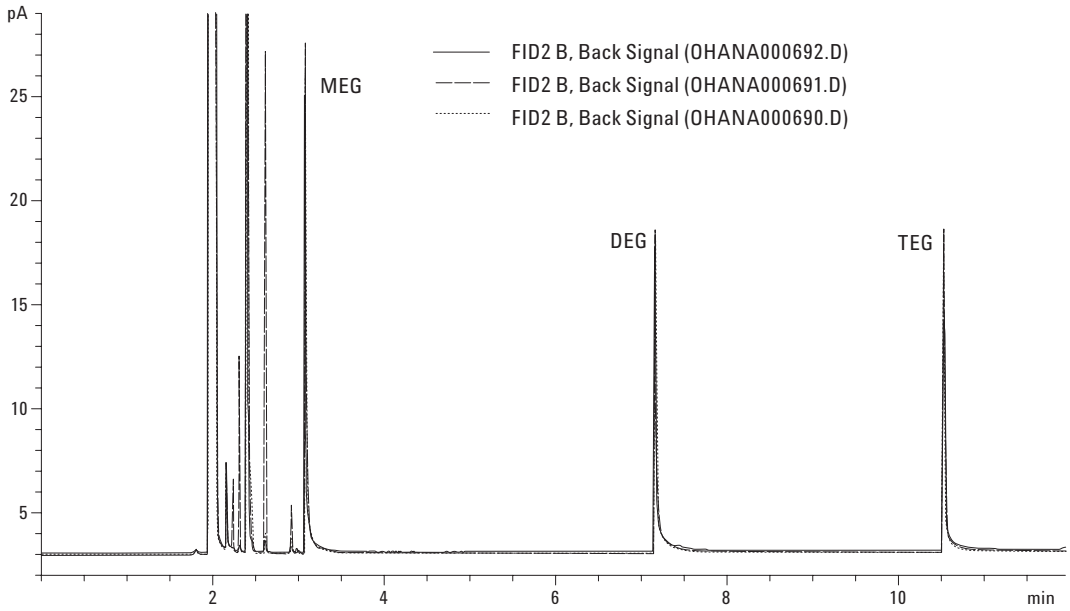


Figure 6. Triplicate run of 100 ppm each of MEG, DEG, and TEG in IPA.

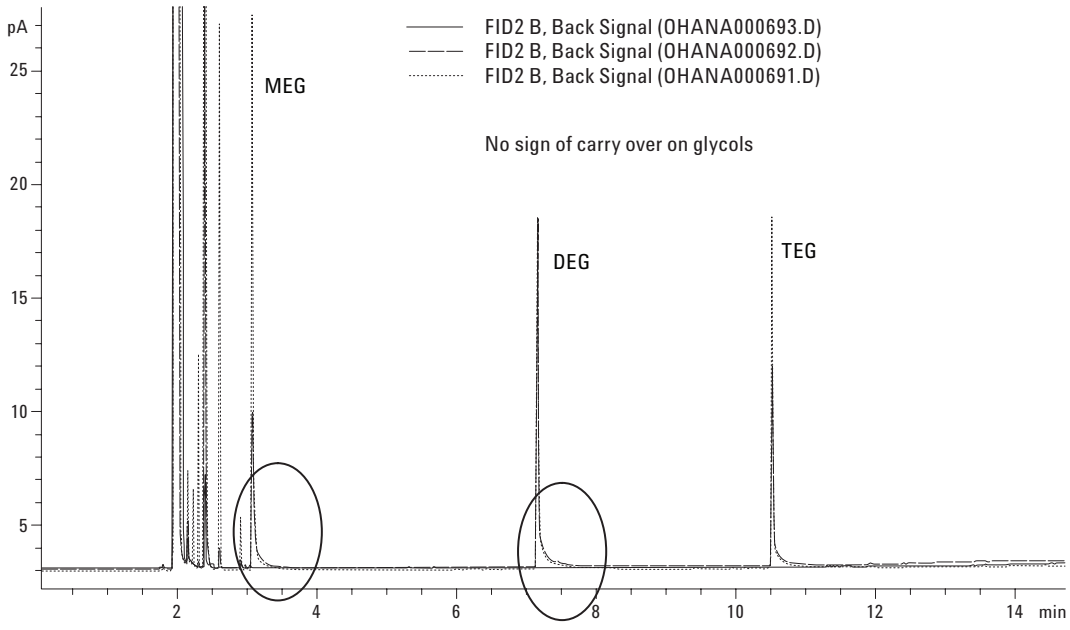


Figure 7. Glycols versus blank. Two standard duplicates, blank run immediately after injection of standard.

A. Liquefied Natural Gas

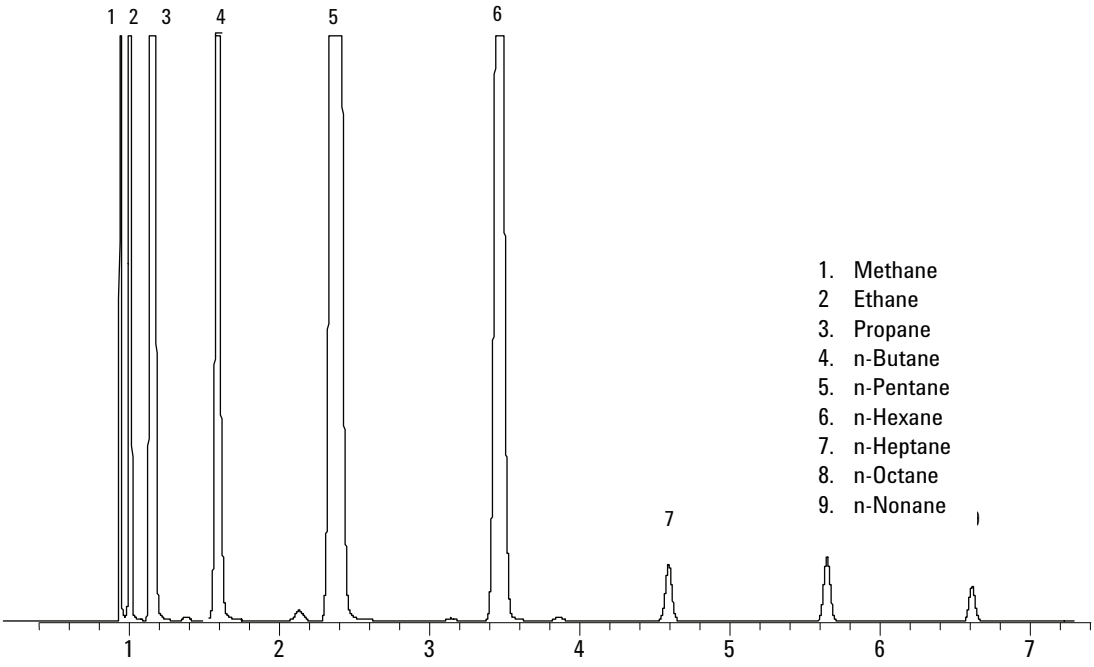


Figure 8. Chromatogram of liquefied natual gas (calibration standard).

Low discrimination is seen in Figure 8 for liquefied natural gas (LNG). Excellent repeatability is obtained with RSDs of less than 1%.

B. Liquefied Ethylene

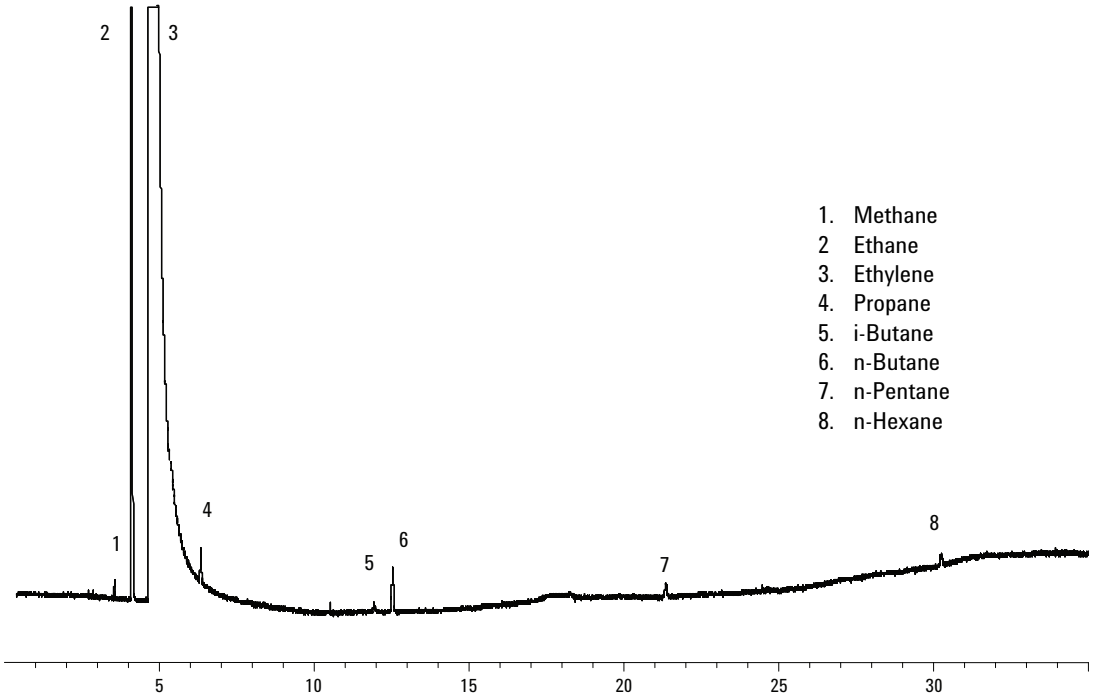


Figure 9. Chromatogram of liquefied ethylene.

The sample in Figure 9 is analyzed by ASTM D6159, "Standard Test Method for Impurities in Ethylene by Gas Chromatography." The method detection limits (MDLs) for the two methods are listed in Table 3.

The MDL using the HPLI device is 10 times lower than reported in the ASTM method due largely to the lack of peak tailing.

Table 3. MDLs (ppm V) by ASTM D6159 and HPLI

Components	ASTM D6159	HPLI
Methane	5.57–62.3	0.27
Ethane	35.1–338	0.78
Propane	8.07–59.7	0.88
i-Butane	7.74–48.4	0.38
Butane	4.97–56.1	1.61
n-Pentane		0.61
n-Hexane		0.74

C. Pressurized Propylene

This sample is analyzed by the same conditions as in ASTM D6159 (above method for ethylene analysis). The chromatogram is shown in Figure 10.

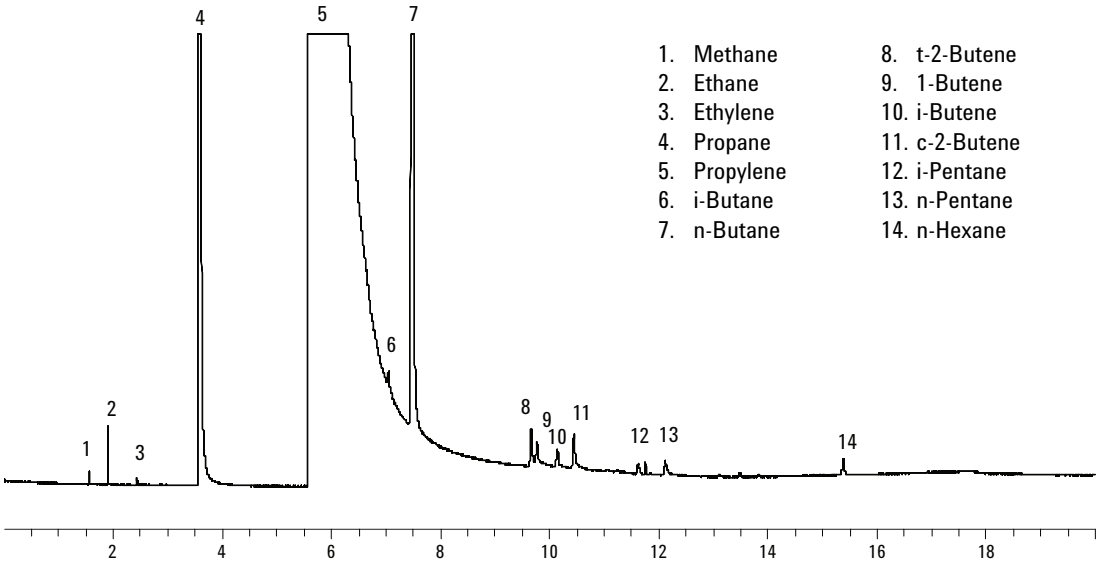


Figure 10. Chromatogram of pressurized propylene.

D. Pressurized 1,3-Butadiene

As an example of C4 hydrocarbons analysis,
Figure 11 shows a typical result for 1,3-Butadiene.

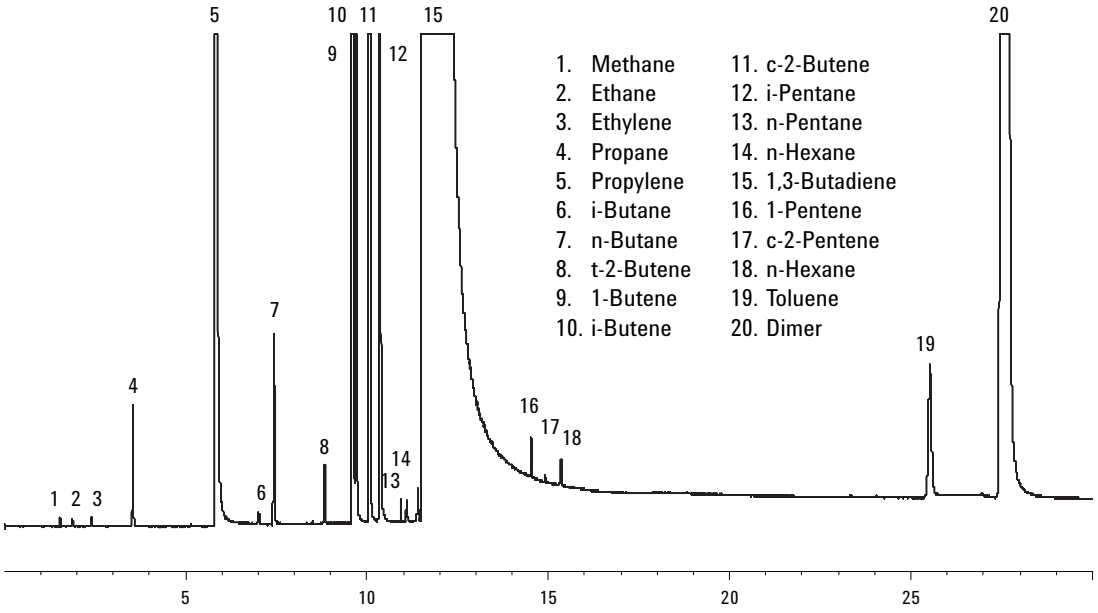


Figure 11. Chromatogram of pressurized 1,3-butadiene.

E. Pressurized Propane + n-Butane

This is a quantitative calibration sample:
Propane:n-Butane = 50%:50%.
The chromatogram is shown in Figure 12 with the results of a quantitative analysis shown in Table 4.

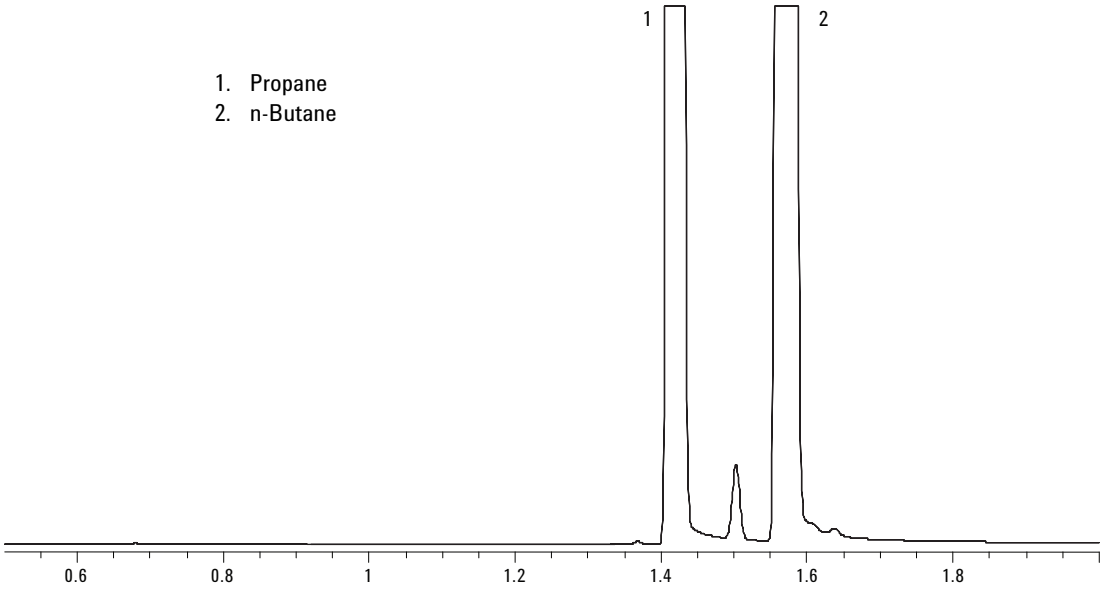


Figure 12. Chromatogram of pressurized propane + n-butane.

Table 4. Quantitative Analysis of Pressurized Propane 50.0% + n-Butane 50.0%. One Percent Difference Between the Blend (actual) and the Analysis Result

	Propane	n-Butane
Response factor	1.03	1.01
Density	0.5139	0.5788
Blend by V%	50.0	50.0
By wt%	47.031	52.969
Analysis		
By area%	45.441	54.559
By wt%	45.927	54.073

F. n-Hexane + 1.0% BP Standard (C5-C18)

To check the quantitative results, a small amount (1.0% BP standard) of C5 to C18 hydrocarbons was added to n-hexane (Figure 13). Table 5 shows the analytical results obtained by adding the C5 to C18 hydrocarbons with both the HPLI device and the automatic liquid sampler (ALS). In Figure 14, chromatograms by HPLI (top) and by ALS (bottom) are shown.

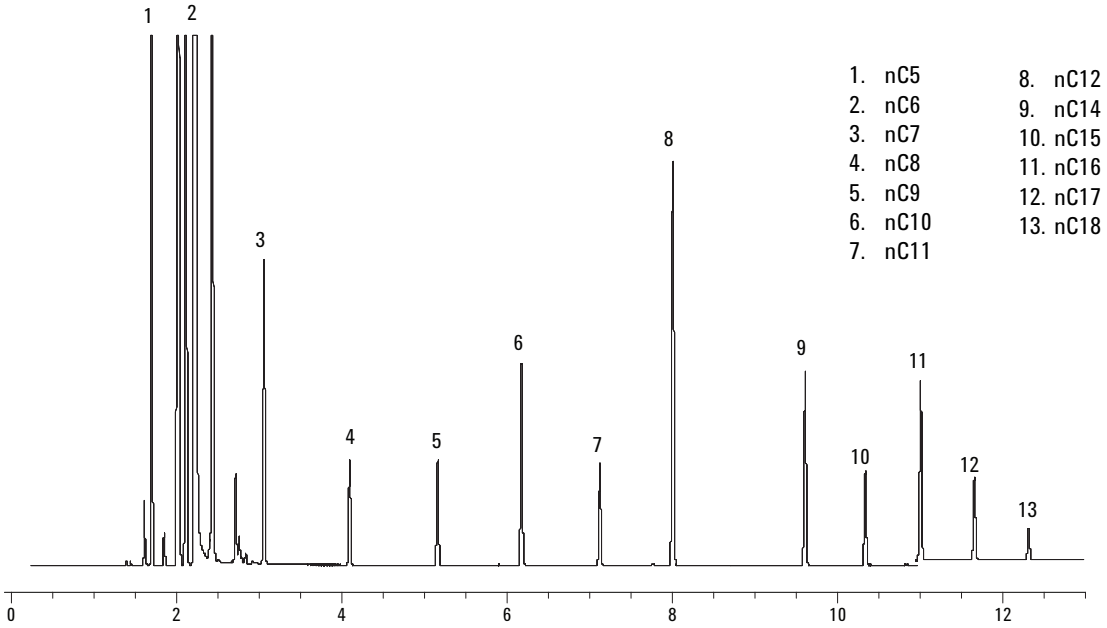


Figure 13. Chromatogram of n-hexane + 1.0% BP standard.

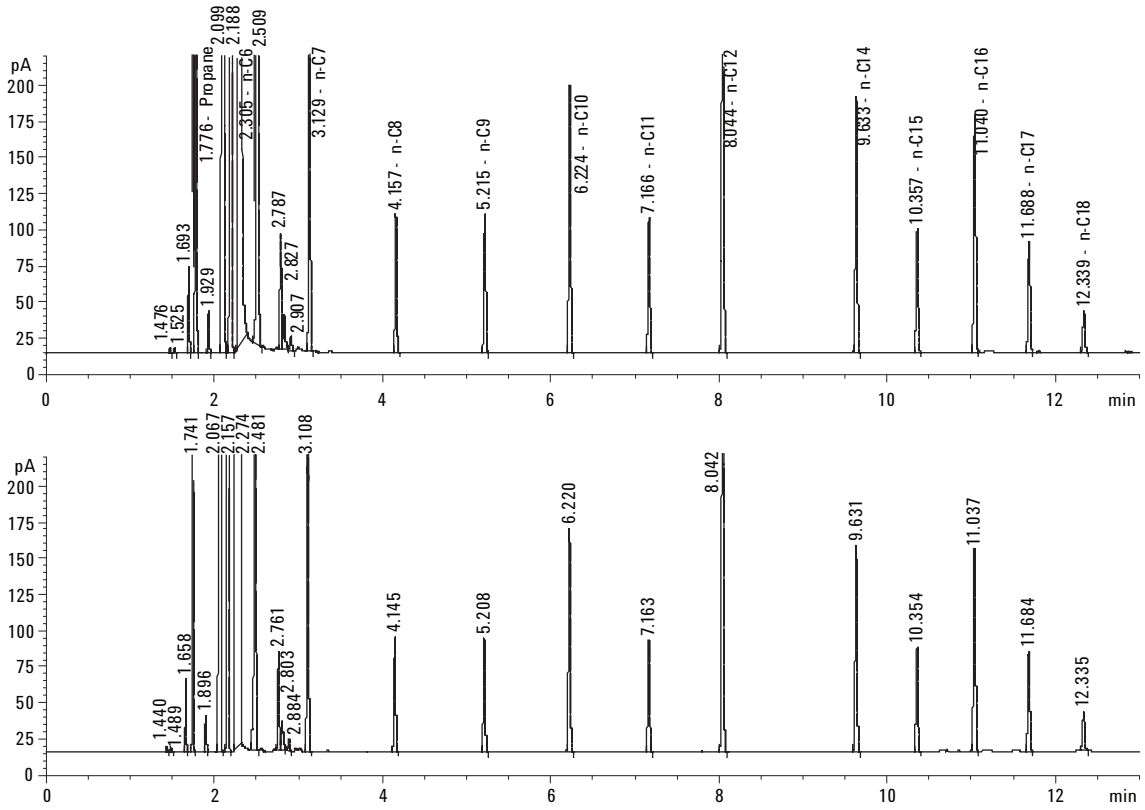


Figure 14. Chromatograms of n-hexane + 1.0% BP standard. Top: HPLI. Bottom: ALS (syringe).

Table 5. Analytical Results for C5-C18 by HPLI and ALS

	HPLI		AUTO INJECTOR	
COMPONENTS	**Area %**	**Width (min)**	**Area %**	**Width (min)**
nC5	0.282		0.279	
nC6	96.950	0.0209	96.922	0.0195
nC7	0.146		0.148	
nC8	0.0524		0.0532	
nC9	0.0537		0.0548	
nC10	0.109		0.111	
nC11	0.0550		0.0559	
nC12	0.219		0.221	
nC14	0.109		0.110	
nC15	0.0532		0.0547	
nC16	0.102		0.109	
nC17	0.0484		0.0546	
nC18	0.0203		0.0239	

The peak width of hexane at top: 0.0209 min
The peak width of hexane at bottom: 0.0195 min

There are no significant differences in quantitative results up to nC14. Compared with the results from an ALS injection, the HPLI device yields results about 10% lower in response above approximately nC16.

G. nC5-nC40 (D2887 BP Standard Diluted by CS_2)

A sample with hydrocarbons (nC5-nC40 D2887 1# BP standard diluted by CS_2) is also run on HPLI. The chromatogram is shown in Figure 15.

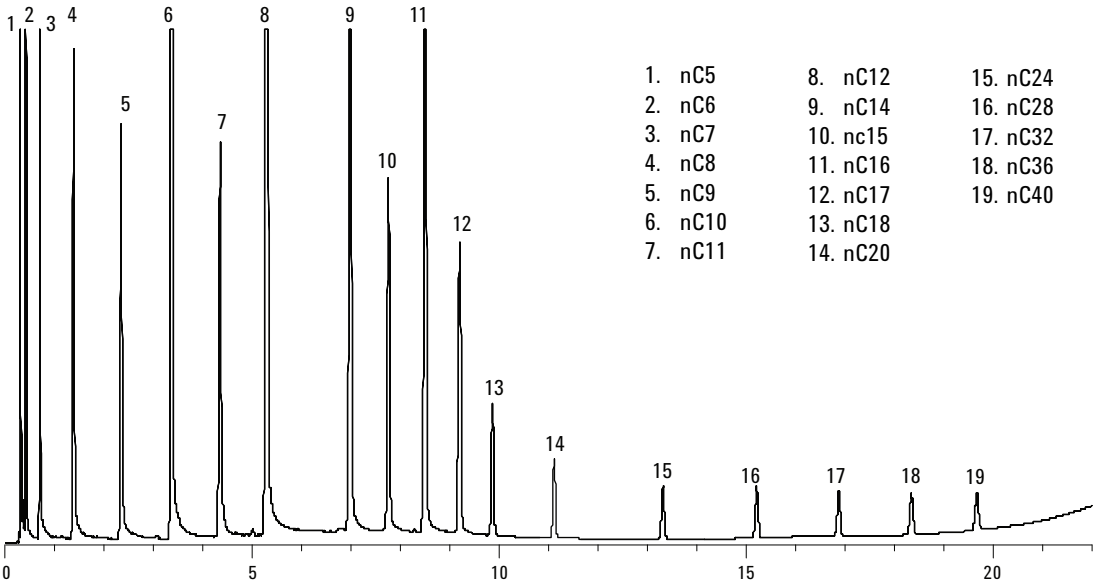


Figure 15. Chromatogram of nC5-nC40 (D2887 BP standard diluted by CS_2).

A lack of discrimination is seen with the HPLI device. In the future, it would be interesting to run some unstable condensates for evaluating the device.

From the above GC evaluation, excellent analytical results could be obtained using the HPLI device. These are summarized below.

1. Excellent repeatability
2. Capable of quantitative results
3. No significant peak width broadening
4. The wide boil point hydrocarbon samples could be analyzed by this device with minimal discrimination.

Conclusions

A unique sample injection device for the Agilent 7890A GC based on a unique deactivated interface and liquid rotary valve has been designed for sampling light petroleum matrices with broad boiling point distributions from methane to as high as C40. It is installed directly over a split/splitless GC inlet. The maximum sample pressure is 3,000 psig, although typical samples will have pressures under 1,500 psig. Various pressurized liquid samples have been tested on this device with high accuracy and precision. The sampler is quick to install and easy to operate. As with all high-pressure sampling systems, appropriate safety precautions must be followed.

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3. Jim Luong, Ronda Gras, and Richard Tymko, *J. Chromatogr. Sci.,* 41 (2003) 550–5.

Acknowledgement

Figures 1 through 4 are courtesy of Ronda Gras and Jim Luong, Dow Chemical Canada, Analytical Sciences.

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Agilent Technologies

Parallel GC for Complete Refinery Gas Analysis

Application

Hydrocarbon Processing

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Abstract

An Agilent 7890A gas chromatograph configured with three parallel channels with simultaneous operation provides a complete, high-resolution analysis for refinery gas in six minutes. The system uses an optimized combination of several packed columns and PLOT alumina columns to allow fast separation of light hydrocarbons and permanent gases with the same oven temperature program. A third channel with TCD with nitrogen (or argon) carrier gas improves the hydrogen sensitivity and linearity. This application also shows the excellent performance for natural gas analysis.

Introduction

Refinery gas is a mixture of various gas streams produced in refinery processes. It can be used as a fuel gas, a final product, or a feedstock for further processing. An exact and fast analysis of the components is essential for optimizing refinery processes and controlling product quality. Refinery gas stream composition is very complex, typically containing hydrocarbons, permanent gases, sulfur compounds, and so on. Successful separation of such a complex gas mixture is often difficult using a single-channel GC system. Three parallel channel analyses allow a separation problem to be divided into three sections. Each channel can optimize a particular part of the separation. TCD with helium carrier gas can be used for permanent gases analysis like O_2, N_2, CO, CO_2, H_2S, and COS. However, hydrogen has only a small difference in thermal conductivity compared to helium, making analysis by TCD using helium carrier gas difficult. To achieve full-range capability for hydrogen, an additional TCD with nitrogen or argon as a carrier is required. Light hydrocarbons are separated on an alumina PLOT column and detected on a FID.

The Agilent 7890A GC now supports an optional third detector (TCD), allowing simultaneous detection across three channels; this provides a complete analysis of permanent gases, including nitrogen, hydrogen, helium, oxygen, carbon monoxide, carbon dioxide, and hydrocarbons to nC_5, C_6+ fraction within six minutes.

Experimental

A single Agilent 7890A GC is configured with three channels, including one FID, and two TCDs. Light hydrocarbons are determined on the FID channel. One TCD with nitrogen or argon carrier is used for the determination of hydrogen and helium. The other TCD with helium carrier is used for the detection of all other required permanent gases. Figure 1 shows the valve drawing. The system conforms to published methods such as ASTM D1945 [1], D1946 [2], and UOP 539 [3].

The FID channel is for light hydrocarbon analysis. The sample from valve 4 is injected via the capillary injector into valve 3 to permit an early back-

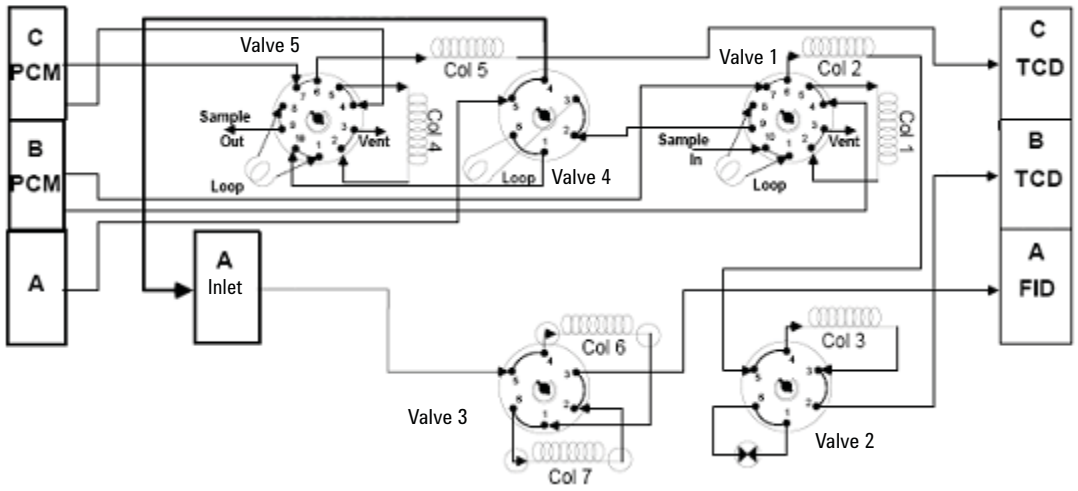
flush of the grouped heavier hydrocarbons (normally C_6+). Valve 3 is a sequence reversal with a short DB1 (column 6) for separating the hexane plus fraction (C_6+) from the lighter components. C_1 through C_5 hydrocarbons are separated on a PLOT alumina column. As soon as the light components C_1 through C_5 pass through the DB1column, valve 3 is switched to reverse the sequence of the DB1 and PLOT aluminum column so that components heavier than nC_6, including nC_6, are backflushed early. As a result, group C_6+ is followed by the individual hydrocarbons from the PLOT alumina column.

A new tube connector based on capillary flow technology is used to connect the valve to the capillary column to enhance the hydrocarbons analysis by improving the peak shape.

The second TCD channel (B TCD) employs three packed columns and two valves for the separation of permanent gases including O_2, N_2, CO, and CO_2 using helium as a carrier gas. Valve 1 is a 10-port valve used for gas sampling and backflushing heavier components; normally components heavier than ethylene are backflushed to vent when H_2S is not required to be analyzed. A six-port isolation valve (valve 2) with adjustable restrictor is used to switch the molecular sieve 5A column in and out of the carrier stream. Initially, the isolated valve is in the OFF position so that unresolved components air, CO, and CH_4 pass quickly through the HayeSep Q (column 2) onto the molecular sieve (column 3). The valve is then switched to the ON position to trap them in column 3 and allow the CO_2 to bypass this column. When the CO_2 has eluted, valve 2 is switched back into the flow path to allow O_2, N_2, CH_4, and CO to elute from the molecular sieve column.

The third TCD channel (C TCD) is for the analysis of H_2. Sample from the 10-port valve (valve 5) is injected into a precolumn (column 4, HayeSep Q) when H_2 with its coeluted compounds O_2, N_2, and CO pass through the short precolumn HayeSep Q onto the molecular sieve 5A column (column 5). Valve 5 is switched so that CO_2 and other compounds will be backflushed to vent, while H_2 is separated on the molecular sieve 5A.

Typical GC conditions for fast refinery gas analysis are listed in Table 1. The refinery gas standard mixture that was used for the method develoment is listed in Table 2.



Column 1 HayeSep Q 80/100 mesh
Column 2 HayeSep Q 80/100 mesh
Column 3 Molsieve 5A 60/80 mesh
Column 4 HayeSep Q 80/100 mesh
Column 5 Molsieve 5A 60/80 mesh
Column 6 DB-1
Column 7 HP-PLOT Al_2O_3
PCM: Electronic pneumatics control (EPC) module

Figure 1. RGA valve system.

Table 1. Typical GC Conditions for Fast Refinery Gas Analysis

Valve temperature	120 °C
Oven temperature program	60 °C hold 1 min, to 80 °C at 20°C/min, to 190 °C at 30 °C/min
FID channel	
Front inlet	150°C, split ratio: 30:1 (uses higher or lower split ratio according to the concentrations of hydrocarbons)
Column	6: DB-1 7: HP-PLOT Al2O3 S
Column flow (He)	3.3 mL/min (12.7 psi at 60 °C), constant flow mode
FID	
Temperature	200 °C
H_2 flow	40 mL/min
Air flow	400 mL/min
Make up (N_2)	40 mL/min
Second TCD channel	
Column	1: HayeSep Q 80/100 mesh 2: HayeSep Q, 80/100 mesh 3: Molecular sieve 5A, 60/80 mesh
Column flow (He)	25 mL/min (36 psi at 60 °C), constant flow mode
Procolumn flow (He)	22 mL/min at 60 °C (7 psi), constant pressure mode
TCD	
Temperature	200 °C
Reference flow	45 mL/min
Make up	2 mL/min
Third TCD channel	
Column	4: HayeSep Q 80/100, mesh 5: Molecular sieve 5A, 60/80, mesh
Column flow (N_2)	24 mL/min, (26 psi at 60 °C), constant flow mode
Procolumn flow (N_2)	7 psi, (24 mL/min at 60 °C), constant pressure mode
TCD	
Temperature	200 °C
Reference flow	30 mL/min
Make up	2 mL/min

Table 2. RGA Calibration Gas Standards

	Compound	% (V/V)		Compound	% (V/V)
1	Methane	5.98	15	i-Pentane	0.101
2	Ethane	5.07	16	n-pentane	0.146
3	Ethylene	2.99	17	1,3-Butadiene	1.46
4	Propane	8.04	18	Propyne	0.476
5	Cyclopropane	0.50	19	t-2-Pentene	0.195
6	Propylene	3.04	20	2-Methyl-2-butene	0.149
7	i-Butane	2.71	21	1-Pentene	0.094
8	n-Butane	2.11	22	c-2-Pentene	0.146
9	Propadiene	0.94	23	n-Hexane	0.099
10	Acetylene	1.72	24	H_2	15.00
11	t-2-Butene	1.55	25	O_2	2.00
12	1-Butene	1.00	26	CO	1.50
13	i-Butene	0.808	27	CO_2	3.00
14	c-2-Butene	1.230	28	N_2	BL

Results and Discussion

Enhance Gas Analysis with Union Connector

The system uses the new union connector based on capillary flow technology for connecting the capillary column to the valve, enhancing the peak shapes in gas analysis and making the connections easier. Figure 2 shows the comparison of peak shapes obtained from a traditional polyamide connector and the new union connecter. With the new union connecter the improvement in peak shape is readily apparent.

Fast Refinery Gas Analysis (RGA)

Use of an optimized combination of several packed columns and a PLOT alumina column allows fast separation of light hydrocarbons and permanent gases with the same oven temperature program without the need of an additional oven.

The separation results from each channel are illustrated in Figure 3.

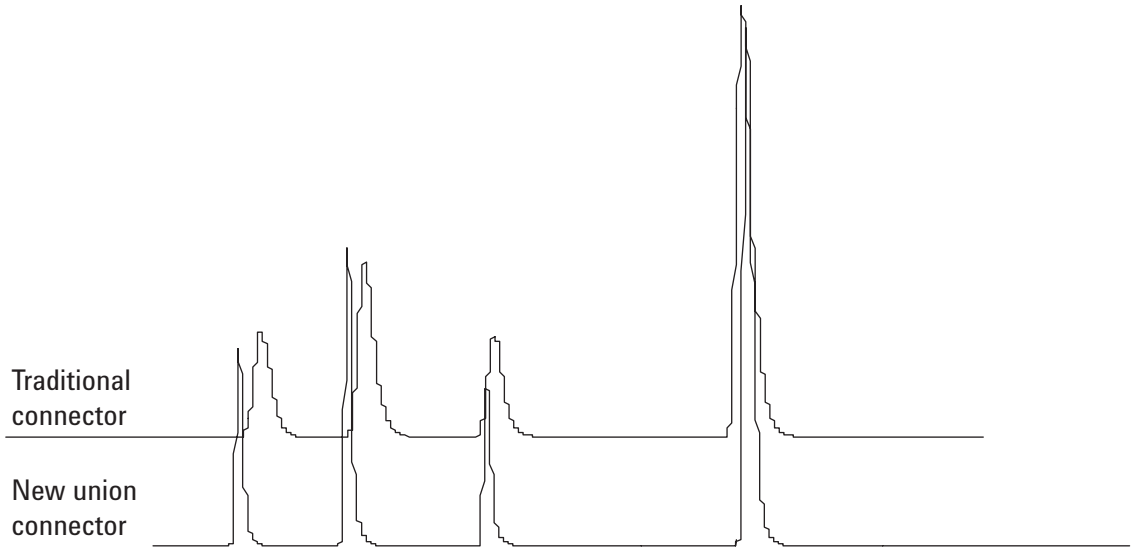


Figure 2. Hydrocarbon peaks obtained from traditional tube connector and new union connector.

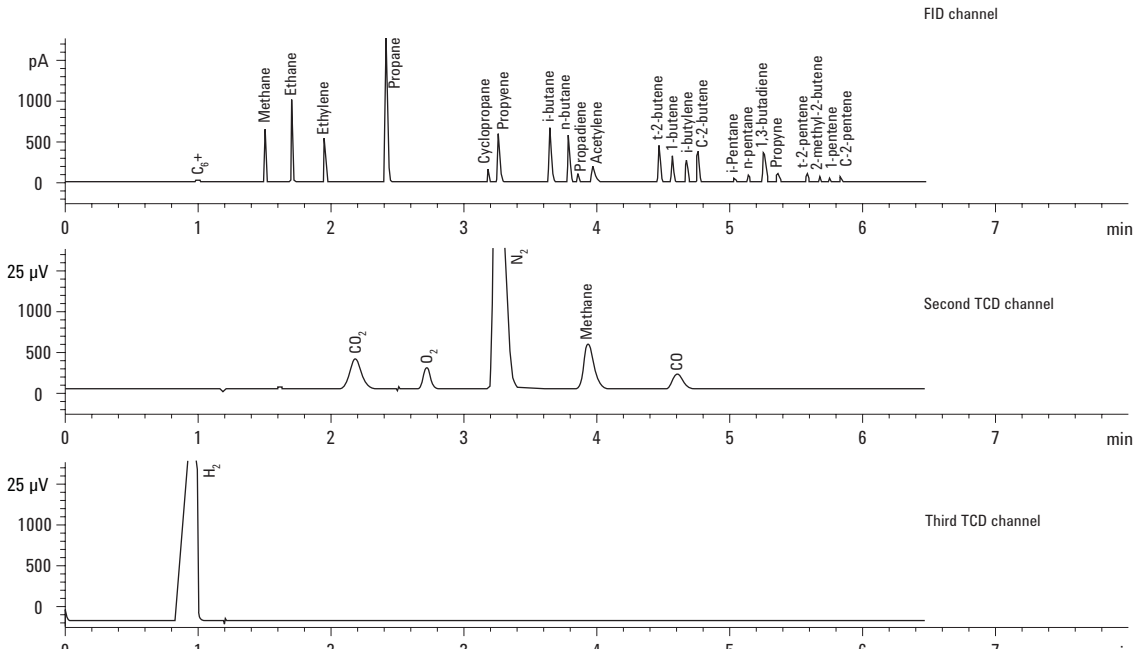


Figure 3. Refinery gas calibration standards analysis. The concentrations for each compound are shown in Table 2.

The top chromatogram (FID channel) is the hydrocarbon analysis. The PLOT alumina column provides excellent separation of hydrocarbons from C_1 to nC_5, including 22 isomers. Components heavier than nC_6 are backflushed early as a group (C_6+) through the precolumn. The middle chromatogram (second TCD channel) is the separation of permanent gases using helium as a carrier gas. The bottom chromatogram (third TCD channel) is the separation of hydrogen, since hydrogen has only a little difference in thermal conductivity compared to helium. Use of an additional TCD with nitrogen (or argon) as a carrier gas improves the hydrogen detectability and linearity.

Table 3 shows very good repeatability for both retention time and area for analysis of the refinery gas standard.

Table3. Repeatability-Refinery Gas Analysis (6 runs) with 1 Run Excluded

	Retention time			Area		
Compounds	**Average**	**Std. dev.**	**RSD%**	**Average**	**Std. dev.**	**RSD%**
C_6+	0.99648	0.00031	0.03	59.01	1.10	1.86
Methane	1.50780	0.00046	0.03	490.02	1.45	0.30
Ethane	1.70788	0.00052	0.03	807.40	2.35	0.29
Ethylene	1.95732	0.00071	0.04	472.31	1.31	0.28
Propane	2.41706	0.00075	0.03	1950.35	5.96	0.31
Cyclopropane	3.18506	0.00075	0.02	145.62	0.45	0.31
Propyene	3.26195	0.00072	0.02	732.90	2.01	0.27
i-butane	3.64883	0.00055	0.02	885.04	3.15	0.36
n-butane	3.79161	0.00070	0.02	682.13	2.59	0.38
Propadiene	3.86098	0.00095	0.02	109.08	0.65	0.60
Acetylene	3.96990	0.00120	0.03	348.17	2.39	0.69
t-2-butene	4.47301	0.00106	0.02	507.88	2.59	0.51
1-butene	4.57118	0.00110	0.02	332.39	2.03	0.61
i-butylene	4.67529	0.00121	0.03	260.95	1.95	0.75
c-2-butene	4.76367	0.00112	0.02	403.80	3.47	0.86
i-pentane	5.03923	0.00090	0.02	45.03	0.05	0.11
n-pentane	5.14583	0.00099	0.02	69.23	0.40	0.58
1,3-butadiene	5.25906	0.00122	0.02	485.49	3.66	0.75
Propyne	5.36385	0.00155	0.03	101.08	0.41	0.40
t-2-pentene	5.58664	0.00121	0.02	82.85	0.66	0.79
2-methyl-2-butene	5.68220	0.00117	0.02	62.54	0.61	0.98
1-pentene	5.75553	0.00126	0.02	39.57	0.38	0.96
c-2-pentene	5.83970	0.00131	0.02	59.08	0.50	0.85
CO_2	2.18561	0.00221	0.10	2040.33	2.37	0.12
O_2	2.72634	0.00060	0.02	930.68	6.53	0.70
N^2	3.25170	0.00044	0.01	22500.18	68.87	0.31
CO	4.61692	0.00083	0.02	903.09	2.77	0.31
H_2	0.9869	0.00099	0.10	16097.38	106.53	0.66

Typical natural gas also can be characterized with the system using the same conditions for the fast RGA. The chromatograms of natural gas on the three channels are shown in Figure 4; hydrogen (3% Mol) and helium (1% Mol) are separated on the third TCD channel.

Flexibility for Hydrocarbon Analysis

The system is very flexible for hydrocarbon analysis. By setting up different valve (valve 3) switch times, the early backflush group can be C_6+ followed by individual C_1 to C_5 hydrocarbons as mentioned in fast RGA, or C_7+ followed by individual C_1 to C_6 hydrocarbons, or no backflush to separate C_1 to C_9 individual hydrocarbons. The top chromatogram in Figure 5 is the result with backflush group of C_6+, the middle one is that of C_7+, and the bottom one is that of no backflush. With such flexibility, a wide range of refinery gas and natural gas compositions can be measured reliably without hardware or column changes.

H_2S and COS Analysis

H_2S and COS (methyl-mercaptan) can be analyzed on the rear TCD channel by adding an additional delay to the backflush time (valve 1) to allow H_2S and COS to elute onto column 2 (HayeSep Q). The analysis time is extended an additional 3 to 4 minutes, and requires a sample containing no water. Figure 6 shows the chromatogram of H_2S at approximately 500 ppm and COS 300 ppm with 1 mL sample size. The Nickel tubing packed columns and Hastelloy-C valves can be chosen for high concentration of H_2S analysis to minimize corrosion.

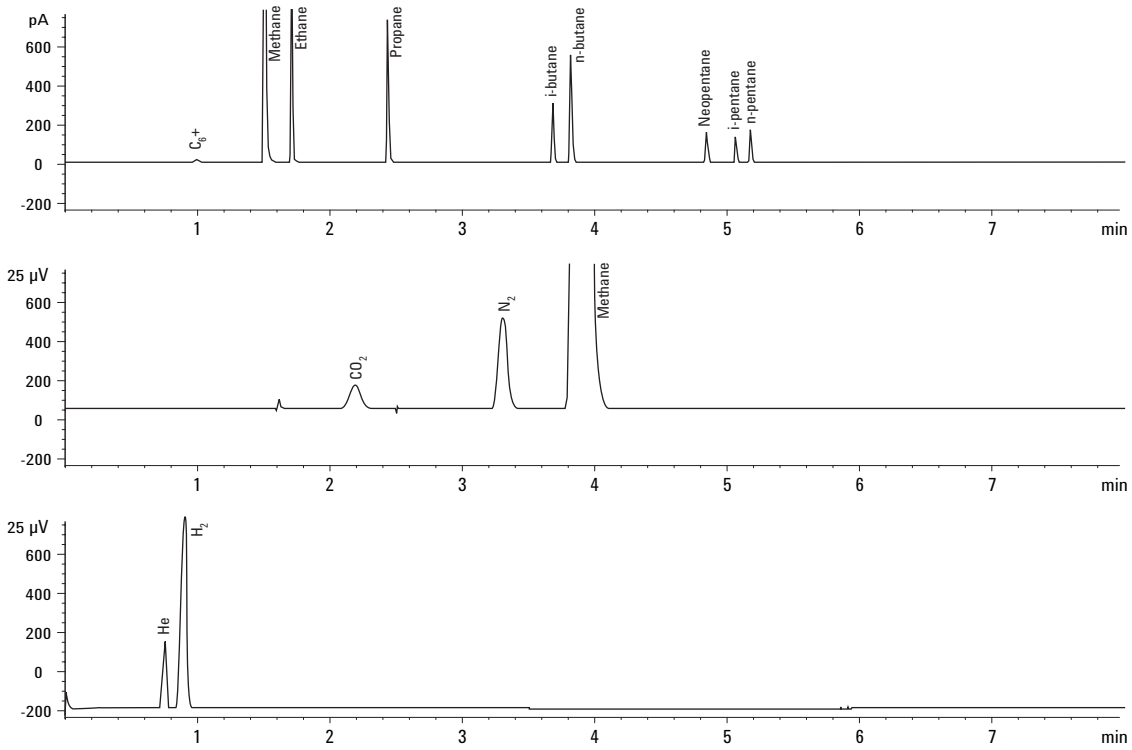


Figure 4. Natural gas analysis of a calibration gas.

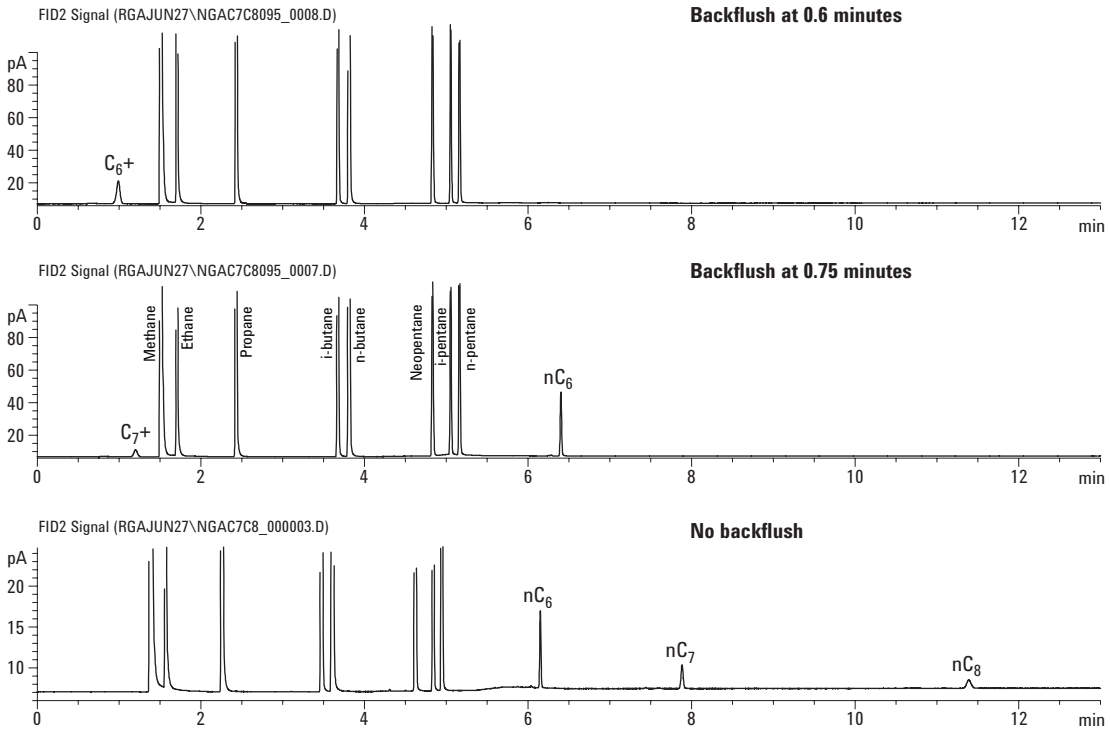


Figure 5. Chromatograms of light hydrocarbons on FID channel with different backflush times .

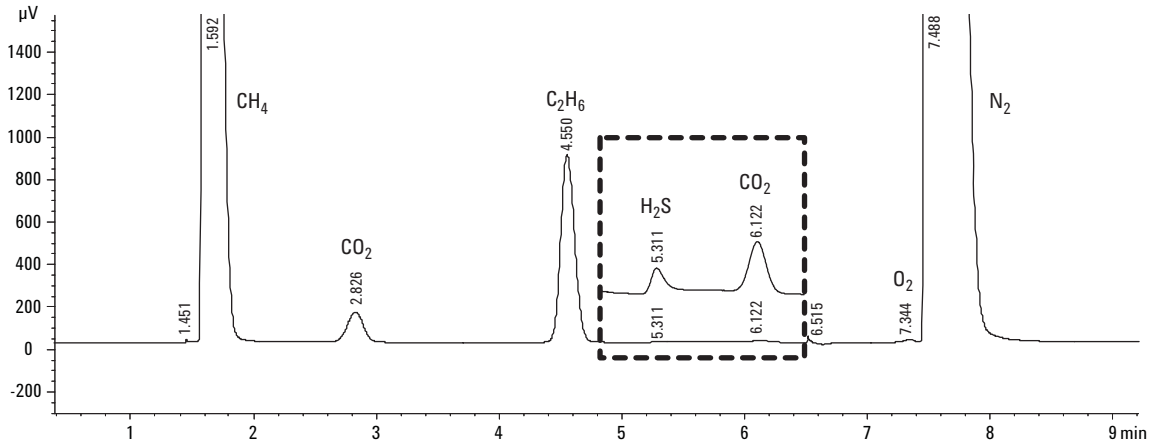


Figure 6. H_2S at approximately 500 ppm and COS 300 ppm on second TCD channel.

Oven program: 50 hold 2 minutes, to 150 °C at 30 °C/min, hold 3 minutes, to 190 °C at 30 °C/min, hold 1 minute
Sample loop: 1 mL

Reporting

A macro program provides automated gas properties calculation. It gives a report in mole %, weight %, volume %, or any combination of the three. If required, heat values for the gas analyzed and other standard calculations are also available. Reports can be calculated using formulas given in the ASTM/GPA or ISO standards.

Conclusions

An exact and fast analysis of the components in refinery gas is essential for optimizing refinery processes and controlling product quality.

One 7890A GC configured with three parallel channels with simultaneous operation provides complete analysis of permanent gases, including nitrogen, hydrogen, helium, oxygen, carbon monoxide, carbon dioxide, and all hydrocarbons to C_5 and C_6+ as a group within six minutes. A second TCD with nitrogen or argon as a carrier gas improves the hydrogen sensitivity and linearity.

The configuration is very flexible for hydrocarbon analysis, different backflush times may be set to obtain the early backflush group for C_6+ or C_7+, or no backflush to separate C_1 to C_{10} individual hydrocarbons. In these cases, the analysis time is increased by 6 minutes. H_2S and COS can be analyzed on the same GC configuration; it requires 3 to 4 minutes of additional time.

A macro program provides automated gas properties calculation. Reports can be calculated using formulas given in the ASTM/GPA or ISO standards. It gives a report in mole %, weight %, volume %, or any combination of the three.

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Agilent Technologies

Parallel GC for Complete RGA Analysis

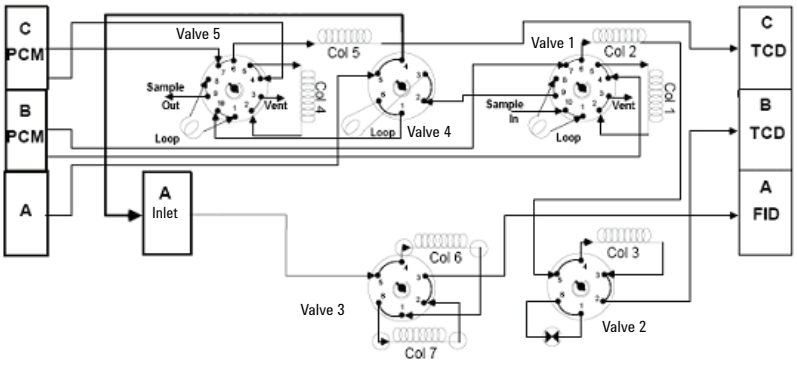
Application Brief

Chunxiao Wang

A previous application brief [1] has shown that a 7890A GC configured with three parallel channels provides a complete refinery gas analysis (RGA) within six minutes. The configuration for fast RGA in the brief has been updated by adding a fifth valve, which can now be supported by the 7890A GC. The updated configuration is almost the same as the previous one except for the third channel (TCD) for H_2 analysis using N_2 or Ar as carrier gas to improve H_2 detectability and linearity. The updated configuration uses a 10-port valve with a pre-column for backflushing late-eluting components while H_2 is separating on the molsieve column instead of a three-way splitter plus split/splitless inlet.

Refinery gases are mixtures of various gas streams produced in refinery processes. They can be used as a fuel gas, a final product, or a feedstock for further processing. The composition of refinery gas streams is very complex, typically containing hydrocarbons, permanent gases, sulfur compounds, etc. An exact and fast analysis of the components is essential for optimizing refinery processes and controlling product quality.

The Agilent 7890A GC now supports an optional detector (TCD), allowing simultaneous detection across three channels. This provides a complete analysis of permanent gases, including nitrogen, hydrogen, oxygen, carbon monoxide,



Column 1 HayeSep Q 80/100 mesh
Column 2 HayeSep Q 80/100 mesh
Column 3 Molsieve 5A 60/80 mesh
Column 4 HayeSep Q 80/100 mesh
Column 5 Molsieve 5A 60/80 mesh
Column 6 DB-1
Column 7 HP-PLOT Al_2O_3
PCM: Electronic pneumatics control (EPC) module

Figure1. RGA valve system.

Highlights

- One 7890A GC configured with three parallel channels with simultaneous detection provides a comprehensive, fast, and high-resolution analysis of refinery gas in 6 minutes.
- Use of optimized columns allows faster analysis of hydrocarbons and permanent gases using a single oven temperature program without the need for an additional column oven.
- A third TCD channel can be used for improving hydrogen detection and linearity by using nitrogen (or argon) as carrier gas.
- A new, easy-to-use union tubing connector based on capillary flow technology is used to connect valves and capillary columns to improve the chromatographic performance, including peak shape.
- Excellent results are achieved. The lowest detection limit is 50 ppm for all compounds, 500 ppm for hydrogen sulfide.
- ChemStation macro program is supplied for RGA reporting.
- The system can be obtained by ordering option SP1 7890-0322 for the standard fast RGA and 7890-0338 for the fast RGA with Hastelloy valves and nickel tubing for H_2S containing samples on the 7890A.

carbon dioxide, and hydrocarbons to nC6. The total run time is less than 6 minutes. The configuration is suitable for most refinery gas streams such as atmospheric overhead, FCC overhead, fuel gas, and recycle gases.

In this analysis, a single Agilent 7890A GC is configured with three channels, including an FID channel and 2 TCD channels. Light hydrocarbons are determined on the FID channel using an alumina column. One TCD is used with nitrogen or argon carrier gas for improved determination of hydrogen and helium; the other TCD is used with helium carrier for the detection of all other required permanent gases. The configuration is shown in Figure 1. An Agilent union tube connector, based on capillary flow technology, is used to quickly and easily connect the valve and capillary column for improved performance. The system conforms to published methods such as ASTM D1945 [2], D1946 [3], and UOP 539 [4].

Separation resulting from each channel is illustrated in Figure 2. The top chromatogram shows the hydrocarbon analysis. A PLOT AL2O3 column provides excellent separation of hydrocarbons from C1 to nC5 containing 22 isomers. Components heavier than nC6 are backflushed early in the run as a group (C6+) through a short DB-1 pre-column.The middle chromatogram shows the separation of permanent gases using helium as the carrier gas on the second TCD channel (B TCD). H_2S and COS can be analyzed on the second TCD channel as well, requiring 3 to 4 additional minutes. The bottom chromatogram shows the separation of hydrogen. Because hydrogen has only a small difference in thermal conductivity compared to helium, it requires an additional TCD with nitrogen or argon as the carrier gas to improve the hydrogen detectability and linearity. All channels operate simultaneously to provide a comprehensive, fast analysis with high resolution of components. A macro program automatically provides the calculation of gas properties. Reports can be generated using formulas specified in the ASTM/GPA and/or ISO standards. Reports in mole%, weight%, volume%, or any combination of the three are available.

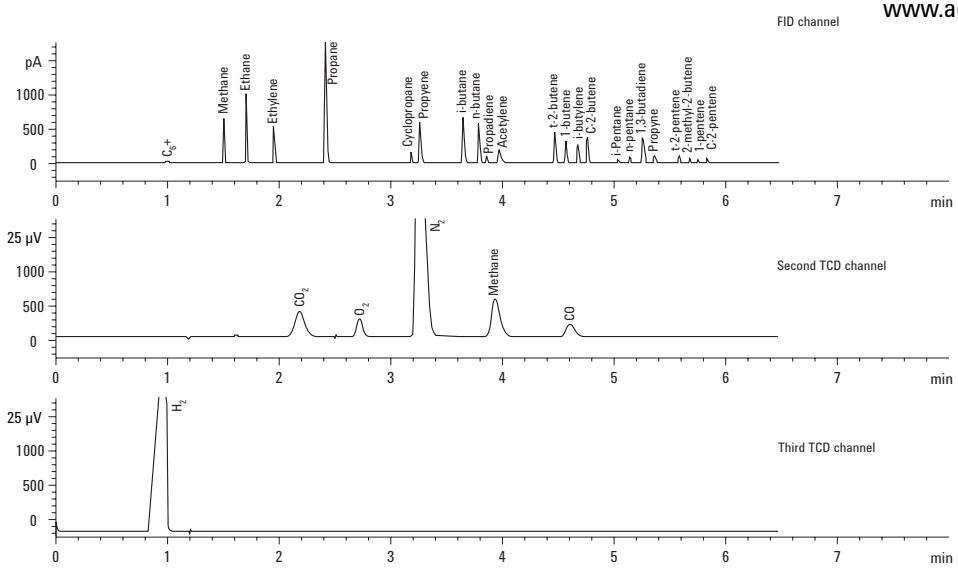


Figure 2. Refinery gas calibration standards analysis.

For More Information

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1. Chunxiao Wang, "Parallel GC for Complete RGA Analysis,"Agilent application brief, 5989-6103EN, January 19, 2007
2. ASTM D1945-03, "Standard Test Method for Analysis of Natural Gas by Gas Chromatography," ASTM International, 100 Bar Harbor Drive, West Conshohocken, PA 19428 USA.
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5989-7438EN

High-Pressure Injection Device for the Agilent 7890A and 6890 Series Gas Chromatographs

Accessory G3505A

Introduction

Gas chromatography sampling and representative analysis of highly volatile liquefied hydrocarbons with high precision and accuracy can be challenging. In the solution described here, a unique sample injection device based on a needle interface and liquid rotary valve, has been designed for sampling light petroleum matrices with broad boiling point distributions. The 7890A GC-based system consists of a 4-port liquid valve, a deactivated removable needle, and an auxiliary flow. The needle is directly installed on one port of the valve. This compact device is installed directly over the top of a split/splitless inlet. The unit is operated automatically just like a typical liquid autosampler; however, the needle is not withdrawn. Various pressurized liquid samples have been run on this device, such as liquefied natural gas (calibration standard), ethylene, propylene, and butadiene. Excellent repeatability is obtained with RSDs typically below 1% in quantitative analyses.

Injection Device

The high-pressure injection device (HPLI) consists of components as shown in Figure 1.

- **Valve:** Internal sample valve from Valco Instruments Co. Inc. 4-port equipped with a sample volume of 0.06 µL. Other rotor sizes are available from Valco Instruments Company.
- **EPC:** An auxiliary flow from a 7890A Aux module is connected to port P. In sample analysis, the flow can be set at 50 mL/min to 200 mL/min. The higher auxiliary flow gives better peak shape.

Ordering Information

Order accessory G3505A. The accessory is compatible with both the 7890A and 6890 series GCs.

The following components are recommended. These are not supplied in the accessory kit.

- **Filter:** To remove particles from samples.
- **Restrictor:** To maintain sample pressure, a metering valve (Agilent PN 101-0355) is connected to the end of the sample exit line tubing. Restrictor is not included in accessory kit.

Guideline for choosing Aux flow source

7890AGC

G3471A Pneumatic Control Module (PCM) or

G3470A Aux EPC module

6890GC

G1570A Aux EPC or

G2317A PCM module

The PCM is the preferred source for both GCs.

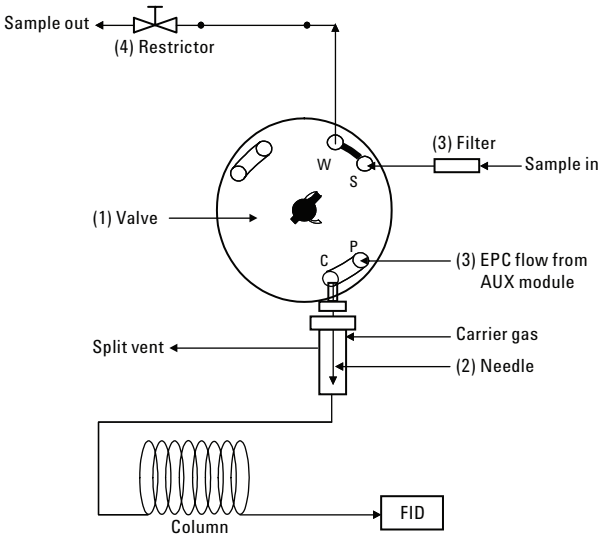


Figure 1. Flow diagram of the high-pressure injection device (HPLI).

Typical Instrumental Conditions

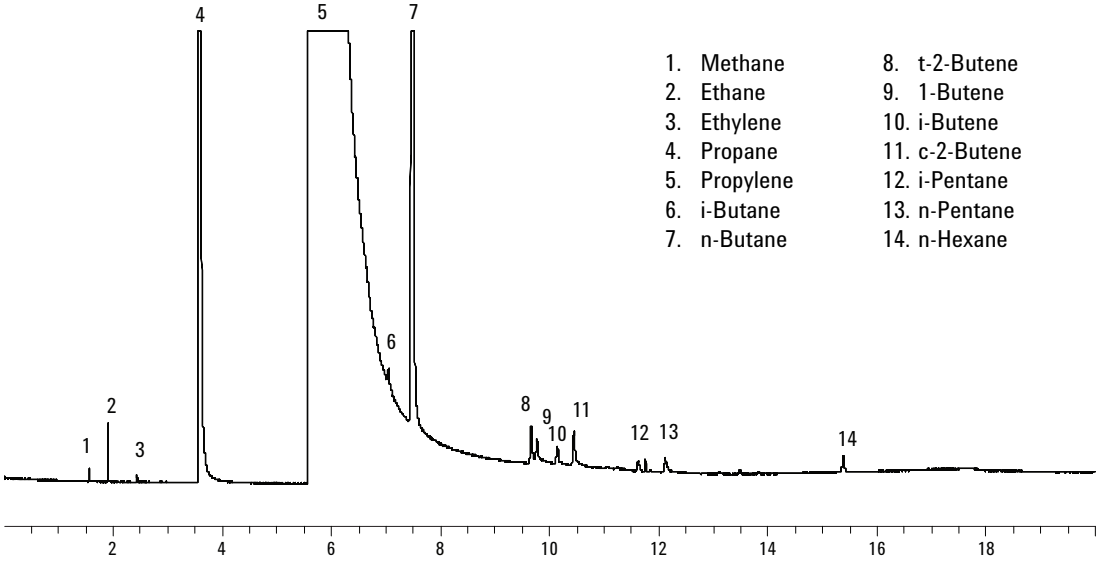
Gas chromatograph	Agilent 7890A
Injection source	High-pressure injection device (HPLI) at near ambient temperature
Injection port	Split/splitless, 250 °C (350 °C for C5–C40)
Sample size	0.06 µL
Carrier gas	Helium
Aux or PCM	150 mL/min (Helium)
FID	250 °C (350 °C for C5–C40) H_2, 35 mL/min Air, 400 mL/min

Agilent pneumatic air actuator/valve assembly installed on the 7890A.

Sample Chromatograms

Pressurized Propylene

This sample is analyzed by the same conditions as in ASTM D6159. A typical chromatogram is shown in Figure 2.



1. Methane
2. Ethane
3. Ethylene
4. Propane
5. Propylene
6. i-Butane
7. n-Butane
8. t-2-Butene
9. 1-Butene
10. i-Butene
11. c-2-Butene
12. i-Pentane
13. n-Pentane
14. n-Hexane

Figure 2. Chromatogram of pressurized propylene.

Pressurized 1,3-Butadiene

Figure 3 is an example of C4 hydrocarbons analysis showing 1.3 butadiene purity.

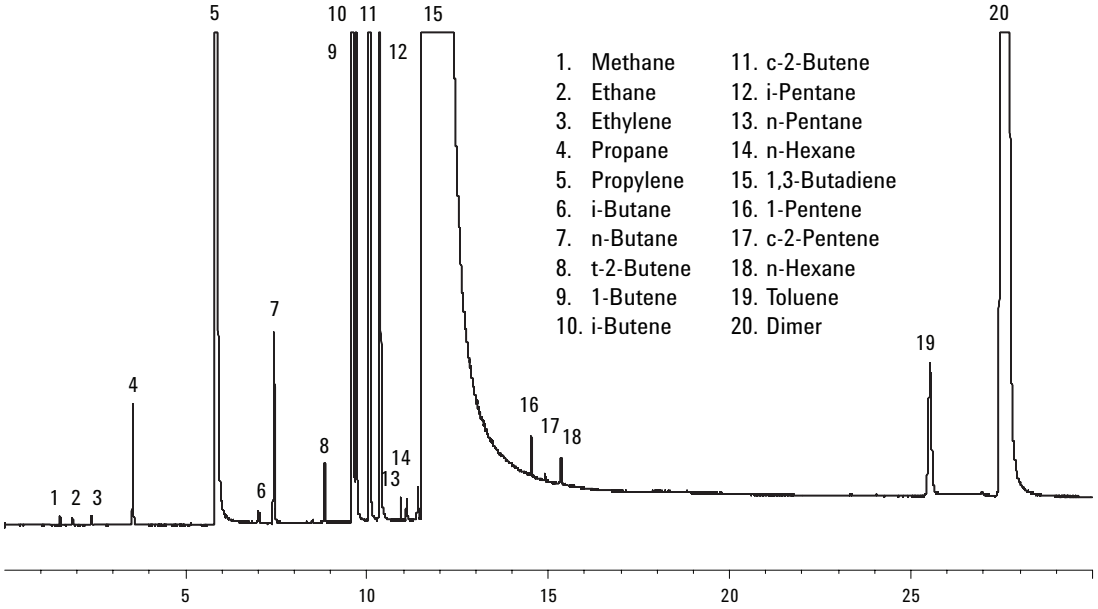


Figure 3. Chromatogram of pressurized 1,3-butadiene.

Summary

A unique sample injection device for the Agilent 7890A GC based on a unique deactivated interface and liquid rotary valve has been designed for sampling light petroleum matrices with broad boiling point distributions from methane to as high as C40. It is installed directly over a split/splitless GC split/splitless inlet in a few minutes. The maximum sample pressure is 3,000 psig, although typical samples will have pressures under 1,500 psig. Various pressurized liquid samples have been tested on this device with high accuracy and precision. The sampler is quick to install and easy to operate. As with all high-pressure sampling systems, appropriate safety precautions must be followed.

Competitive Advantages

The HPLI can be used with a wide variety of sample streams or pressurized vessels. Because the sampling valve is interfaced directly to the inlet with an inert needle, loss or adsorption of analytes is minimized compared to conventional liquid sample valve systems. Compared to other gas chromatographic vaporizers for handling pressurized or nonpressurized samples, the Agilent HPLI has the following advantages:

- Better results with polar analytes such as glycols
- Superior inertness
- Low discrimination (no discrimination up to C_{16})
- Flexibility: Install or uninstall in less than 10 minutes
- Good for trace impurity analysis with 0.5 µL rotor
- Excellent repeatability, typically RSDs below 1 %

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Crude Oil & Natural Gas

Sulfur & Odorants

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Volatile Sulfur in Natural Gas, Refinery Gas, and Liquified Petroleum Gas

Application

Gas Chromatography

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Abstract

An Agilent 6890 gas chromatograph equipped with an FPD (flame photometric detector) is used to characterize low level sulfur compounds in natural gas, refinery gas, and liquified petroleum gas (LPG) using a J&W 105 m × 0.53 mm × 5.0 μm DB-1 column. Analysis of volatile sulfur to less than 100 ppb can easily be performed with a volatiles interface (VI) connected to a 6-port gas-sampling valve. The system as configured provides a cost-effective solution for the determination of odorants in natural gas. Coelutions of hydrocarbons and sulfur compounds that result in signal quenching are documented.

Introduction

Monitoring of low-level volatile sulfur compounds in light hydrocarbon streams such as refinery gas, and in fuels including natural gas and LPG, persist as measurement challenges. To highlight one application area, odorant monitoring is an essential measurement need of the natural gas industry. Table 1 lists a number of the commonly used additives in the United States and Europe. Europe currently favors t-butyl mercaptan, methyl ethyl sulfide, ethyl mercaptan and tetrahydrothiophene. Odorant quality, including characterization of contaminants and possible reaction byproducts, is also important. Optimal odorization is also dependent on the quality of the natural gas stream, making measurement of the naturally occurring sulfur important for optimal metering of odorant addition and for monitoring odor threshold.

Table 1. Common Odorizers in Natural Gas

Methyl mercaptan	Ethyl mercaptan
Dimethyl sulfide	Isopropyl mercaptan
Methyl ethyl sulfide	Normal propyl mercaptan
Tertiary butyl mercaptan	Secondary butyl mercaptan
Diethyl sulfide	Tetrahydrothiophene
Ethyl isopropyl sulfide	

Sulfur selective measurements can assist in blending operations to assure proper ratios of components are injected into the pipeline, and to ensure that effects such as pipeline oxidation are understood.

Natural gas and other light hydrocarbon streams are finding use as fuel feedstocks for a variety of fuel cell technologies. Fuel cells and the reformer catalysts are generally not sulfur tolerant. Depending on the technology employed, sulfur can be a poison at single digit ppm levels. The need for low level sulfur measurement in the fuel cell industry will continue to grow as the various technologies see wider deployment. Odorant monitoring at various locations within a gas distribution system can also be important.

Gas chromatography plays an important role in sulfur measurement. The flame photometric detector (FPD) is ideal for many of these applications, given its low cost and ease-of-use, provided coelution can be avoided. Selection of the appropriate column, temperature program, and sample introduction system are key to the deployment of a successful system. This work illustrates what can be done with a methyl silicone column (105 m × 0.53 mm × 5.0 µm DB-1) without use of cryogenic oven cooling.

ASTM method D 5504-94 details a chemiluminescence approach to the analysis of sulfur in various gaseous streams including natural gas. Other sulfur selective detectors are not excluded from the method provided they meet criteria for sensitivity and hydrocarbon interference. The system described in this paper generally follows the method, pointing out situations where particular hydrocarbon matrices can cause quantitative problems. A subset of the sulfur compounds listed in the ASTM method is used.

Experimental

An Agilent 6890 gas chromatograph equipped with a FPD operating in a hydrogen rich mode for optimal sensitivity was used in this work. Sample introduction consisted of a 6-port Hastelloy C gas sample valve (GSV) interfaced directly to the volatiles interface (VI) with Sulfinert tubing (Figure 1). Instrument conditions are given in Table 2. A point-of-use gas blending system was used for preparation of ppb level sulfur compounds in the hydrocarbon matrices. Figure 2 illustrates the basic components and configuration of the gas blending hardware. The details of this system have been described

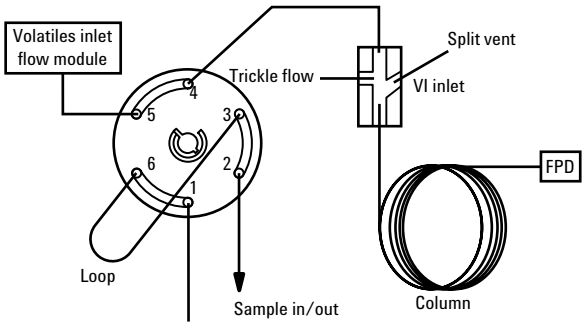
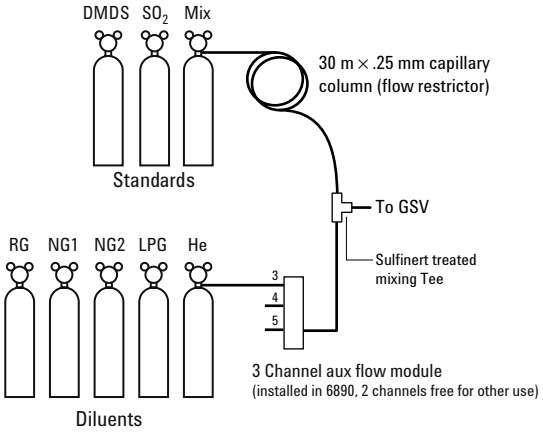


Figure 1. Sample introduction scheme.

Table 2. Instrument Conditions

Agilent 6890 Gas Chromatograph	
Detector	**Flame Photometric**
Temperature	250 °C
Hydrogen Flow	50 mL/min
Air Flow	60 mL/min
Makeup	N_2 60 mL/min, constant mode
Filter	393 nm
Injection Source	**6-port Gas Sampling Valve**, Hastelloy C
Temperature	120 °C
Loop	0.50 cc Sulfinert treated (replaces standard loop)
Injection Port	**Volatiles Interface**
Temperature	120 °C
Split Ratio	0.2 to 1 typical
Carrier Gas	Helium
Constant Flow Mode	
Columns	**105 m × 0.53 mm × 5.0 µm DB-1, J&W Cat. No. 125-10B5**
Oven Program	
Initial Temperature	35 °C
Initial Time	5 min
Temperature Ramp	25 °C/min
Final Temperature	240 °C
Final Time	5 min
Aux EPC	
Restrictor	Medium flow resistance frits, Part no. 19231-60700



Cylinder codes:
- RG - Refinery gas
- NG1 - High methane natural gas
- NG2 - High ethane natural gas
- LPG - Liquified petroleum gas
- Mix - 8 component sulfur mix
- DMDS Dimethyl disulfide

Figure 2. Point-of-use automated blending system.

previously.[1] Sulfur components and their respective cylinder concentrations in the calibration mix are listed in Table 3. The mix was obtained from DCG Partnership 1, LTD., Pearland, TX, 281-648-1894, The GPA natural gas mixtures were purchased from Scott Specialty Gases.

Table 3. Sulfur Calibration Mix

Number	Compound	Conc.(ppm)
1	Hydrogen sulfide	5.00
2	Carbonyl sulfide	4.96
3	Methyl mercaptan	5.00
4	Ethyl mercaptan	5.04
5	Dimethyl sulfide	4.91
6	Carbon disulfide	5.01
7	t-Butyl mercaptan	5.04
8	Tetrahydrothiophene	5.05

Results

Sensitivity will always be the first and perhaps most important attribute of a selective detector. This should be well understood prior to tackling complex application problems. First, note that the FPD is a non-linear detector due to the mechanism of S2 formation from sulfur atoms in the flame. Excited S2 is responsible for light emission at approximately 393 nm, which gives the detector its selectivity. A comprehensive review of various sulfur selective detectors and applications have been previously discussed.[2] To establish the performance potential of the 6890-FPD system, specifically in terms of sensitivity, a dilution study was conducted where the 8 component mix was systematically diluted in helium to obtain concentrations from 50 ppbv to approximately 400 ppbv. Programming the Aux EPC over a pressure range from 60 psig to 10 psig automatically does this at a sulfur calibration mix flow of 0.9 mL/min. The pressure needed to achieve this mix flow is set from the cylinder regulator. Four methods were setup, each with a different Aux pressure setting, and subsequently used in the ChemStation sequence table. The resulting calibration curve in log-log format for one of the components, ethyl mercaptan, is shown in Figure 3. Figure 4 shows an FPD chromatogram of the sulfur in helium mix at 78 ppbv per component, obtained from one of the methods used in the automatic dilution sequence. Good signal to noise is seen even at this low sulfur level.

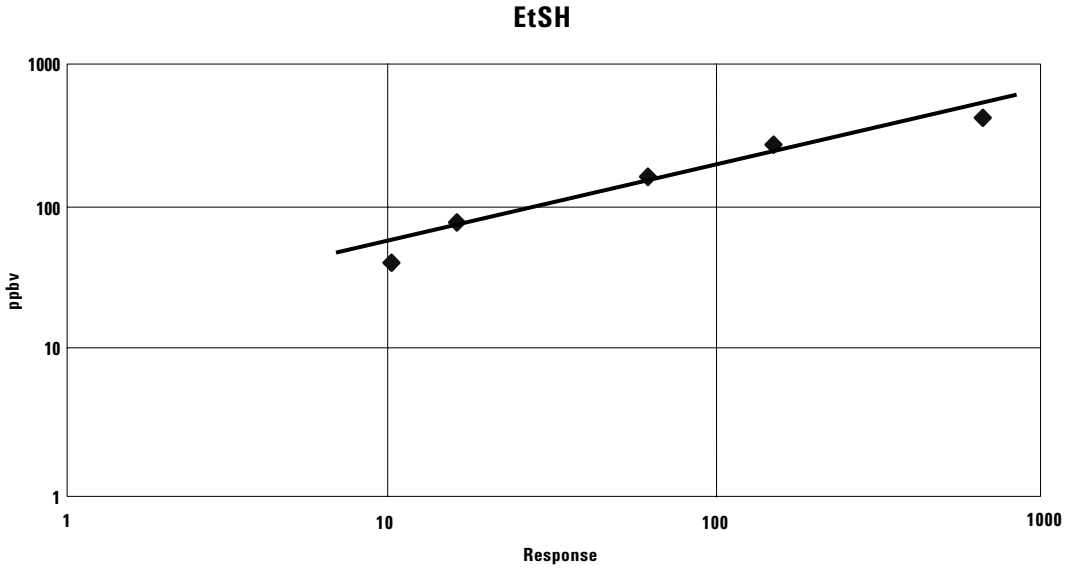


Figure 3. Calibration of ethyl mercaptan in helium from 400 ppbv to 50 ppbv.

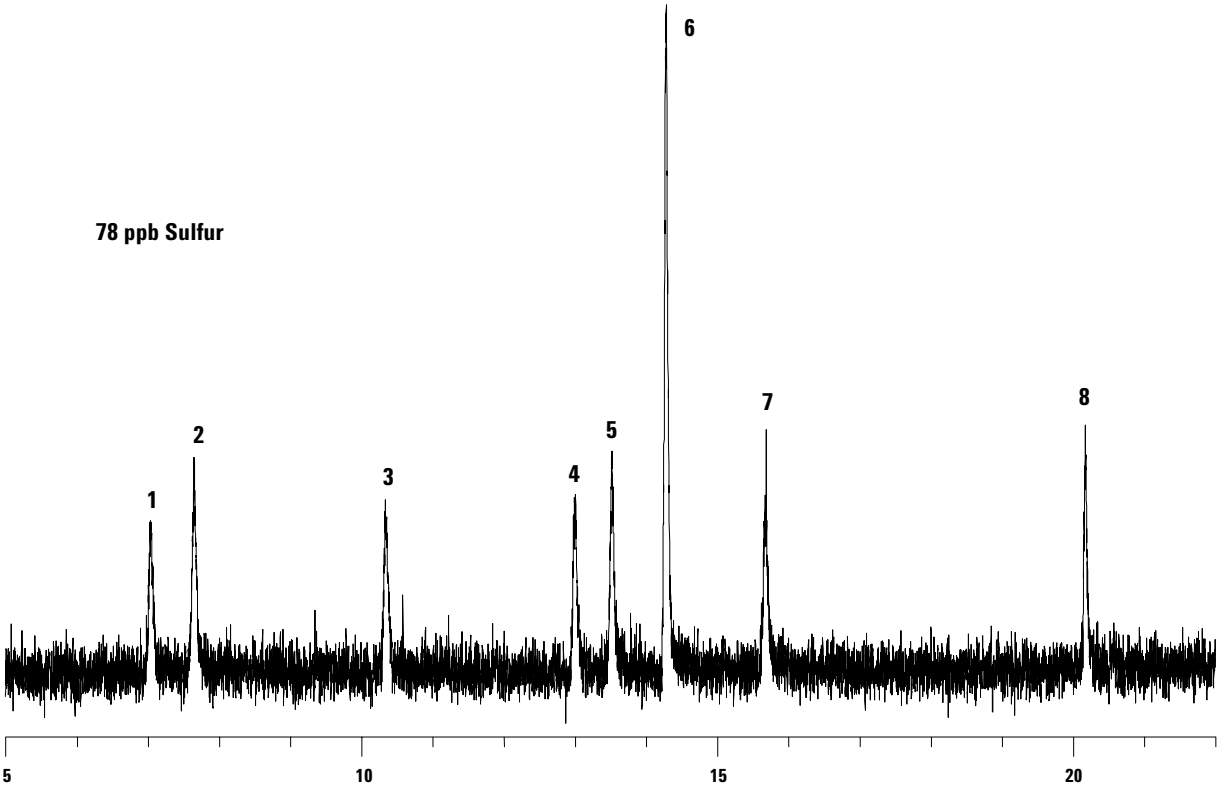


Figure 4. Eight volatile sulfur compounds at 78 ppbv per component. Detector - Flame Photometric. See Table 3 for peak id's.

Prior to use of the FPD, the Agilent atomic emission detector (AED) was used to characterize potential hydrocarbon-sulfur coelutions and false hydrocarbon responses that result when the selectivity of the detector is exceeded. Both carbon and sulfur chromatograms can be collected simultaneously, allowing potential interferences that would lead to signal quenching on the FPD to be quickly identified. Figures 5, 6 and 7 show overlaid sulfur and carbon chromatograms for high ethane natural gas, high methane natural gas, and refinery gas, respectively.

These chromatograms were produced by blending the sulfur mix into the hydrocarbon matrices to produce sulfur levels of 145 ppbv per component. The AED carbon chromatograms shown are due to the hydrocarbon matrix since the contribution of the carbon in the sulfur compounds is exceedingly small.

Coelutions of carbonyl sulfide/propane and methyl mercaptan/t-2-butene are clearly identified. Therefore, in natural gas streams, analysis of low level COS will be problematic on the FPD when using the methyl silicone column. This is not a major limitation since COS is normally not found in natural gas streams beyond the well head. However, most other volatile sulfur compounds found naturally or added as odorants should be quantifiable over the sensitivity range of the detector. For more complex hydrocarbon streams such as refinery gas, the additional coelution of methyl mercaptan/ t-2-butene must be watched.

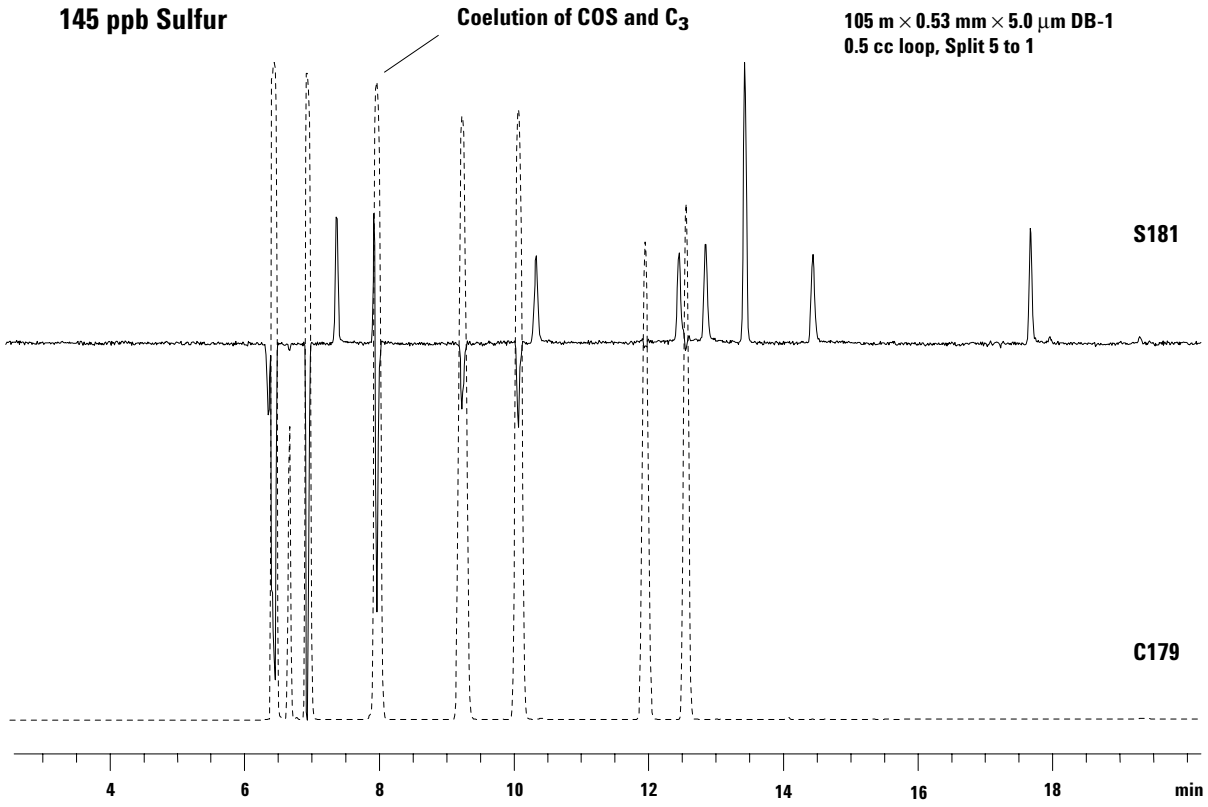


Figure 5. AED carbon and sulfur chromatograms of high ethane (9%) natural gas blended with the eight component sulfur mix. Dashed line is carbon. The carbon and sulfur chromatograms are not drawn to the same scale.

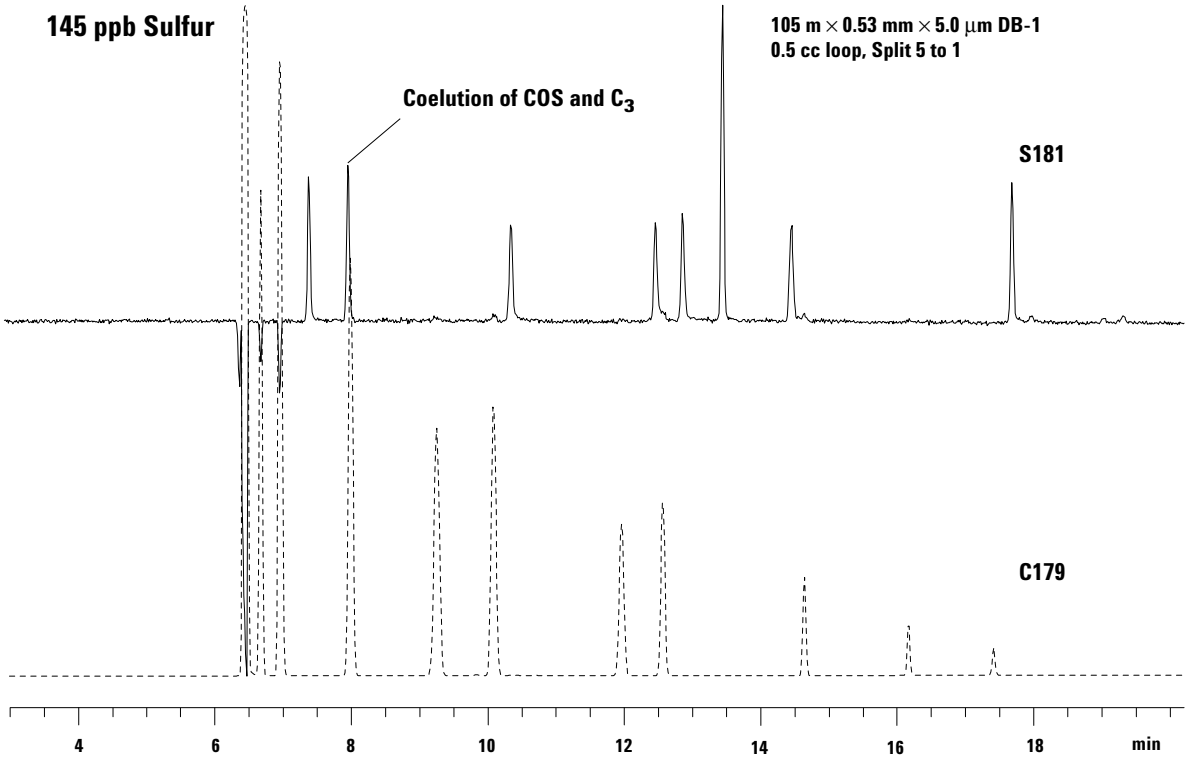


Figure 6. AED chromatograms of high methane natural gas blended with the sulfur calibration mix. Dashed line is carbon.

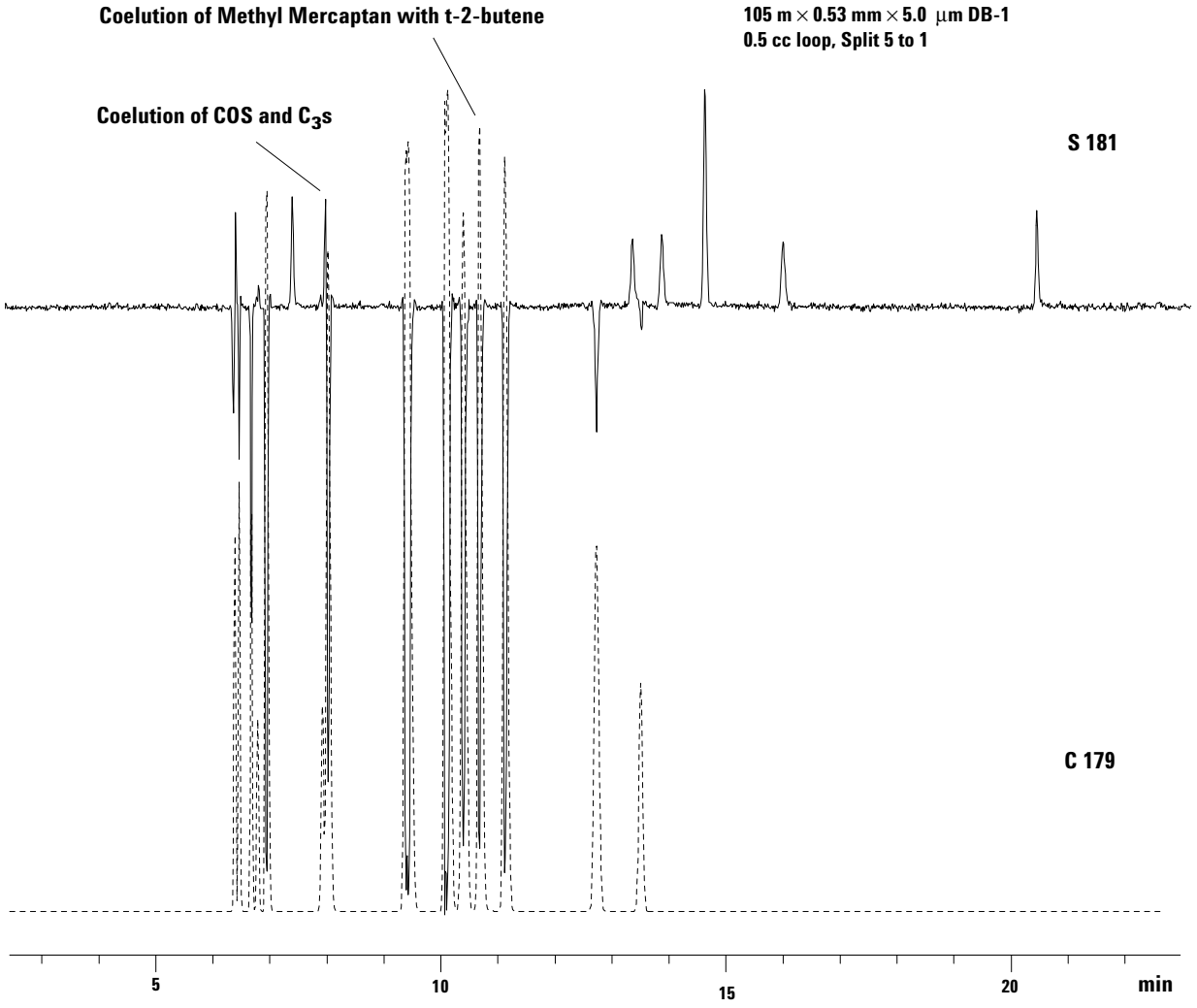


Figure 7. AED chromatograms of refinery gas blended with the sulfur calibration mix. Dashed line is carbon.

Once potential interferences have been characterized, the dynamic blending system can be used to mix various hydrocarbon matrices with the sulfur calibration mix to simulate real world samples and analytical problems. With this information in hand, the method developer and routine user can confidently use the system to identify and quantify a variety of low-level volatile sulfur compounds.

Examples of sulfur compounds blended with high methane (2 ppm and 410 ppb/sulfur compound) and high ethane natural gas (120 ppb/sulfur compound) are shown in Figures 8 and 9, respectively. The upper chromatogram in Figure 8 shows sulfur components at 2 ppm in high methane natural gas. This is representative of a typical range of odorant addition. Only COS cannot be reliably quantified at these levels due to quenching. All common natural gas odorants are cleanly separated from hydrocarbons and should be easily quantified with the FPD.

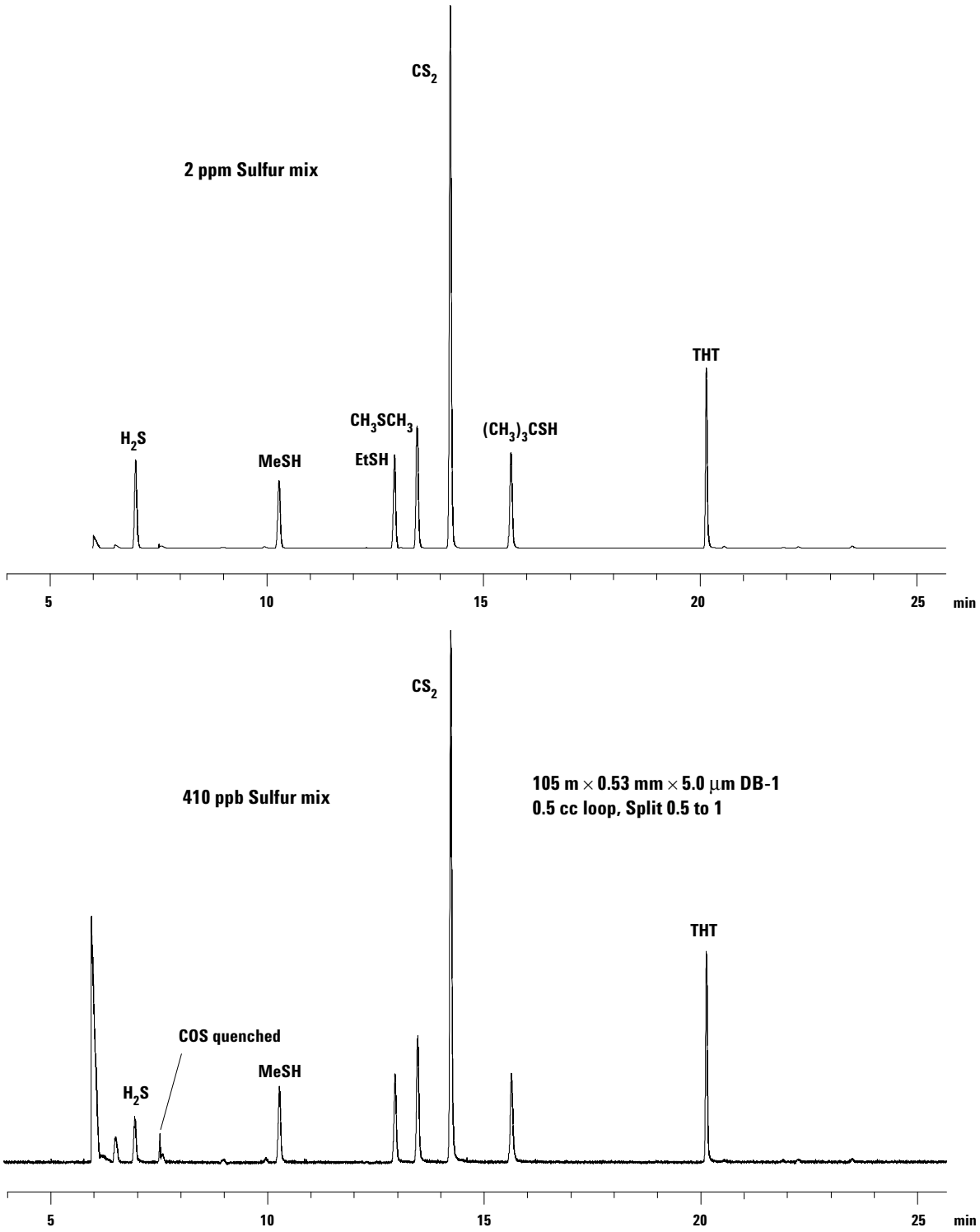


Figure 8. Sulfur mix blended with high methane natural gas at 2 ppm and 410 ppb. Detector - Flame Photometric.

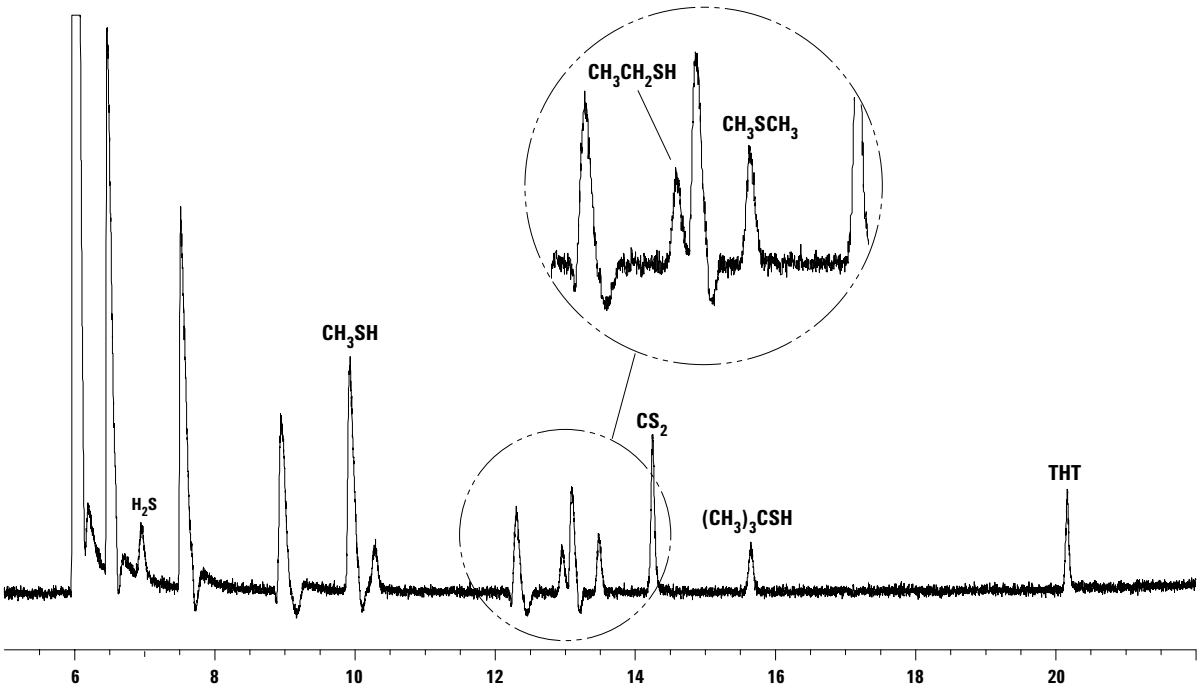


Figure 9. Sulfur mix blended with high ethane natural gas. Sulfur level: 120 ppb. Detector - Flame Photometric.

Refinery gas presents a more challenging matrix from potential sulfur coelutions with the relatively large number of C4 and C5 isomers. In Figure 10, 120 ppb sulfur mix in a refinery gas qualitative standard is shown. From the AED work, measurement of COS and CH_3SH at these 100 ppb sulfur levels is expected to be erroneous. Peaks labeled 1, 4, 5, 6, 7, and 8 (see figure) identifies the six sulfur compounds from among the false hydrocarbon response peaks. These six sulfur species can be easily quantified.

The last example shown in Figure 11, illustrates the measurement of sulfur in LPG. Ethyl mercaptan, the most common odorant used in LPG is seen at approximately 2.5 ppm. The presence of methyl mercaptan seen at approximately 10 minutes RT may be naturally occurring in origin. Two peaks at 20.5 and 22.0 minutes are unidentified sulfur compounds.

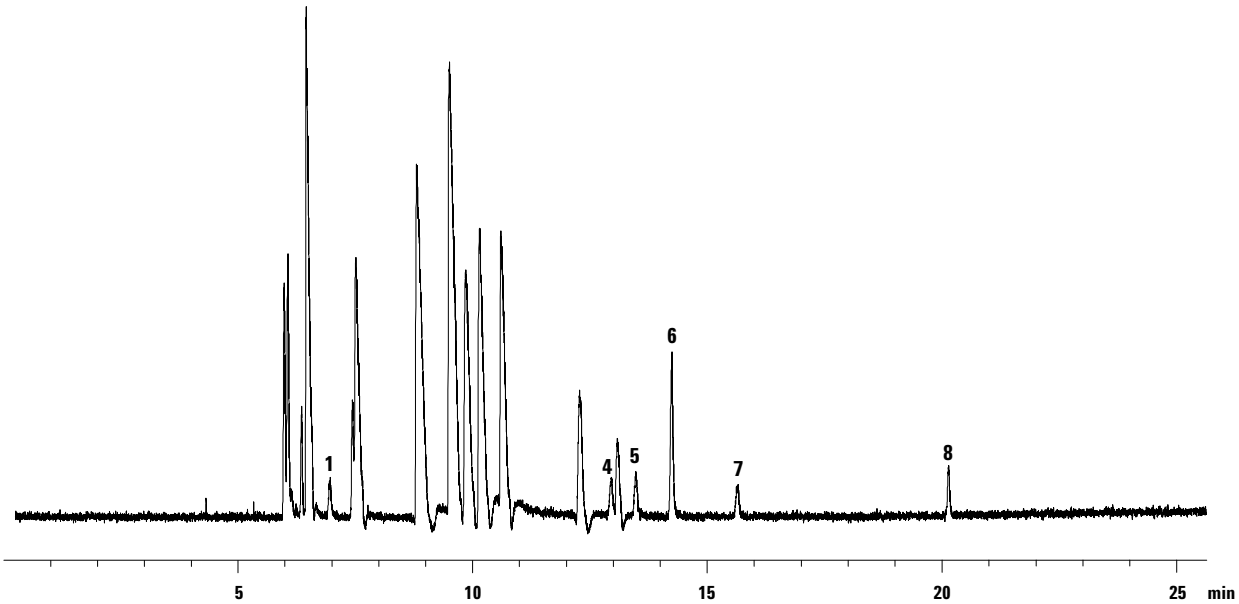


Figure 10. Sulfur mix blended with refinery gas. Sulfur level: 120 ppb. Detector - Flame Photometric. See Table 3 for peak id's.

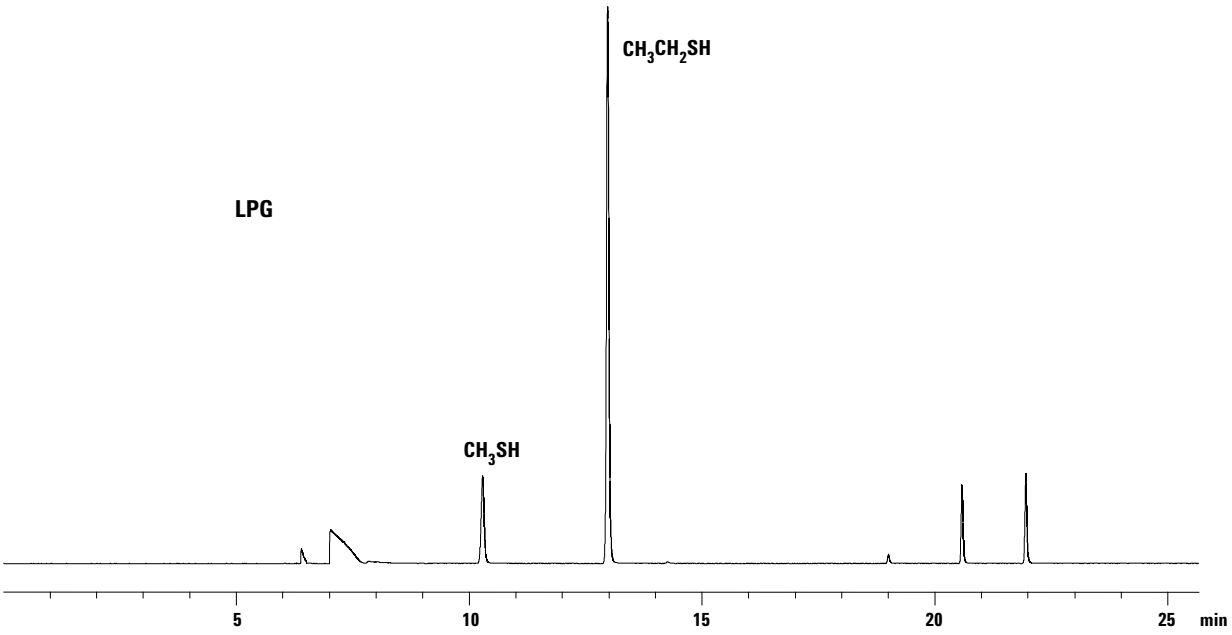


Figure 11. FPD analysis of LPG showing ethyl mercaptan at 2.5 ppm.

Conclusions

Many sulfur selective detectors cannot be characterized as easy to use or low maintenance instruments. The FPD is an exception to this rule with setup, operation, and stability on par with a standard FID. When the gas chromatograph is carefully configured with inert sample path components and optimized sample introduction hardware, reliable routine detection of volatile sulfur components under 50 ppb is achievable. Although the FPD is subject to quenching by high hydrocarbon concentrations, careful selection of the column can largely eliminate the problem. The 105 m × 0.53 mm × 5.0 µm DB-1 offers a high level of inertness, capacity, and efficiency for volatile sulfur analysis. Dynamic blending, controlled by the Aux EPC offers an automatable means of system calibration.

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2. R. L. Firor and B.D. Quimby, *A Comparison of Sulfur Selective Detectors for Low Level Analysis in Gaseous Streams*, Publication Number 5988-2426, April 2001 (Downloadable from www.agilent.com)

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Agilent Technologies

Use of GC/MSD for Determination of Volatile Sulfur: Application in Natural Gas Fuel Cell Systems and Other Gaseous Streams

Application

Fuel Cells, Petrochemicals

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Abstract

The mass selective detector is an ideal tool for the analysis of trace level volatile sulfur compounds. It is differentiated from other sulfur-selective detectors in that structural information is provided. When operated in the Selected Ion Monitoring mode, excellent sensitivity and selectivity is obtained. Eight volatile sulfur compounds are used to demonstrate low parts-per-billion analysis in a variety of hydrocarbon matrices. The system is well suited for fuel cell developers for characterization of fuel feedstocks and the analysis of impurities that can poison critical catalytic processes. Measurement of carbonyl sulfide in propylene is also demonstrated.

Introduction

Sulfur detectors are finding widespread use in a broad range of applications that cut across many industries. Demand for low-level sulfur detection will only increase in the future in response to more stringent quality control and regulation. The significance and need for low level sulfur measurements have been detailed in previous Agilent application literature [1, 2, 3, 4].

Emerging needs are found in alternative energy applications such as the fuel cell industry. Fuel processors serve a vital role in many fuel cell systems and are sensitive to feedstock composition and impurities. Potential fuels include hydrogen, natural gas, propane, methanol, gasoline and other hydrocarbon streams. Near-term development is concentrating on reformed hydrocarbon fuels creating a need to monitor composition and impurities. Fuel contaminants can adversely affect performance of the fuel cell system. This is especially true for Polymer Electrolyte Membrane (PEMFC) and Molten Carbonate (MCFC) types, although Phosphoric Acid (PAFC) and Solid Oxide (SOFC) technologies are also subject to sulfur poisoning. For example, natural gas feeds to external or internal catalytic reformers need to be desulfurized since low ppm sulfur levels can poison the reformer catalyst and fuel cell stack. Potential breakthrough of sulfur from the desulfurization beds needs to be closely monitored.

The mass selective detector (MSD) is usually not considered when the need for low-level volatile sulfur quantitation and speciation arises in the analytical laboratory or plant. Selective detectors such as the flame photometric (FPD), pulsed flame photometric (PFPD), and sulfur chemiluminescence (SCD) have traditionally dominated these applications [1]. The 6890N/5973N GC/MSD system is a very capable alternative to these detectors providing the added benefit of positive compound identification. Details on how to set up the

system for optimum sensitivity and selectivity are discussed in this paper. The specific hardware configuration reviewed is applicable to a wide range of applications.

MSDs are now widely used in many routine applications including QA/QC environments. The 5973N is easy to use, compact in size, and stable over long time periods. Tuning is software controlled and automatic, a significantly easier task than what is needed for some sulfur-selective detectors.

A common problem with many sulfur-selective detectors is hydrocarbon interference, especially from chromatographic coelution [4]. The measurement challenge is acute when the interfering hydrocarbon comprises the majority of the sample, as in the analysis of impurities in ethylene and propylene. In most cases, an accurate determination of the sulfur compound is not possible. However, the use of the MSD and selected ion monitoring (SIM) can largely overcome the coelution problem for many applications.

Experimental

Networked versions of the 6890 and 5973, designated by the N following the product number were used in this work; replacing the previously HPIB-interfaced models. Well known benefits of LAN include reliability, lack of distance limitations and simple configuration.

The sulfur calibration mix consisted of the following components at 5 ppm each: Hydrogen sulfide, carbonyl sulfide, methyl mercaptan, ethyl mercaptan, dimethyl sulfide, carbonyl sulfide, t-butyl mercaptan, and tetrahydrothiophene. The blend in helium was purchased from DCG Partnership, Pearland, TX.

A 6-port gas-sampling valve was connected directly to the volatiles interface on the 6890N with Sulfinert 1/16-inch tubing. See the sample introduction diagram in Figure 1. The sample loop, tubing and inlet are either Sulfinert or Silcosteel treated for inertness. Table 1 contains the instrument conditions.

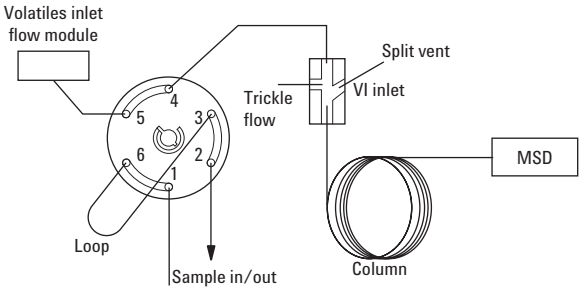

Figure 1. Sample introduction scheme.

Table 1. Instrument Conditions

Injection port	**Volatiles interface**
Temperature	150 °C
Split ratios	1 : 1 up to 50 : 1
Carrier gas	Helium
Constant flow mode	1.9 mL/min
Injection source	**6-Port sampling valve**
Material	Hastelloy C
Temperature	150 °C
Loop	Sulfinert, 0.5 cc
Column	**60 m × 0.320 mm × 5.0 µm DB-1**
Initial temperature	40 °C
Initial time	5 min
Temperature ramp	25 °C/min
Final temperature	270 °C
Final time	2 min
5973 MSD	
Mass range	33 to 100 and 12 to 100
Scans	13.1/sec and 15.9/sec
Samples	2
Threshold	150
EM voltage	BFB.u tune voltage
Solvent delay	3 min
Source temperature	230 °C
Quad temperature	150 °C
Transfer line	280 °C

Gaseous blends of the sulfur standard in helium or other matrices such as natural gas, propylene, and refinery gas were prepared using dynamic blending at the point and time of use. Diluent (matrix) gases are mixed with the calibration standard using an Aux EPC module on the 6890N GC. This system and the hardware employed were described in detail previously [2].

Positioning of the column in the MSD must be carefully done to avoid loss of sulfur sensitivity. To position the column just inside the source, 2 to 3 millimeters of the column should be visible at the MSD end of the transfer line. See reference 5 for installation details.

Results and Discussion

System Calibration

First, the system was calibrated and checked for linearity by analyzing the sulfur mix at various concentrations. The dynamic blending system was used to prepare seven and five level calibrations using helium and natural gas as diluents, respectively. Table 2 lists the concentrations used. Calibrations were focused in the ppb range since this is where most analytical problems for sulfur analysis are found. SIM acquisition mode, discussed later in this section, was used.

Table 2. Calibration levels for checking system linearity. Sulfur concentrations in ppbv.

Cal Level	1	2	3	4	5	6	7
Conc. in helium	21	35	46	57	95	1600	3600
Conc. in nat gas	88	242	475	880	1170	--	--

Calibrations are linear in both matrices for all eight sulfur compounds. This is seen in Table 3 where the regression coefficient, r^2 values appear. This is an indication not only that the system response is linear but also that calculated concentrations from the blending system are accurate. Unlike some sulfur-selective detectors, the MSD does not show equimolar response. Each compound will have its own response characteristics, requiring each component's response factor to be determined.

Table 3. Calibration Regression Coefficient r^2 Values

Compound	Helium	Natural gas
H_2S	0.998	0.998
COS	0.998	0.999
CH_3SH	0.997	0.999
EtSH	0.996	0.998
DMS	0.998	0.998
CS_2	0.998	0.998
t-ButylSH	0.996	0.993
THT	0.996	0.992

One of the calibration plots as produced by the MSD Chemstation is shown in Figure 2 for the calibration of H_2S in natural gas.

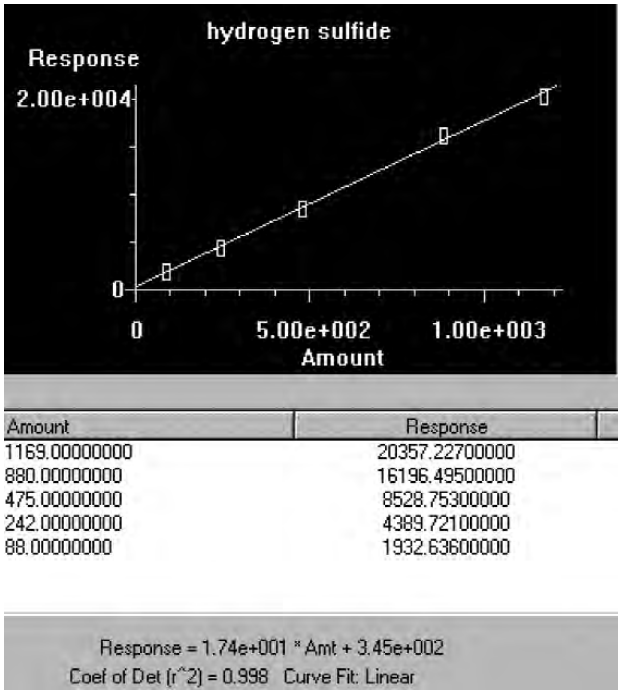

Figure 2. Five level calibration plot of H_2S using natural gas as the diluent. Calibration range is from 88 to 1170 ppb.

Scan Results

The total ion chromatogram (TIC) of the eight-component sulfur mix at 1.3 ppm in helium is shown in Figure 3 using a split ratio of 0.5 to 1. As is evident in the figure, H_2S is close to the minimum detectable limit (MDL) for this particular set of operating conditions. While operating in scan mode is useful for initial method development, unknown identification and retention time determinations, use of extracted ions from a scan and/or SIM are required to improve overall sensitivity and selectivity.

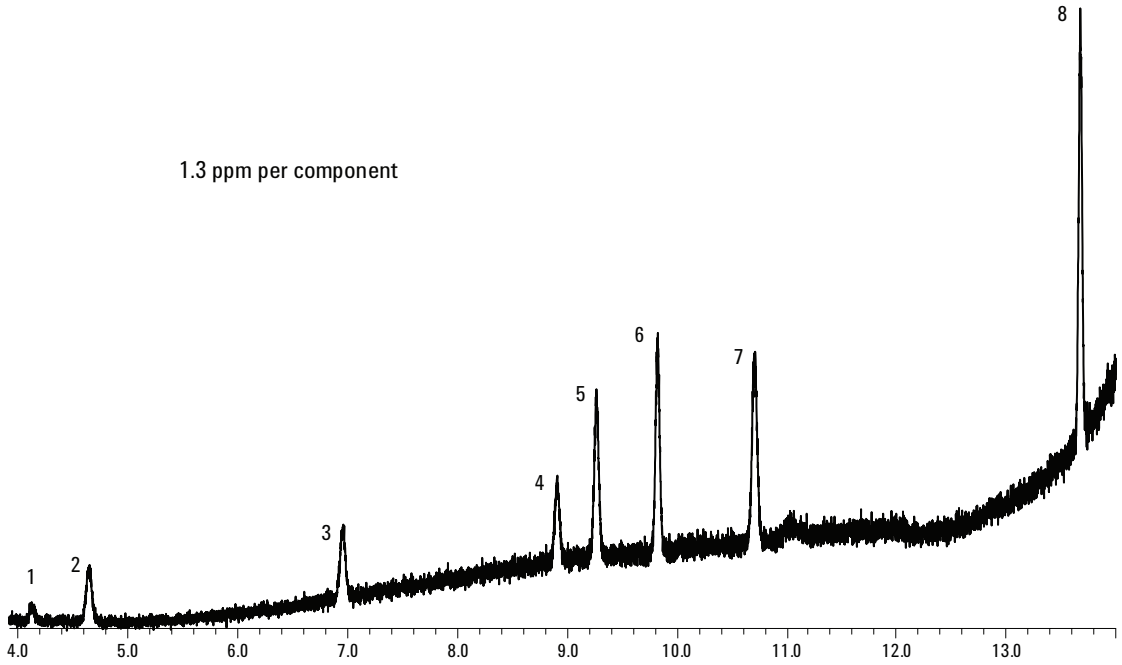

Figure 3. Total ion chromatogram of the eight-component sulfur mix at 1.3 ppm per component. Scan 33-100 amu. Peak labels: 1. hydrogen sulfide, 2. carbonyl sulfide, 3. methyl mercaptan, 4. ethyl mercaptan, 5. dimethyl sulfide, 6. carbon disulfide, 7. t-butyl sulfide, 8. tetrahydrothiophene.

Extracted Ion Results

In Figure 4, extracted ion chromatograms are shown for ions 60 and 62. Three of the eight sulfur compounds are found with these target ions. Ion 60 is present in COS and tetrahydrothiophene, and ion 62 is found in ethyl mercaptan and dimethyl sulfide. The concentration of the sample was 86 ppb per component in helium. Extracted ion chromatograms for the other sulfur compounds show similar signal to noise ratios at the concentration level. A considerable improvement in sensitivity is achieved by using extracted ions. In cases where this does not provide sufficient sensitivity, the next step should be SIM.

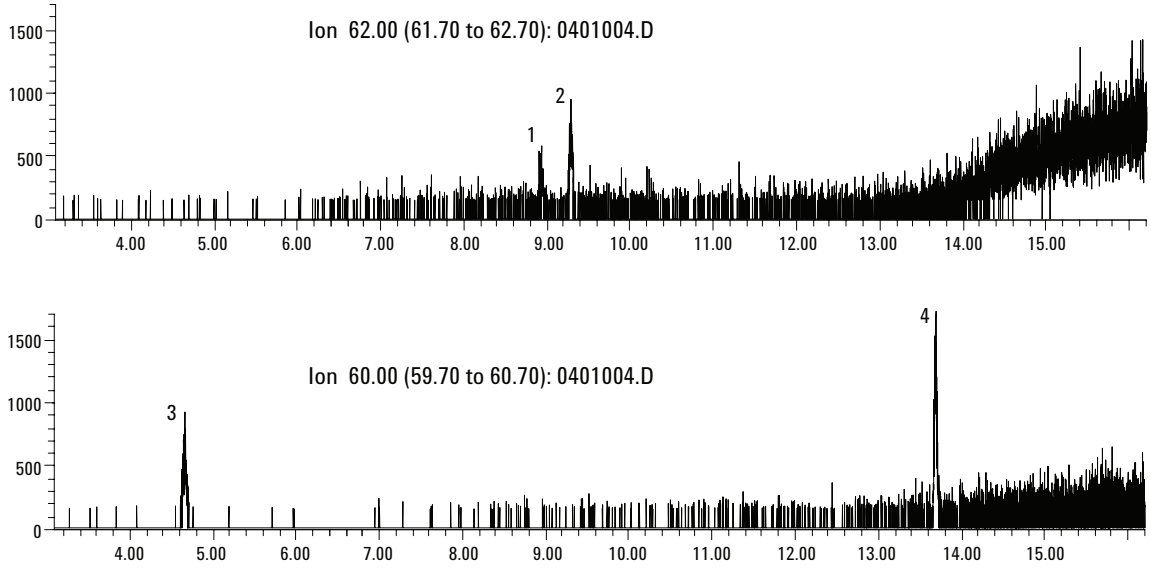

Figure 4. Extracted ion chromatograms for ions 60 and 62. Concentration is 86 ppb per component. Split ratio 1:1. Peak labels: 1. EtSH, 2. DMS, 3. COS, 4. THT.

Application of SIM

SIM provides superior sensitivity and selectivity. Since sulfur determinations will normally be done in hydrocarbon matrices, care must be taken to select ions that ideally have no hydrocarbon contribution. If this can be done, excellent selectivity can be achieved even in cases where coelution of sulfur species and hydrocarbon occur. This is an important distinction and advantage of the MSD compared to some of the common gas chromatographic sulfur-selective detectors. Both the FPD and PFPD will suffer from quenching if coelution occurs making accurate quantitation of low-level sulfur impossible [2]. Even the SCD will have problems measuring low ppm sulfur in the presence of a dominant coeluting hydrocarbon. In situations where a unique sulfur ion cannot be found, refinement of the method and chromatographic column/conditions to achieve separation from the interfering hydrocarbon should be tried [2]. Also, when operating the MSD in SIM mode, it is usually best to select low resolution for maximum sensitivity at the expense of some mass selectivity loss.

The SIM ions used for each sulfur compound are listed in Table 4. These ions were chosen to minimize interference from hydrocarbons. To arrive at the ions shown in the table, a scan of the sulfur mix in helium is acquired to identify target ions. Library spectra can also be consulted. Hydrocarbon mixes such as natural gas and refinery gas are then run separately using the SIM table to look for ions that may match those selected for the sulfur. The table may be further refined if hydrocarbon interferences appear. Retention times of the sulfur compounds are also needed to set up the time-programmed groups. These are not the only possible ions that can be used. For some of the compounds other choices or additional ions could be included in the SIM table. While not necessary for this relatively simple sulfur example, the use of second and third qualifier ions may give the analyst a higher level of confidence of a compound's identity by comparing ion ratios to library spectra for a particular compound.

Table 4. Optimized SIM table for selective sulfur detection in hydrocarbon streams. Dwell time for each ion is 100 ms.

GROUP	START TIME (min)	TARGET and QUALIFIER IONS	COMPOUND
1	3.00	33,34	H_2S
2	4.20	60	COS
3	6.00	45,47	MeSH
4	8.00	47	EtSH
5	9.10	45,47,62	DMS
6	9.70	44,76	CS_2
7	10.20	57,90	t-ButylSH
8	11.80	45,60,88	THT

Fuel Cell Natural Gas Feedstocks: Composition and Impurities

The TIC of a natural gas scan and sulfur mix SIM runs are overlaid for illustration purposes in Figure 5. Note that with the 60 m × 0.32 mm × 5.0 µm DB-1 column, all hydrocarbons and CO_2 are separated. Natural gas compounds in order of elution are: O_2/N_2, CH_4, CO_2, ethane, propane, i-butane, n-butane, i-pentane, and n-pentane. From the overlay, it can be seen that seven of the eight sulfurs do not coelute with natural gas components; only COS and propane show potential overlap. This also demonstrates the utility of the system for fuel cell feed streams, providing both hydrocarbon composition and gas impurity analysis.

The chromatogram shown in Figure 6 of the sulfur mix in helium was produced using the SIM parameters in Table 3. The offsets seen in the baseline are a result of the MSD switching from group to group and should not be interpreted as a chromatographic problem. Excellent signal to noise is seen for all components at the 46 ppb level. The sulfur mix was then further diluted to 16 ppb per component. The resulting chromatograms for H_2S and COS, the most challenging analytes, and tetrahydrothiophene are shown in Figure 7.

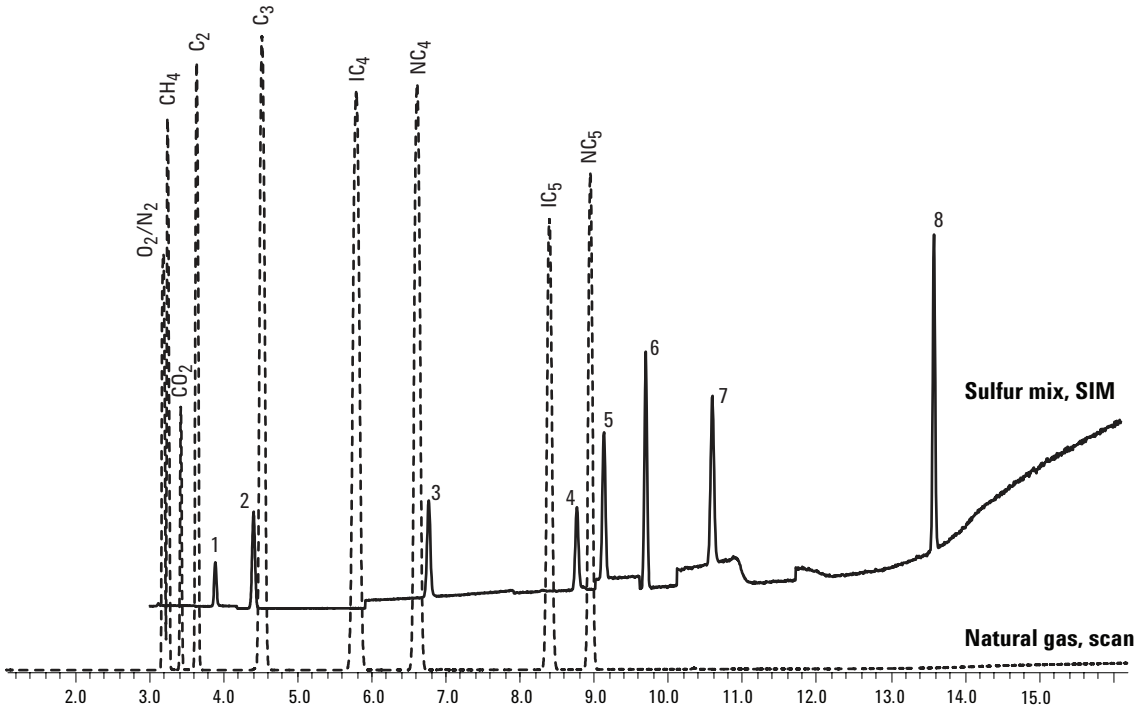

Figure 5. Overlay of two runs: natural gas scan (12 to 100 amu) and sulfur mix at 4.5 ppm in SIM mode. Split ratio 20:1. Sulfur peak labels same as in Figure 3.

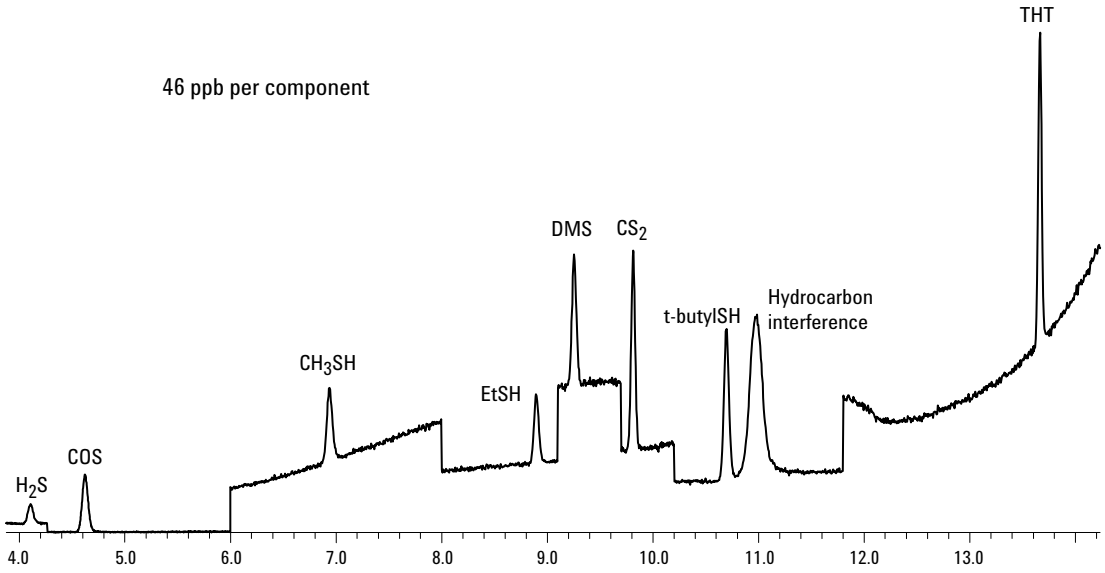

Figure 6. Eight-component sulfur mix in helium at 46 ppb per component in SIM mode. Split ratio 0.5:1.

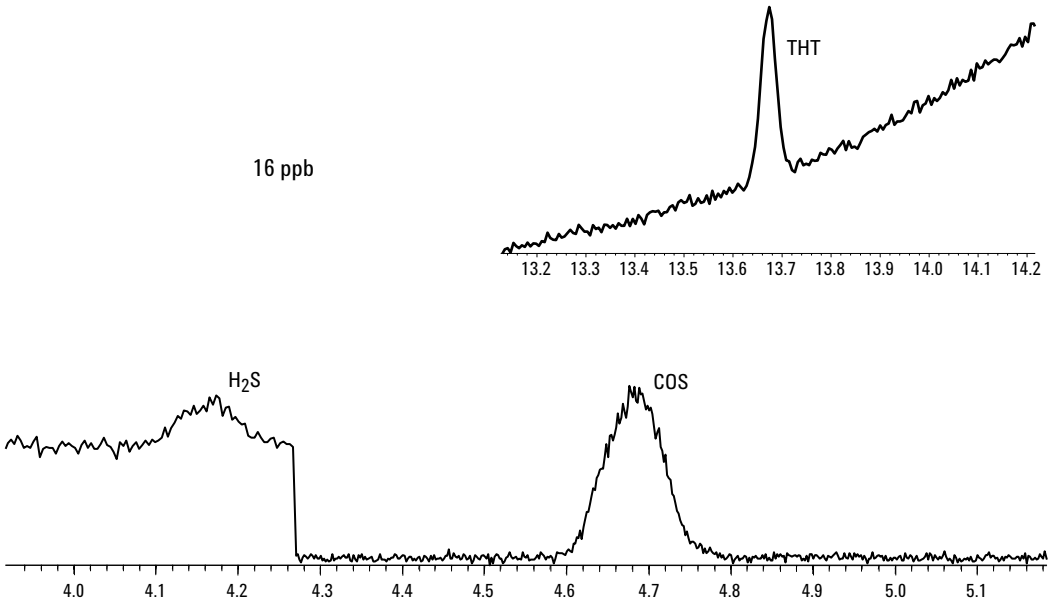

Figure 7. H_2S, COS and tetrahydrothiophene (insert) at 16 ppb each. SIM was used.

For ppb sulfur analysis, it is recommended that the pure matrix be run separately using the sulfur SIM acquisition parameters. Ideally, no response would be seen. If ions of the hydrocarbon matrix are seen, they can be noted and not mistaken for sulfur compounds. This is illustrated in Figure 8 for natural gas streams. Chromatograms of the sulfur mix in scan mode and pure natural gas in SIM mode are overlaid for illustrative purposes. Both are drawn to the same scale. This is a good practice to follow not only for sulfur but also for any impurity analysis using SIM.

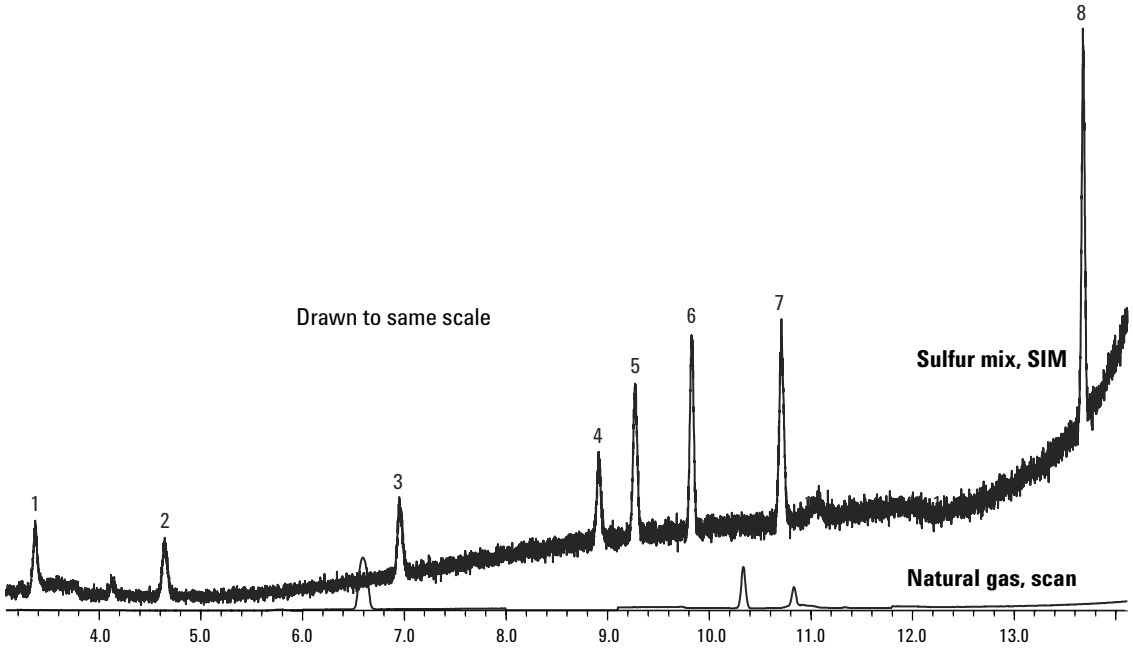

Figure 8. Overlay of sulfur mix in scan (33-100 amu) and natural gas (using sulfur SIM table). Ideally the natural gas chromatogram would be blank. Same scale used for both.

Analysis of COS in Propylene and Propane

Measurement of ppb COS in propylene and propane can be a challenging analytical problem due to coelution of COS/propylene on the preferred methyl silicone columns. This coelution is illustrated in Figure 9 where two independent (separate runs) are overlaid. Both the FPD and PFPD will be unsuccessful with this analysis due to quenching. The SCD's selectivity can also be exceeded for low ppb COS analysis

SIM (ion 60) was employed for the analysis of COS. To avoid overloading the source, the split ratio was increased to 50:1. To determine the effect of coeluting propylene on COS response, two runs were performed at identical concentrations of 105 ppb COS. The diluents for the first and second runs were helium and propylene, respectively. Chromatograms for both runs are shown in Figure 10. The helium chromatogram shows the true COS area unaffected by any other coeluting compound. This area is then compared to that of COS in propylene diluent using the area ratio (COS propylene/COS helium) to indicate how coelution has affected the MSD response. This ratio of 0.77 indicates that COS in propylene response is suppressed by only 23%, probably due to a reduction in ionization efficiency. Moreover, a subsequent experiment that constructed a five level calibration of COS in propylene showed linear behavior over the range of 20 to 1200 ppb. Therefore, using a carefully constructed SIM method, the MSD has the capability of quantifying ppb level COS in coeluting 99+% propylene. It follows, in the general case, that coeluting analytes do not preclude quantification even when concentration differences exceed 10^5 provided unique ions can be identified for the component of interest.

These results and conclusions are relevant to fuel cell developers who are using high propane (for example 50 to 99%) as a feedstock. The performance, chromatographic behavior, and minimal detectable impurity levels will be very similar. Under the conditions used the retention time of propane will differ by less than 0.1 minute from propylene (see propane retention time in Figure 5). Sulfur impurities other than COS can be easily measured.

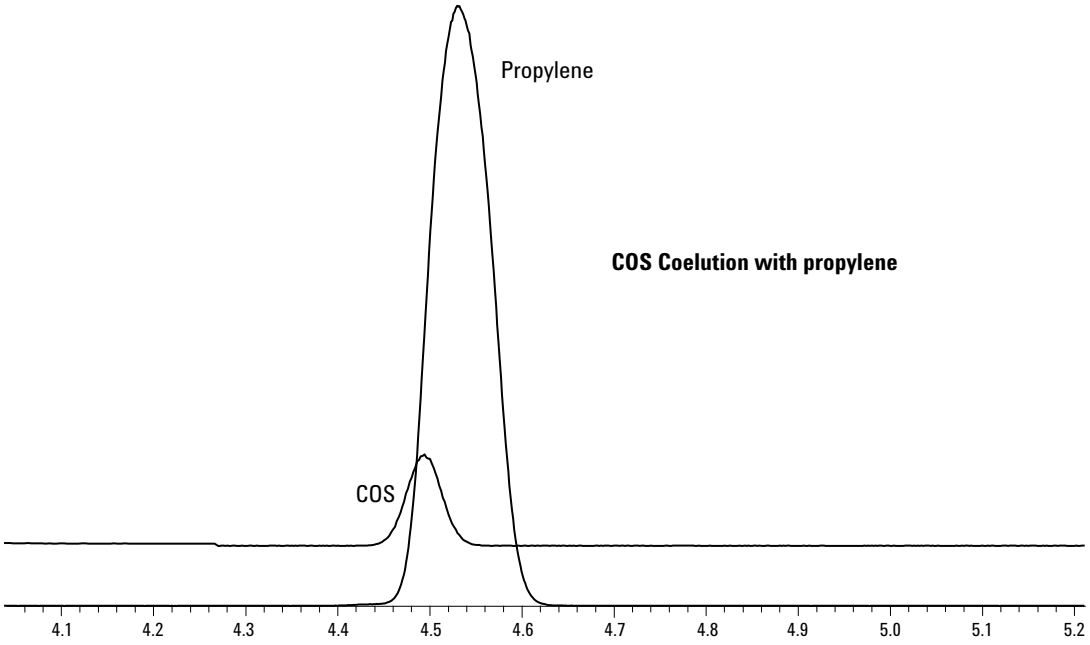

Figure 9. Two separate chromatograms (from separate runs) superimposed showing the coelution of COS with propylene. Split ratio 50:1.

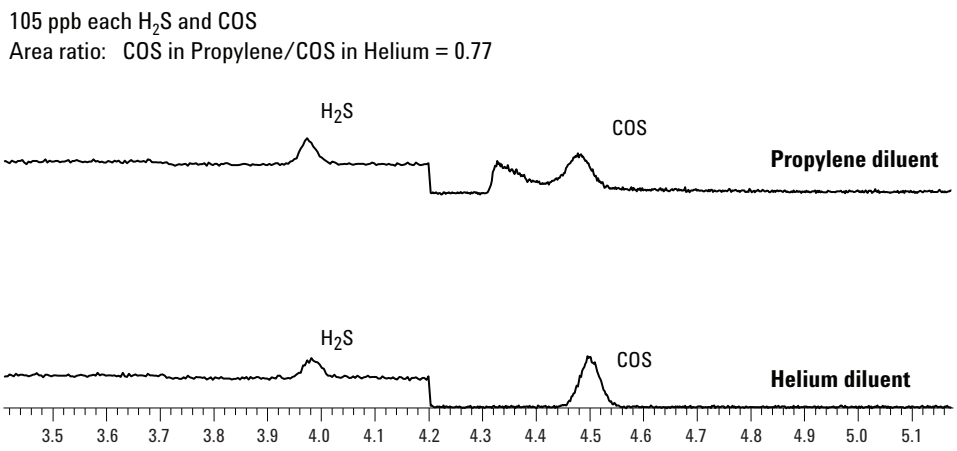

Figure 10. Comparison of COS response (SIM mode) in helium and propylene. Split ratio 50 to 1.

Conclusions

The hardware and associated methods outlined in this paper demonstrate the MSD's capabilities as a sensitive and selective detector for gaseous analytes. It has the added advantage of providing structural information. Sulfur detection at low ppb levels is easily achieved through use of a time programmed SIM table consisting of unique ions for the compounds of interest. This minimizes hydrocarbon interference making it possible to quantitate low-level analytes such as COS with coeluting propylene.

The 6890N/5973N system is also a powerful tool for fuel cell developers, providing detailed composition and impurity analyses of common fuels. The examples shown here demonstrate how natural gas feed could be characterized providing complete speciation of sulfur compounds including odorants or naturally occurring impurities such as H_2S. The system can also be used to monitor the performance of desulfurization beds and reformer output.

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Agilent Technologies

Dual-Channel Gas Chromatographic System for the Determination of Low-Level Sulfur in Hydrocarbon Gases

Application

Hydrocarbon Processing

Authors

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Abstract

A 6890N equipped with dual flame photometric detectors is described for the analysis of ppb level volatile sulfur compounds in a variety of hydrocarbons using thick film DB-1 and GS-GasPro columns. Enhanced performance flame photometric detectors are employed that can achieve detection of sulfur compounds below 20 ppb. Examples of arsine and phosphine analysis with the same hardware are also discussed.

Introduction

Gas chromatography with sulfur selective detection is finding widespread application in many segments of the petroleum, petrochemical, and specialty chemical industries. Demand for low-level sulfur detection will increase in the future in response to more stringent regulations and tighter quality control.

Sulfur compounds can be significant poisons for various catalytic processes involved in hydrocarbon conversion. Monitoring these low-level poisons can lead to considerable saving in terms of improved yields, increased catalyst lifetime, and higher quality products. In looking at the future of fuel cells, fuel contaminants can adversely affect performance of fuel cell systems and fuel processors that are powered by natural gas or other fossil fuels. Finally, environmental regulatory issues in certain regions will continue, necessitating the need to monitor fuel impurities.

A common problem with many gas chromatographic sulfur selective detectors is hydrocarbon interference, especially from co-elution. The measurement challenge is acute when the interfering hydrocarbon comprises the majority of the sample, as in the analysis of impurities in ethylene and propylene, or sulfur in natural gas [1, 2]. In most cases, an accurate determination of the sulfur compound is difficult or not possible even with highly selective sulfur detectors. However, the use of a dual-channel system employing two very different separation columns (in terms of selectivity) largely avoids the interference problem. The configuration is shown in Figure 1. Sulfur compounds that have a severe interference on one column are likely to be separated from that interference on the other column. By assuring that a given sulfur compound will be separated on at least one of the columns, the system can use a reliable, stable, and relatively inexpensive flame photometric detector (FPD) for detection. If the hydrocarbons can be chromatographically separated from the sulfur compounds of interest, enhanced FPDs can quantitate sulfur to less than 20 ppb.

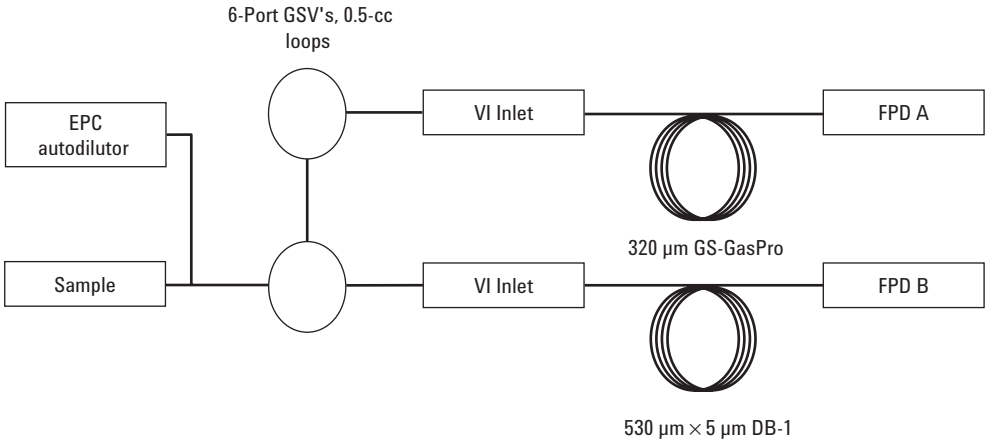

Figure 1. System configuration on the Agilent 6890N. Valves (plumbed in series) are Hastelloy C and all plumbing is Silcosteel® or Sulfinert™ treated.

Experimental

Selection of the appropriate capillary column is often key to the solution of a particular analysis problem, and this is especially true for this system. Four columns are employed (two for any given analysis) as described in Table 1.

Table 1. Recommended Column Combinations by Application

Applications	Column set
Natural gas, fuel cell gases	60 m × 530 µm × 5.0 µm DB-1
	30 m × 320 µm GS-GasPro
Ethylene, propylene, C4 streams	105 m × 530 µm × 5.0 µm DB-1
	60 m × 320 µm GS-GasPro

Recommended GC oven programs are 40 °C (5 min) to 290 °C (5 min) at 25 °C/min for natural gas, fuel cell gases and ethylene, and 35 °C (7 min) to 290 °C (5 min) at 20 °C/min for propylene. Somewhat lower detection limits can be achieved for sulfur in a propylene stream by employing cryo oven programs such as: –35 °C (7 min) to 290 °C (5 min) at 20 °C/min. Split ratios, as set in the GC method, vary from 0.5:1 to 2:1.

Each valve was interfaced to a specialized inert (Silcosteel treated) volatiles interface for accurate sample introduction at low split ratios into a capillary column. Due to the tendency for organosulfur compounds (especially H_2S) to adsorb to metal surfaces, great care must be used in selecting and constructing the chromatographic sample introduction system. The sample loop, tubing, and inlet are either Sulfinert or Silcosteel treated for inertness.

A factory modified FPD, with enhanced sensitivity, was used for each channel. The FPD is optimized for the analysis of trace sulfur gases, arsine, and phosphine in gaseous samples. See Table 2 for appropriate gas flow settings. These detectors achieve detection limits that are roughly four times better than standard. The sensitivity advantage is illustrated in Figure 2, where standard and modified FPDs are compared using a standard calibration blend. Minimum detection level (MDL) calculated on methyl mercaptan using linearized data and the 60 m DB-1 column is better than 15 ppb.

Table 2. FPD Gas Flow Settings

Analysis	Gas	Flow rate (mL/min)
Sulfur	Air	60
	Hydrogen	50
	Makeup	58
Arsine	Air	150
	Hydrogen	50
	Makeup	100
Phosphine	Air	110
	Hydrogen	150
	Makeup	58

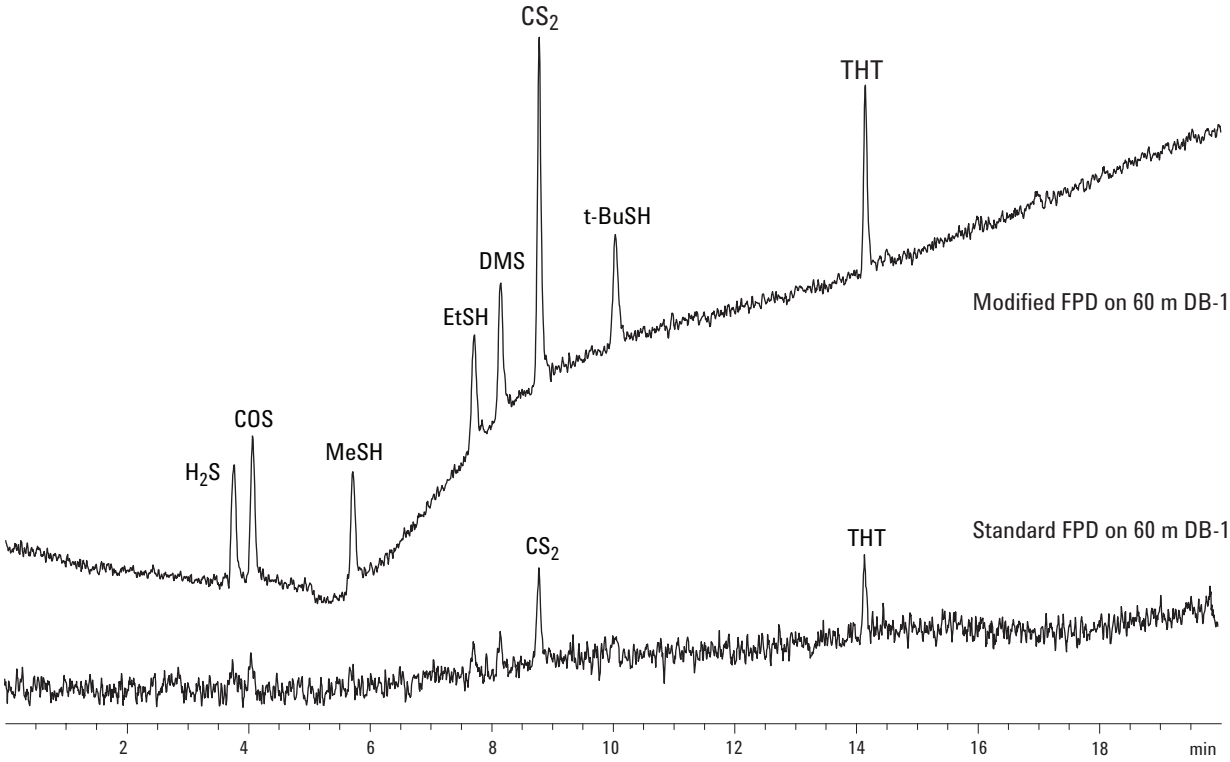

Figure 2. Sensitivity comparison of standard and enhanced FPDs. Concentrations are 33 ppb per component (v/v) in helium.

Due to the use of all available heated zones on the 6890N GC for either inlet or detector heating, the 6-port sample valves are not actively heated. This does not pose a problem for the light gaseous streams studied in this work. However, if desired, the valves can be heated by an auxiliary stand-alone temperature controller (Agilent model 19265B). The system is designed only for gaseous samples containing significant concentrations of hydrocarbons of C_6 or below.

Discussion

Channel 1 employs the GS-GasPro column, using a unique bonded PLOT technology, where COS is separated from C_2 and C_3 hydrocarbons, allowing measurement at trace levels. However, H_2S and the C_3s coelute. Channel 2 uses a thick film DB-1 column where H_2S is well separated from C_2s and C_3s, making low-level measurements of this sulfur impurity possible. COS and C_3s will coelute on this column. In summary, using a dual-column approach with the unique separation capabilities of GS-GasPro and thick film DB-1, both COS and H_2S can be measured in one chromatographic analysis at low ppb levels regardless of the concentrations of light hydrocarbons present in the sample. The elution order difference between the two columns is illustrated in Figure 3.

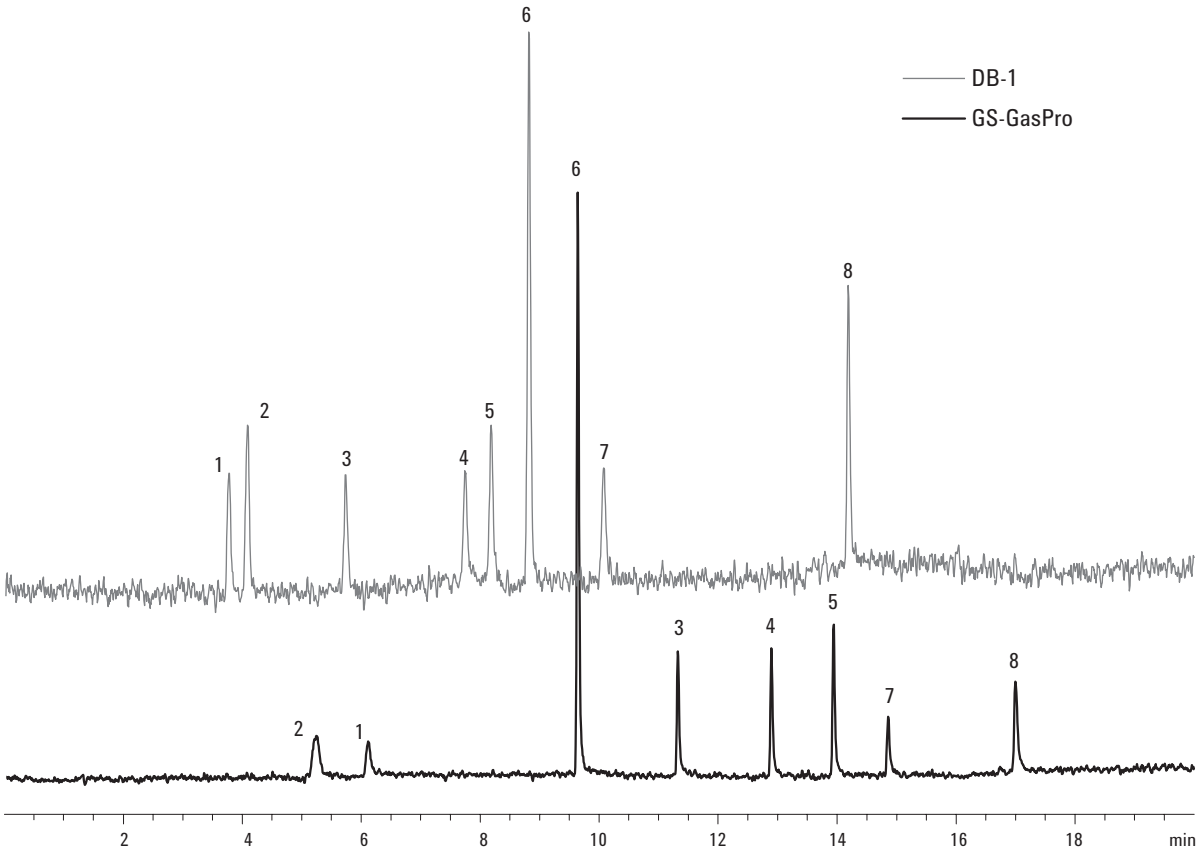

Figure 3. The dual-column advantage. Sulfur mix at 90 ppb per component in helium. 1. H_2S, 2. COS, 3. MeSH, 4. EtSH, 5. DMS, 6. CS_2, 7. t-BuSH, 8. THT.

Other potential interferences or coelutions between light sulfur compounds and hydrocarbons are avoided with this approach. A coeluting pair on one column will likely be separated on the other. Split ratios were set depending on the application from 0.5:1 to 2:1 in order to achieve the reported detection limits.

The sulfur calibration mix consisted of the following components at 5 ppm each: Hydrogen sulfide (H_2S), carbonyl sulfide (COS), methyl mercaptan (MeSH), ethyl mercaptan (EtSH), dimethyl sulfide, carbonyl sulfide (DMS), t-butyl mercaptan (t-BuSH), and tetrahydrothiophene (THT). The blend in helium was purchased from DCG Partnership, Pearland, TX. These compounds are representative of the most common light sulfur species encountered in gaseous fuels or petrochemical feedstocks.

Some adsorption of H_2S on the GS-GasPro column is possible. Priming the system a few times with a low ppm sulfur stream such as the calibration mix described here can largely eliminate the loss in sensitivity that can result from adsorption. This priming is usually only necessary for low ppb analyses where the active sites in the column could adsorb most of the sulfur present in the sample during an initial run.

Gaseous blends of the sulfur standard in helium or other matrices such as natural gas, propane, liquidfied petroleum gas (LPG), propylene, and refinery gas were prepared using dynamic blending at the point and time of use. Diluent (matrix) gases were mixed with the sulfur calibration standard using an Aux EPC module on the 6890N GC. Accurate concentrations from low ppb to ppm levels can be easily prepared by knowing the flow rates of the two streams as they mix in a Tee fitting prior to the gas sampling valves on the GC. This system and the hardware employed were described previously in detail [3].

Sulfur in Fuel Cell Gases, Natural Gas, and Proypylene

Figure 4 shows the chromatograms from the eight-component sulfur standard diluted with a fuel cell mix to 45 ppb (v/v) each component. The fuel cell

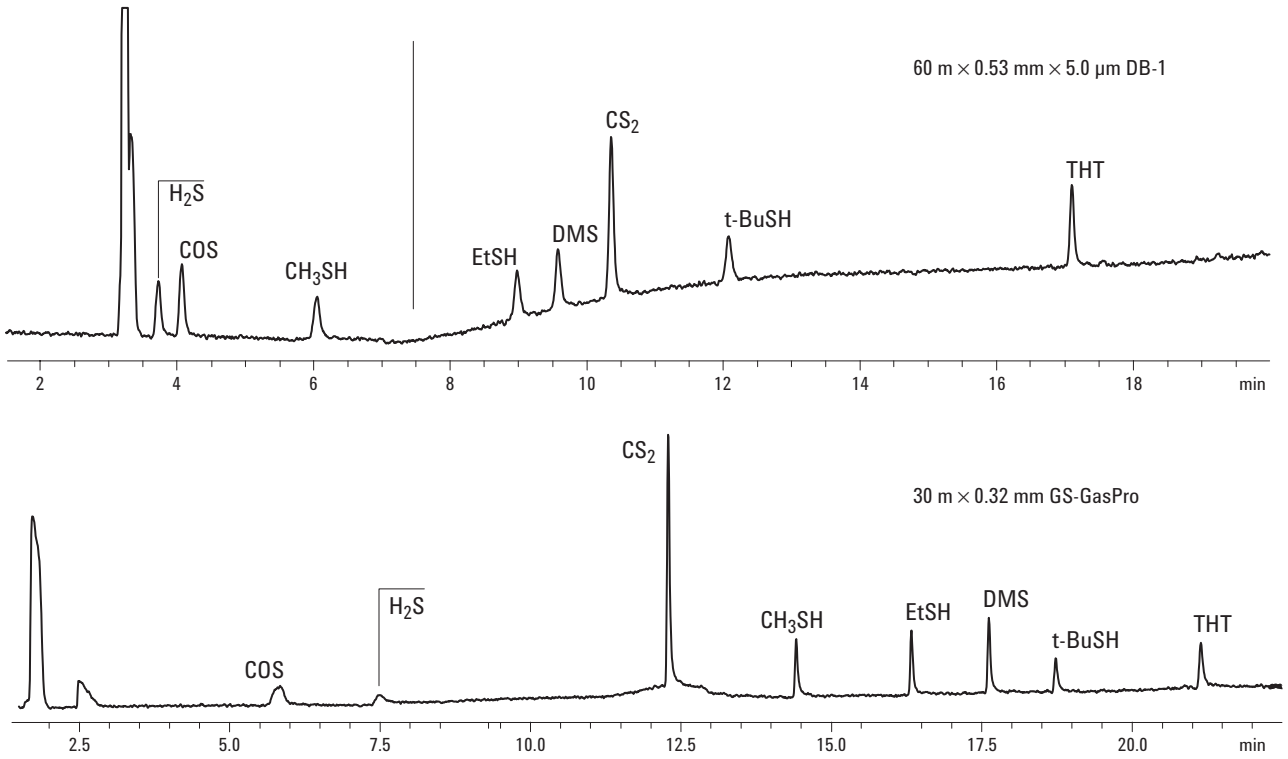

Figure 4. Simultaneous dual column analysis of fuel cell mix containing 45 ppb (v/v) each of the eight sulfur compounds. Split ratio is 0.5:1.

mix is 50% hydrogen, 10% carbon dioxide, and 5% methane. This mix is often used to simulate the output stream of a natural gas reformer used as the feed to a fuel cell. This matrix is one of the easier ones because the large hydrocarbon (methane) elutes before all of the sulfurs on both columns. Note that elution order of the sulfurs is significantly different on the GS-GasPro column compared to the DB-1 (see Figure 3). All eight compounds are clearly detectable at 45 ppb.

Natural gas is a much more challenging matrix because of the high concentrations of several hydrocarbons. These interferences extend out into the retention time range of the sulfur compounds.

Figure 5 shows the chromatograms from the eight-component sulfur standard diluted with sulfur free natural gas to 45 ppb (v/v) each component. There are more peaks evident in these chromatograms than just the eight sulfur compounds. The additional peaks are interference responses from the large hydrocarbons in the natural gas.

In the DB-1 chromatogram, H_2S is clear but COS is lost to a severe overlap with a large C_3 peak. Ethyl mercaptan is also overlapped with n-pentane. On the GS-GasPro column, however, only the H_2S is occluded by interference. The COS and EtSH are free from interferences. With the dual-column approach, all eight compounds can be measured down to 45 ppb.

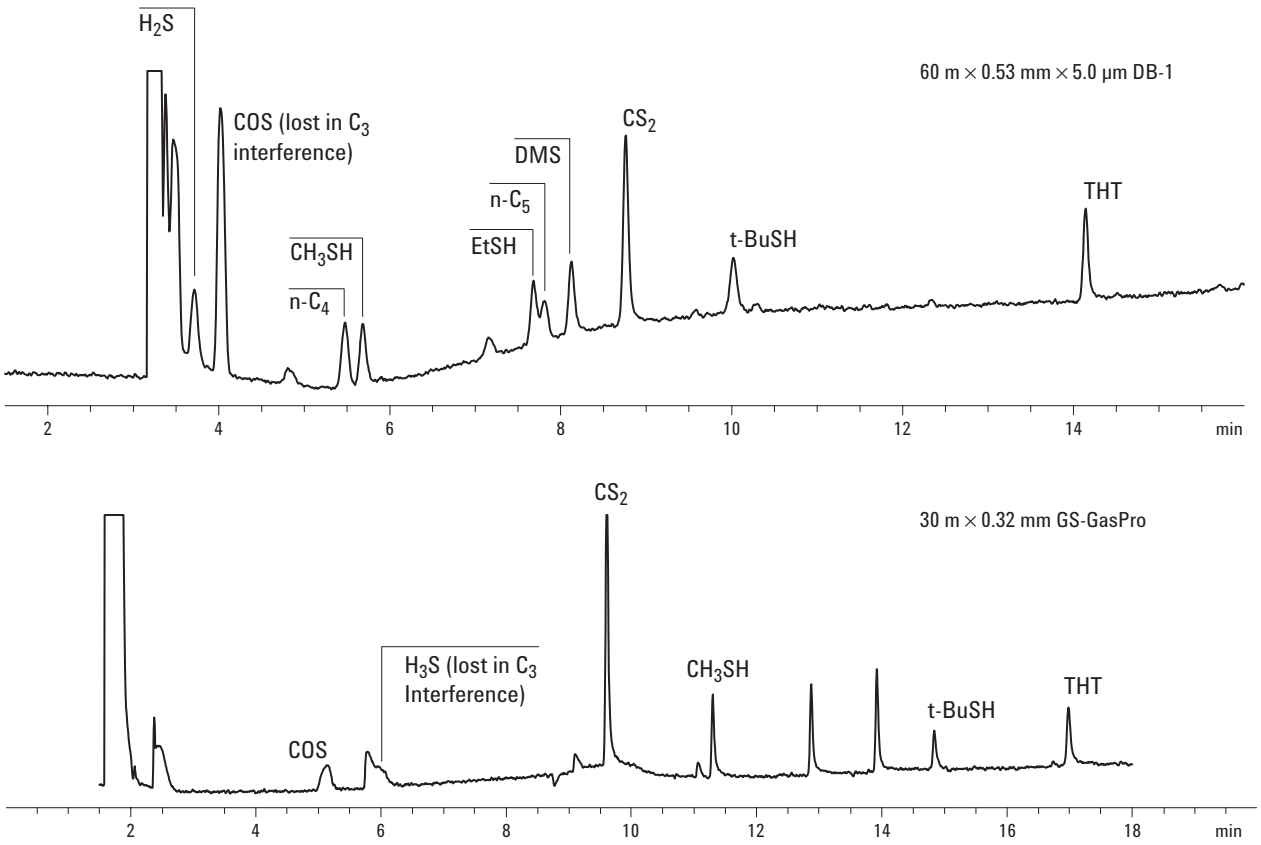

Figure 5. Natural gas blend containing 45 ppb (v/v) each of the eight sulfur compounds. Split ratio is 0.5:1.

Propylene monomer offers another interesting challenge. The huge C_3 peaks interfere with both the H_2S and COS on both columns used above. To address this, longer versions of the same columns were used (Table 1). The oven temperature and split ratio are also modified (see Experimental on page 2) to improve resolution of the H_2S and COS from the C_3s.

Figure 6 shows the chromatograms from the eight-component sulfur standard diluted with polymer-grade propylene to 45 ppb (v/v) each component. By using longer DB-1 and GS-GasPro columns, lower oven temperature, and a higher split ratio, the H_2S and COS can be measured with somewhat poorer detection limits.

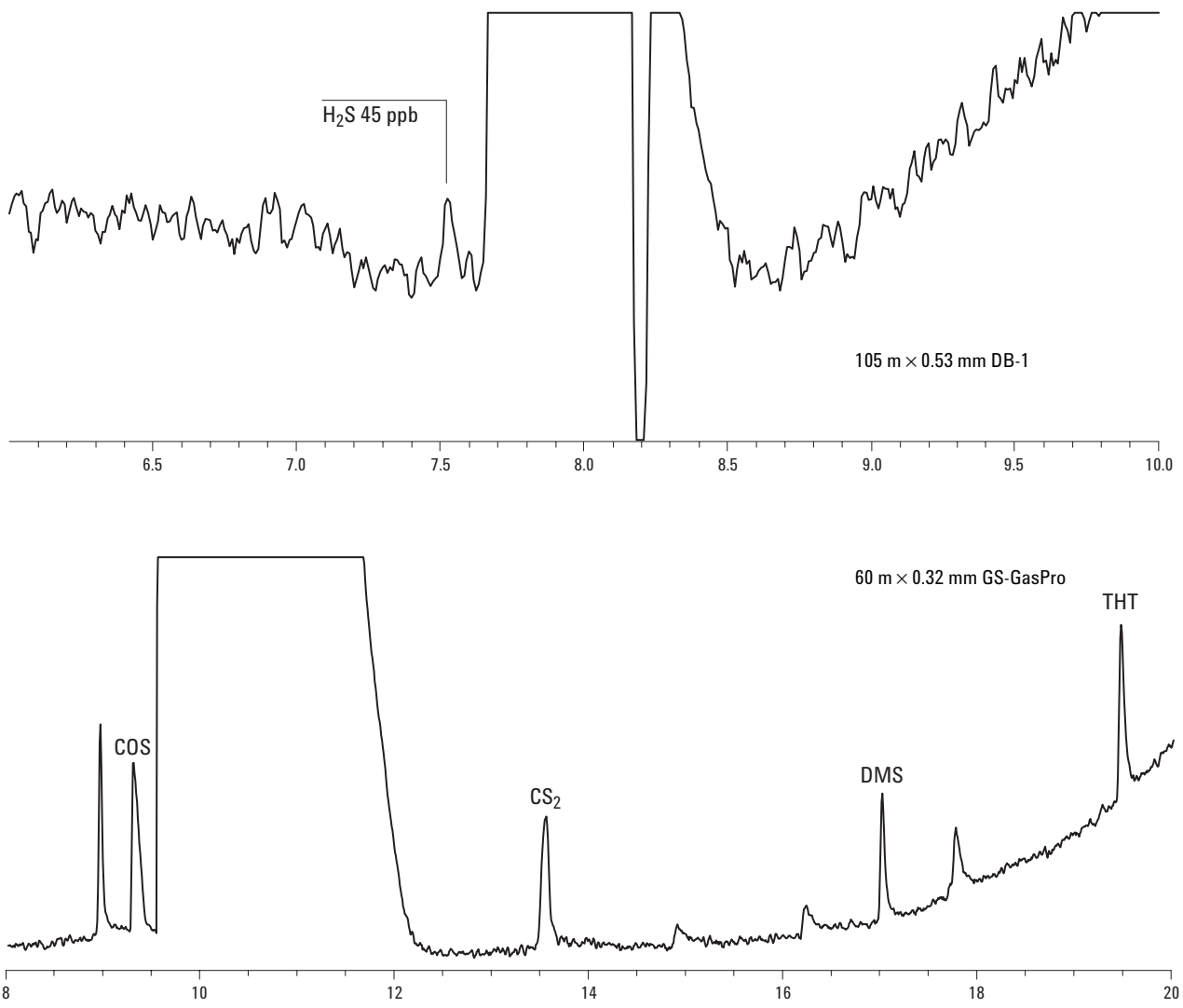

Figure 6. Polymer-grade propylene blend containing 45 ppb (v/v) each of the eight sulfur compounds. Split ratio is 2:1. Top chromatogram: 105 m × 530 µm DB-1 showing only H_2S, bottom: 60 m GS-GasPro.

Cryogenic oven temperatures were evaluated to see if the separation of H_2S and COS could be improved enough to allow use of the more sensitive 0.5:1 split ratio. The oven program tested was: -35 °C for 7 min, 20 °C/min to 300 °C, hold for 5 min. The separation was improved enough to allow the analysis of H_2S on the DB-1 column with the 0.5:1 split ratio, but COS was still occluded by the C_3s on the GS-GasPro. A DB-1 chromatogram illustrating the increased separation between H_2S and propylene is given in Figure 7.

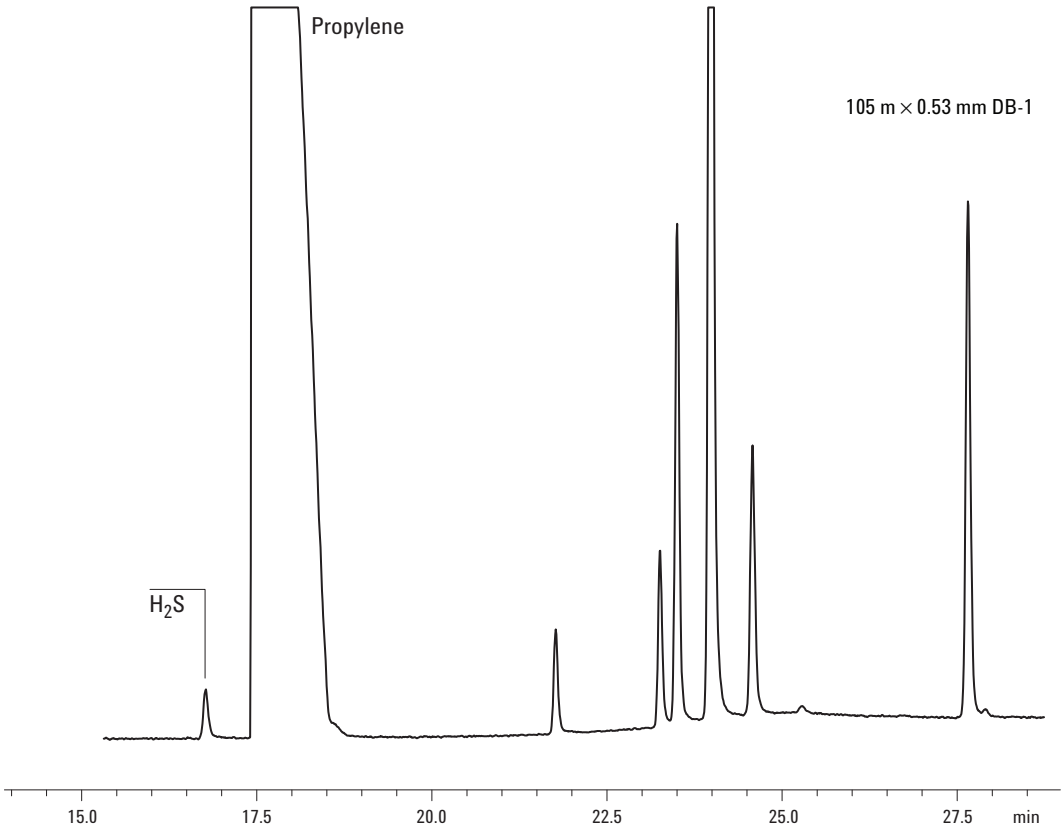

Figure 7. Use of cryogenic oven temperatures for analysis of H_2S (400 ppb) in propylene at 0.5:1 split.

Phosphorus and Arsenic on the Same System

One interesting characteristic of the modified FPD is that the filter used also passes the emissions for phosphorus and arsenic. This means that the same detectors can also be used to measure arsine and phosphine in polymer grade ethylene and propylene. A change of detector gas flows to that optimum for each element, followed by a rerun of the sample is all that is required. Since the 6890N detector flows are controlled by EPC, these reruns can be automated.

Figure 8 shows the chromatograms from an arsine and phosphine standard (DCG Partnership) diluted with polymer grade propylene to 36 ppb (v/v) each component. These are run under the same chromatographic conditions as in Figure 6, except that the FPD detector flows are set to those listed for phosphorus detection and the split ratio is back to 0.5:1. The detection limit under these conditions for phosphine in helium is under 5 ppb. If the detector flows are set to those listed for arsenic detection, the detection limit for arsine is about 60 ppb measured in helium. This system is well suited for gas analysis, however it is not really applicable to pesticide analysis due to the lack of selectivity between sulfur, phosphorus, and arsenic.

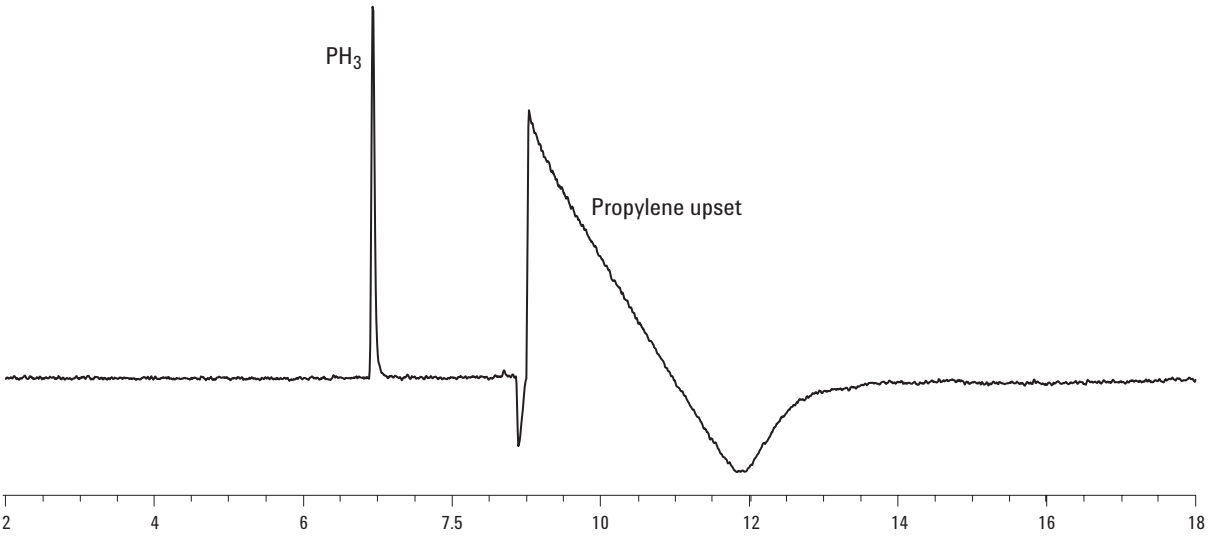

Figure 8. Polymer-grade propylene blend containing 36 ppb (v/v) each of arsine and phosphine. Split ratio is 0.5:1. Note longer 105 m DB-1 columns are used.

An example of arsine detection in propylene is shown in Figure 9.

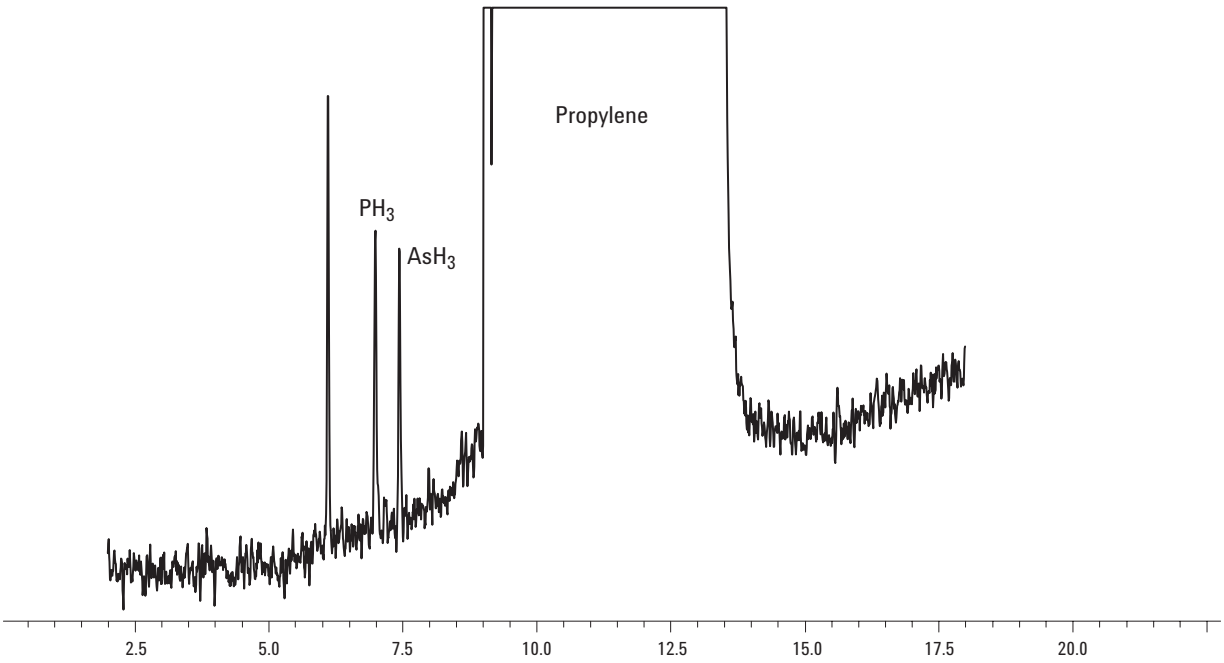

Figure 9. Arsine optimized FPD flows. H_2: 50 mL/min, air: 150 mL/min. 60 m × 0.32 mm GS-GasPro, 0.5 to 1 split. 90 ppb each of AsH_3 and PH_3.

How to Order and Configure a Dual-Channel FPD System

The Dual-Channel FPD System, including columns and valves, can be ordered as a special (SP-1) option on any new Agilent 6890N GC. This special also includes the enhanced performance FPD. Contact your local Agilent representative for more information.

Learn more about low-level sulfur detection from these application notes available from any Agilent sales office or Agilent's Web site at www.agilent.com/chem. Just click "Library" in the menu listing, and type "sulfur" in the keyword field.

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1. Roger L. Firor and Bruce D Quimby, "A comparison of Sulfur Selective Detectors for Low Level Analysis in Gaseous Streams," Agilent Technologies, publication 5988-2426EN www.agilent.com/chem
2. Roger L. Firor, "Volatile Sulfur in Natural Gas, Refinery Gas, and Liquefied Petroleum Gas," Agilent Technologies, publication 5988-2791EN, www.agilent.com/chem
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Agilent Technologies

Detection of Sulfur Compounds in Natural Gas According to ASTM D5504 with Agilent's Dual Plasma Sulfur Chemiluminescence Detector (G6603A) on the 7890A Gas Chromatograph

Application

Hydrocarbon Processing

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Abstract

An Agilent dual plasma sulfur chemiluminescence detector (DP SCD) combined with an online dilutor was used for the analysis of sulfur compounds. By using this method, the detection limits of the sulfur compounds achieved the ppb level. The stability of the DP SCD was also investigated. The long-term and short-term stability show that the performance of DP SCD is stable, and no hydrocarbon interference was found during the analysis of natural gas samples.

Introduction

Many sources of natural gas and petroleum gases contain varying amounts and types of sulfur compounds. The analysis of gaseous sulfur compounds is difficult because they are polar, reactive, and present at trace levels. Sulfur compounds pose problems both in sampling and analysis. Analysis of sulfur compounds many times requires special treatment to sample pathways to ensure inertness to the reactive sulfur species. Sampling must be done using containers proven to be nonreactive. Laboratory equipment must also be inert and well conditioned to ensure reliable results. Frequent calibration using stable standards is required in sulfur analysis [1].

GC SCD configuration with inert plumbing is one of the best methods to detect sulfur compounds in different hydrocarbon matrices. Sulfur compounds elute from the gas chromatographic column and are combusted within the SCD burner. These combustion products are transferred to the SCD detector box via vacuum to a reaction cell for ozone mixing. This detection technique provides a highly sensitive, selective, and linear response to volatile sulfur compounds.

Agilent Technologies DP technology is the detector of choice for sulfur analysis when dealing with a hydrocarbon matrix. The burner easily mounts on the 6890 and 7890A GCs and incorporates features for easier and less frequent maintenance. In this application, the Agilent 355 DP SCD was used to analyze the gaseous sulfur compounds in natural gas. Detection limits, stability and linearity were investigated.

Experimental

An Agilent 7890A GC configured with a split/splitless inlet (Sulfinert-treated), and an Agilent 355 DP SCD were used. Sample introduction was through a six-port Hastelloy C gas sample valve (GSV) interfaced directly to the sulfur-treated inlet with Sulfinert tubing. An online dilutor was used for preparation of ppb-level sulfur compounds in

different matrices. Two four-port valves were used — one for sample introduction and one for static sample injection. The valves were installed sequentially prior to the GSV. Figure 1 illustrates the configuration of the gas blending system and GC SCD.

The sulfur standards were blended in helium at 1 ppm (V/V) and were purchased from Praxair, Inc. (Geismar, LA). See Table 1 for component details.

Table 1. Sulfur Standards in Helium

1.	Hydrogen sulfide	H_2S
2.	Carbonyl sulfide	COS
3.	Methyl mercaptan	CH_3SH
4.	Ethyl mercaptan	CH_4CH_3SH
5.	Dimethyl sulfide	CH_3SCH_3
6.	Carbon disulfide	CS_2
7.	2-propanethiol	$CH_3SHC_2H_5$
8.	Tert-butyl mercaptan	$(CH_3)_3CSH$
9.	1-propanethiol	$CH_3(CH_2)_2SH$
10.	Thiophene	C_4H_4S
11.	n-butanethiol	$CH_3(CH_2)_3SH$
12.	Diethyl sulfide	$CH_3CH_2SCH_2CH_3$
13.	Methyl ethyl sulfide	$CH_3SCH_2CH_3$
14.	2-methyl-1-propanethiol	$(CH_3)_2CHCH_2SH$
15.	1-methyl-1-propanethiol	$CH_3CH_2CHSHCH_3$

Experimental Conditions

GC Conditions

Front Inlet	Split/splitless (Sulfinert-treated capillary inlet system)
Heater	150 °C
Pressure	14.5 psi
Septum purge flow	3 mL/min
Mode	Splitless
Gas saver	20 mL/min after 2 min
Sample loop	1 mL
Oven	30 °C (1.5 min), 15 °C/min 200 °C (3 min)
Column	HP-1 60 m × 0.53 mm × 5 µm
Injection mode	Static flow and dynamic flow modes

SCD Conditions

Burner temperature	800 °C
Vacuum of burner	372 torr
Vacuum of reaction cell	5 torr
H_2	40 mL/min
Air	53 mL/min

Results and Discussion

From the comparative results of the sulfur detectors' sensitivity, it could be seen that SCD is the best detector for sulfur components, especially at low levels [3]. The Agilent DP technology is the most sensitive and selective detector for sulfur-containing gaseous hydrocarbon samples.

Figure 2 is the chromatogram of low-level sulfur compounds at 1.35 ppb (H_2S), which is prepared by the point-of-use gas blending system. Table 2 is the calculated signal to noise (S/N) of each compound, from the achieved data. It can be seen that DP SCD can detect low-level sulfur compounds.

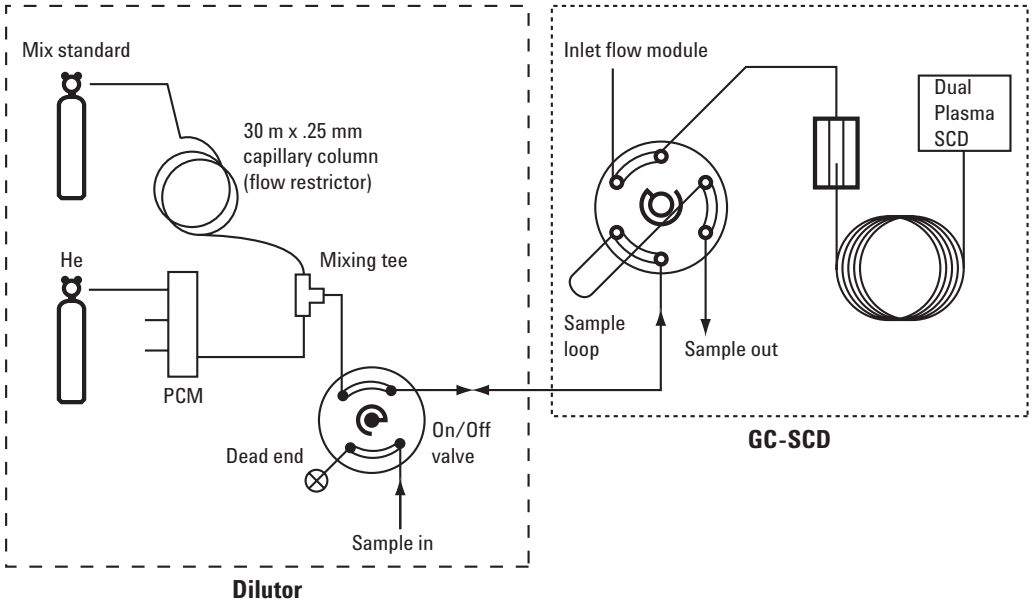

Figure 1. Diagram of online dilutor GC-DP SCD.

Table 2. S/N of Each Sulfur Component at 1.35 ppb (Refer to Table 1 for peak identification.)

Peak No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
S/N	12.0	5.0	2.1	2.6	4.9	11.5	4.0	2.7	3.7	9.1	7.6	2.3	5.7	1.0	1.1

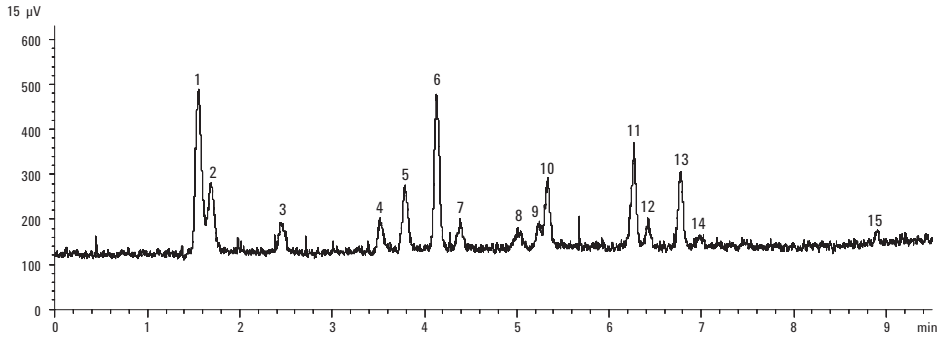

Figure 2. Chromatogram of sulfur compounds in helium at 1.35 ppb. (Refer to Table 1 for peak identification.)

Because the low-level sulfur components were prepared by the online dilutor system, which was prepared by adjusting the aux EPC to get appropriate diluent flow, high diluent flow could have the potential to cause high pressure in the sample loop, which results in the amount of the sample in the loop being different when the diluent flow changes from low to high. In this application, two sample injection modes, static and dynamic, were investigated. The mode is actuated by the on/off valve installed prior to GSV. When using static injection mode, the valve is switched to the off position, the pressure in the sample loop balances to ambient pressure, and then the sample is injected into the GC.

Table 3 shows the linear ranges of the two injection modes. The two injection modes have no difference from a linearity perspective, which means that the two injection modes are both suitable when using the 1-mL sample loop. The 1-mL sample loop's resistance is not high enough to cause variation in the sample injection amount.

Table 3 Linear Ranges of Two Injection Modes (Refer to Table 1 for peak identification.)

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Linear range (ppb)				**6.24-544.5**				
Static mode	1	0.99996	0.99995	0.99999	0.99996	0.99999	0.99996	0.99999
Dynamic mode	1	0.99996	0.99997	0.99997	0.99996	0.99999	0.99998	0.99998
	9	**10**	**11**	**12**	**13**	**14**	**15**	
Linear range (ppb)				**6.24-544.5**				
Static mode	0.99995	0.99994	0.99996	0.99996	0.99996	0.99998	0.99998	
Dynamic mode	0.99998	0.99997	0.99998	0.99998	0.99998	1	0.99998	

Table 4 shows the long-term (72 hours) and short-term (8 hours) stability of the SCD at different concentration levels.

In an effort to investigate the coelution of hydrocarbon and sulfur, the same sulfur standards in natural gas were analyzed on the SCD. Figure 3 shows the chromatogram; no quenching was found.

Table 4 The Long-Term and Short-Term Stability of SCD (Refer to Table 1 for peak identification.)

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
20.79 ppb	2.7	2.6	2.9	3.0	0.9	1.4	2.8	4.0	2.6	1.7	1.7	3.3	3.2	8.6	7.9
S.T. RSD (%)															
L.T. RSD (%)	3.0	2.7	2.4	2.5	1.4	1.5	2.6	4.3	3.8	2.7	2.0	4.9	3.2	7.9	6.9
1.38 ppb	6.6	10.1	11.7	22.8	30.4	4.1	6.9	18.7	10.7	25.1	5.1	11.1	5.8	29.6	24.1
S.T. RSD (%)															
L.T. RSD (%)	14.4	7.5	16.3	20.8	21.7	4.6	6.1	27.7	23.7	25.3	12.2	24.6	6.1	35.7	38.4

ST: Short term (8 hours); LT: Long term (72 hours)

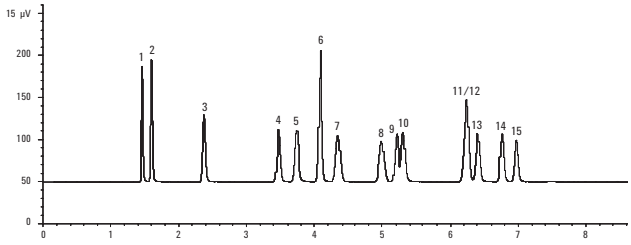

Figure 3. Chromatogram of sulfurs in natural gas. (Refer to Table 1 for peak identification.)

Natural Gas Sample Analysis

Three natural gas samples were analyzed by using the GC DP SCD system. Because the concentration of the target compounds is at ppm level, split mode was used and the method was recalibrated at ppm level. Table 5 shows the result of the three gas samples.

Table 5. Result of the Three Real Samples

Samples		H_2S	COS	Methyl Mercaptan
BLEND AL	Conc. (ppm, v/v)	2.3	2.0	2.0
	RSD (%, n = 5)	2.3	0.3	1.4
BLEND 6	Conc. (ppm, v/v)	27.1	21.9	17.3
	RSD (%, n = 5)	1.2	0.4	2.3
BLEND 12	Conc. (ppm, v/v)	15.0	9.2	10.1
	RSD (%, n = 5)	0.7	0.6	0.6
Standard	Conc. (ppm, v/v)	2.0	0.8	0.9
natural gas	RSD (%, n = 5)	1.7	2.5	1.7

Conclusions

An online dilutor combined with a GC DP SCD is suitable for gaseous sulfur components analysis, especially for the low-level components. The online dilutor offers an automatable means of system calibration and the detection limits for the trace sulfur detection are down to ppb level. By using an on/off valve prior to the GSV, both the static and dynamic injection modes of the sample gas blending system can be used. The static injection mode is important when a small sample loop with a large resistance is used. The diluter system with GC/SCD is available as an Agilent SP1, please refer to SP1 7890-0375 for order information.

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Using a New Gas Phase Micro-Fluidic Deans Switch for the 2-D GC Analysis of Trace Methanol in Crude Oil by ASTM Method D7059

Application

Petrochemical

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Abstract

A new ASTM method was developed for the analysis of trace methanol in crude oil samples. This method relies on the use of two-dimensional heart-cutting gas chromatography to separate methanol from the complex matrix. A new microfluidic Deans switch was developed for the Agilent 6890N GC system that improves the performance of heart-cutting two-dimensional gas chromatography. This system was used to perform the analysis of methanol in crude oil with results that exceed the performance requirements of the ASTM method.

Introduction

The chemical characterization of crude oils present a real challenge to analytical chemists due to the varied and complex nature of the sample matrix. This is especially true when trying to separate and quantify trace amounts of low boiling contaminants or additives that cannot be separated using conventional capillary gas chromatography (GC). For such analyses, two-dimensional (2-D) GC offers a relatively simple yet powerful solution. Recently, ASTM Committee D2 has developed a heart-cutting 2-D GC method for the analysis of methanol in crude between 15 ppm (m/m) and 900 ppm (m/m) [1]. Methanol is added to crude oil to prevent the formation of gas hydrates, but it must be removed since the oxygen can cause problems with further refining processes.

Heart-cutting 2-D GC using a Deans switch has recently experienced a revival due to the advanced technology of modern columns and instruments [2]. The latest GC instruments make heart-cutting GC much easier to set-up, more reliable, and precise. However, the actual hardware used to perform heart-cutting has not kept pace with the advances offered by today's instruments. A typical 2-D manifold still consists of a collection of individual plumbing pieces such as tees, stainless tubing, and graphite/vespel ferrules that are assembled by hand. While this plumbing works well for some applications, especially those with packed columns, it is not optimized for modern capillary chromatography.

The large thermal mass of the device can be difficult to heat uniformly, introducing cold spots in the plumbing resulting in reduced chromatographic performance for higher boiling compounds. While the fittings are machined to reduce dead volume and minimize flow paths, there are still significant plumbing problems that contribute to peak broadening within the device. Capillary columns are also difficult to connect to these fittings and must rely on a graphite/vespel ferrule and sleeve combination to make a tight seal. This connection is difficult to make and can leak with repeated oven temperature cycling from <80 °C to >250 °C. Additionally, the graphite/vespel ferrules

can adsorb solvents and analytical components, resulting in reduced sensitivity, increased peak tailing, and elevated baselines.

To overcome these difficulties, a new micro-fluidic Deans switch was designed that combines the individual switch components into a smaller, single device (Figure 1).

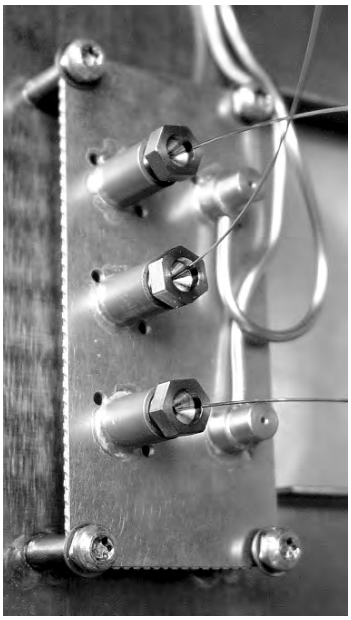

Figure 1. A close-up view of the new micro-fluidic Deans switch in the 6890N GC.

The switch's flow paths and connections are laid out and etched onto a small, thin, stainless steel plate using photolithography and chem-milling technologies. The plate is diffusion bonded, mounted with column connectors, and surface deactivated, resulting in an integrated, micro-fluidic switch that has a number of advantages for heart-cutting 2-D GC. The 4-times smaller thermal mass does not act as a heat sink; therefore, the device works optimally with modern GC ovens, especially for faster applications. The micro-fluidic switch also has far fewer connections, greatly reducing leak potential. Metal ferrules are used to interface capillary columns to the device that are also leak-free in high-temperature cycling applications. These metal ferrules will also not adsorb solvents or sample matrix, improving sensitivity for trace analysis applications. This application note describes the use of the micro-fluidic Deans switch in the analysis of trace methanol in crude oil with ASTM method D7059.

Experimental

An Agilent 6890N gas chromatograph was equipped with a split/splitless injector, a pneumatics control module (PCM), two flame ionization detectors (FIDs), and an automatic liquid sampler (ALS). A DB-1 (polydimethylsiloxane) column was used as the primary column and a CP-Lowox (Chrompack International BV) was used as the secondary column. The two columns were linked using a micro-fluidic Deans switch. Table 1 lists the details of the hardware configuration. The instrument operating conditions for this analysis are outlined in Table 2.

Table 1. Hardware Configuration

6890N GC Hardware	
G1540N	Agilent 6890N Series GC
Option 112	Capillary split/splitless inlet with EPC control
Option 210 (2 of each)	FID with EPC control
Option 309	Pneumatics control module with EPC control
G2855B	Micro-fluidic Deans switch kit
G2613A	Agilent 7683 Autoinjector
Columns	
Primary column	DB-1 column, 5.00-µm film, 10 m x 0.53-mm id (Agilent part no. 125-10H5)
Secondary column	CP-Lowox column, 10 m x 0.53-mm id (Chrompack International BV)
Fixed restrictor	Deactivated fused silica tubing, 0.5 m x 0.25-mm id (Agilent part no. 160-2255-10)
Data System	
G2070A	Agilent Multitechnique ChemStation
Other Consumables	
Agilent part no. 5181-1267	10-µL fixed tapered needle autoinjector syringe
Agilent part no. 5183-4647	Inlet liner optimized for splitless operation
Agilent part no. 5183-4759	Advanced green septa

Table 2. Instrument Conditions

Injection port	Split mode, 7:1 ratio
Temperature	325 °C
EPC pressure	3.51 psi helium, constant pressure mode
Injection size	1 µL
DB-1 column flow	3 mL/min
Pneumatics control module (PCM)	5.07 psi helium, constant pressure mode
CP-Lowox column flow	5 mL/min
FID temperatures	350 °C
Oven temperature program	
Initial temp	150 °C for 3 min
Ramp #1	20 °C to 300 °C for 5 min

Electronic pneumatics control (EPC) pressures, flow rates, and the fixed restrictor dimensions were determined using a Deans switch calculator software program that was designed for this system. This calculator program is included with the Deans switch hardware option for the Agilent 6890N GC.

Crude oil samples spiked with methanol were obtained from Spectrum Quality Standards (Houston, TX, USA). Each sample was prepared according to ASTM Method D7059 by mixing 5.0 g of crude oil sample with 5 mL of ACS grade toluene containing 1000 µg/g of 1-propanol. The 1-propanol was used as an internal standard (ISTD). If the samples were not analyzed immediately, they were stored in glass vials with TFE-fluorocarbon lined caps below 5 °C. During storage there was little or no headspace in the vials to reduce the partition of methanol into the headspace. Seven calibration standards were prepared containing 5 to 1000 ppm (m/m) of methanol in toluene, and each containing 500 ppm (m/m) of 1-propanol. The calibration standards should be used immediately after preparation since the methanol concentration is not stable in toluene. The standards can be stored for several days below 5 °C in glass vials with little or no headspace.

Results and Discussion

Heart-cut times were determined by injecting the 1000-ppm methanol standard onto the primary DB-1 column with no cutting to the Lowox column. The retention time for methanol was 1.82 min and 2.11 min for 1-propanol. Using this data, the cut-time for all standards and samples was 1.70 to 2.35 min. The 1000-ppm standard was then analyzed using this cut time to evaluate the separation of the alcohols on the Lowox column after cutting. The methanol and 1-propanol were easily separated on the Lowox column with retention times of 4.72 and 6.38 min, respectively (Figure 2).

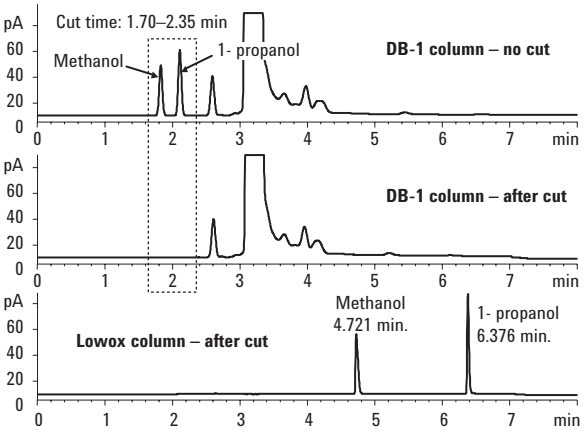

Figure 2. Setting the heart-cut times for the 2-D GC analysis of methanol in crude oil.

Calibration of the systems was performed using seven standards of methanol in toluene at concentrations of 5, 25, 75, 125, 250, 500, and 1000 ppm with 500 ppm of 1-propanol as the ISTD. The ChemStation was used to develop a calibration curve (Figure 3). This calibration exceeded the correlation coefficient of 0.99 required by the ASTM method. The detectability of the system was also checked using a 1-ppm standard of methanol in toluene, with no ISTD. This sample was analyzed and the signal-to-noise of the methanol peak on the second column (Lowox) was found to be 5:1, which exceeded the method requirement of a 5:1 signal to noise for a 2-ppm standard.

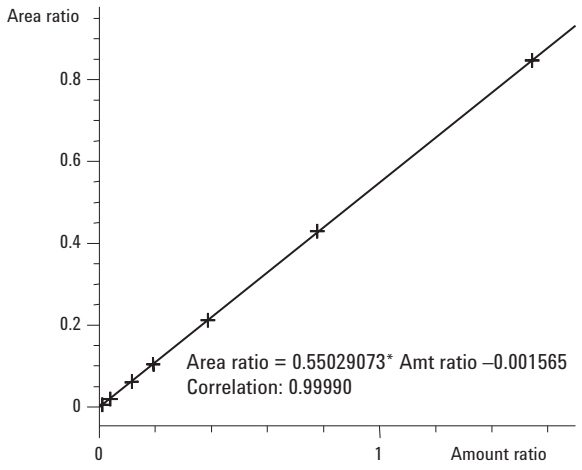

Figure 3. Calibration of methanol from 5 ppm (m/m) to 1000 ppm (m/m) using 2-D heart-cutting GC.

A quality control check of the system was also made using two crude oil samples; one contained 15-ppm methanol, and the other 670 ppm. For the 15-ppm sample, the reported result must be within ±5 ppm and for the 670-ppm sample, within ± 35 ppm. Figure 4 shows the data obtained from the analysis of the crude oil sample containing 15 ppm of methanol in crude oil. Two replicates of the 15-ppm sample yielded results of 10 ppm and 17 ppm. For the 670-ppm samples, the replicates yielded results of 670 ppm and 667 ppm.

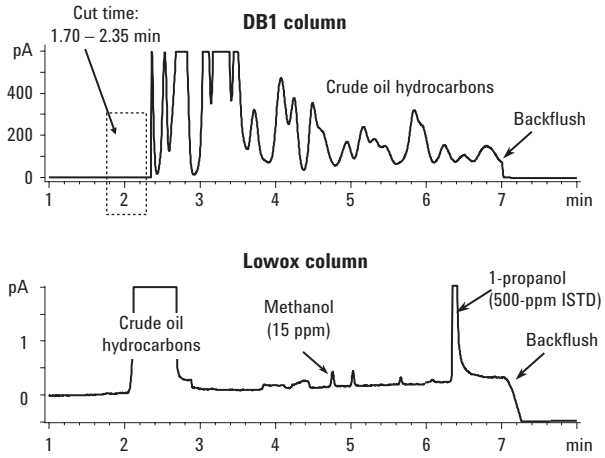

Figure 4. The 2-D GC analysis of 15 ppm (m/m) of methanol in crude oil using a micro-fluidic Deans switch.

The analysis time of the method was reduced by backflushing the primary column to quickly remove the higher boiling crude oil components from the DB-1 column. Backflushing was done after the elution of the 1-propanol peak from the Lowox column. At 7 min, the split/splitless inlet pressure was reduced to 0.5 psi while the PCM pressure was increased to 35 psi. This reversed the flow in the primary DB-1 column so that any remaining compounds at the head of the column were eluted through the split vent (Figure 5).

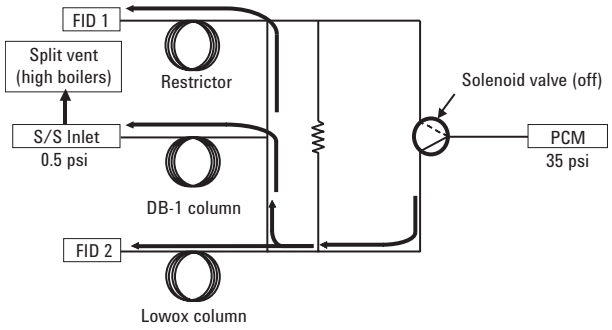

Figure 5. Backflushing the DB-1 column can be done to reduce the analysis time using the EPC on the 6890N Deans system.

Crude oil analysis also requires more maintenance than with more volatile samples. Since crude contains a wide range of compounds, from low boiling to nonvolatile, the inlet liner will need more frequent replacement. It is recommended that the liner be changed after 50 injections. Additionally, one should also inspect the top of the split/splitless inlet body to evaluate any contamination of crude oil tars that can accumulate at the top of the inlet and at the outlet of the split vent line. Depending on the samples, the inlet body may need to be cleaned after 100 injections.

Conclusions

The analysis of any components in crude oil presents a number of challenges due to the difficult nature of the sample matrix. The recently developed ASTM method D7059 uses heart-cutting 2-D GC to separate and quantify trace levels of methanol in crude oil samples. A new micro-fluidic Deans switch designed for the 6890N was shown to be ideally suited to this difficult application. It has 4-times less thermal mass so that it is effectively and uniformly heated, avoiding cold spots where high-boiling crude oil components could be condensed. The shorter flow paths, inert surfaces, and capillary optimized fittings ensure that active compounds like methanol can be separated and detected at trace levels in crude oil.

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The Use Of Automated Backflush on the 7890A/5975A GC-MS System

Setup Example Using Biomarkers

Application

Hydrocarbon Processing

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Abstract

The use of column backflushing in capillary gas chromatography has been sparingly used over the years, primarily due to its added complexity and demands on data system control for use in automated/routine laboratories. The potential of backflushing has been demonstrated in a gamut of applications from environmental, refining, and residues in food where high boiling point and complex matrices are commonplace. This application describes the setup, use and tricks and tips for implementing backflushing on the 7890A/5975A GC-MS system, with the specific example of monitoring biomarkers in crude oil.

Introduction

Until recently, the implementation of capillary column backflush has required a cumbersome conglomeration of parts and separate controllers. The nonintuitive combination of manual pressure regulators, timers, stand-alone valve controllers, and experimentally determined GC setpoints conspired against chromatographers with interest in attempting it. The few who were successful on a given system would rarely consider implementing backflush routinely, even if their efforts met with success the first time. Considerable improvements in implementation of backflush became available with the 6890 GC and 6890/5973 GC MSD systems [1–6]. With the release of the Agilent 7890A/5975A GC-MS system with ChemStation version E.01.00, implementation of capillary column backflush has never been easier. Full electronic control of all backflush parameters is possible in a manner never before offered in a GC-MS system. At the same time, major advancements in fluidic devices now greatly improve the mechanical aspects of implementing routine capillary column backflush.

The benefits of backflush in capillary gas chromatography are myriad:

- More samples/day/instrument
- Better quality data
- Lower operating costs
- Less frequent and faster GC and MSD maintenance
- Longer column life
- Less chemical background

When a mass spectrometer (MS) is employed, a key additional benefit is that backflushing high-boiling components from the capillary column and out of the inlet to waste (usually via a split/splitless inlet or PTV) prevents them from being deposited in the ion source. This improves detection limits for sub-

sequent samples (less background) and greatly increases the number of samples that can be run before ion source cleaning is required.

As illustrated by the many prior examples (see references), backflush technology is relevant in many areas, including the geochemical/hydrocarbon area, wherein samples generally span a large boiling point range and analyses are typically long yet contain only one or two compounds of specific interest. Biomarker determination in crude oils is such an example where backflush can provide several significant benefits. Analytical run times are greatly reduced; high-boiling, less important components are removed from the system and prevented from reaching the mass spectrometer; and the column is exposed to much lower final oven temperatures. In this application, backflushing on a 7890A/5875 system is presented to show the new setup screens and increased ease of setting up backflush conditions.

Experimental

Table 1 shows the analytical conditions used in a traditional GC-MS analysis of crude oil. The boiling point range of this oil sample is very wide (spanning C_4 to C_{50}), with the target components of interest eluting around 30 minutes in a 74-minute analysis (see Results and Discussion).

Table 1. Original Analytical Method Conditions

Column	HP5-MS 30 m × 0.25 µm × 0.25 µm; part number 19091S-433
Carrier gas	Helium, constant flow mode; 1.2 mL/min
Split/splitless inlet	340 °C, split 30:1
Oven	50 °C (1 min) → 320 °C at 5 °C/min hold for 20 minutes
Analysis time	74 min
Sample	Crude oil in CS_2, 1-µL injection
MSD	Scan = 35–700 u Samples = 2^2 Source = 300 °C Quad = 150 °C Transfer line = 320 °C

A 3-way purged splitter (Agilent part number G3183B) Capillary Flow Technology device was used for this application, in part to demonstrate its flexibility. The device has a purge and four connections (Figure 1). As used herein, only two of the ports were used, one for the column outlet (port 3) and the other for the restrictor to the MSD (port 4). The other two ports (1 and 2) were plugged with solid wire instead of column connections. Very reliable connections are a feature of Capillary Flow Technology devices because of the use of soft metal ferrules. Care needs to be taken when making these connections, but the process is very straightforward and easily learned. The manuals provided with the various Capillary Flow Technology devices contain explicit instructions.

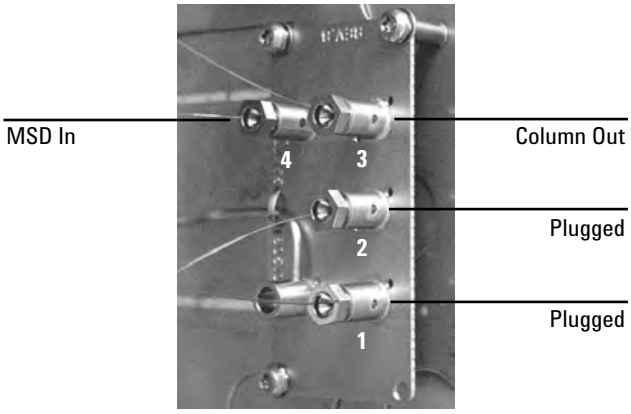

Figure 1. 3-way purged splitter. The column outlet was attached to port 3 and the MSD restrictor was attached to port 4. Ports 1 and 2 were plugged.

Careful consideration must be made before a restrictor internal diameter (ID) and length are chosen for a backflush application. Parameters such as detector type (atmospheric pressure versus vacuum), vacuum pumping capacity (for example, diffusion pump, standard and performance turbo molecular pumps), and Capillary Flow Device pressure and desired split ratio (if splitting detector effluent to multiple detectors) must all be taken into consideration. Such considerations are described in detail in a previous application [1].

In this example with a 5975A MSD, a deactivated restrictor of 1 m × 0.18 mm id (such as Agilent part number 160-2615-1) provided a balanced match for this application.

Table 2 shows the analytical conditions used for this backflush application, and Figures 2 to 7 show the software setup screens for the 7890A/5975A GC-MS system with MSD ChemStation revision E.01.00 software.

Table 2. Backflush Analytical Method Conditions

Column	HP5-MS 30 m × 0.25 µm × 0.25 µm part number 19091S-433
Carrier gas	Helium, constant flow mode; 1.2 mL/min
Split/splitless inlet	340 °C, split 30:1
Oven	50 °C (2 min) → 205 °C at 5 °C/min no hold
Backflush restrictor	1m × 0.18 mm deactivated capillary column tubing
Aux 3 pressure	1 psi
Backflush pressure	75 psi
Analysis time	31 min + 5.47 post run at 205 °C Total time = 36.47 min
Sample	Crude oil in CS_2, 1-µL injection
MSD	Scan = 45–700 u Samples = 2^2 Source = 300 °C Quad = 150 °C Transfer line = 320 °C

By setting up the required analytical column and restrictor with the correct inlet and outlet connections (Figures 2 to 4), the software automatically calculates the inlet pressure required to maintain analytical column flow. By selecting the "evaluate" button (Figure 5), the backflush pressure required for a predetermined number of column "sweeps" or "void volumes" is calculated, displayed for review, and uploaded to the analytical method along with the GC oven hold time (Figures 6 to 8). As a general guide, 10 void volumes is effective for most applications. As few as two void times can effectively backflush a capillary column under certain conditions (for example, high oven ramp rates prior to backflush). However, some applications may require more than 10 void volumes to backflush everything, so the onus is on the user to validate appropriately backflush times for a given application. A blank run (that is, pure solvent as sample) following a sample run with backflush is helpful during method validation to see that all components are effectively removed from the analytical column by the chosen backflush conditions.

In this application, a 75 psi backflush pressure resulted in a backflush flow of approximately 6 mL/min through the capillary column and 75 mL/min into the performance turbo molecular pump. A figure shown later in this application illustrates that these backflush conditions were effective.

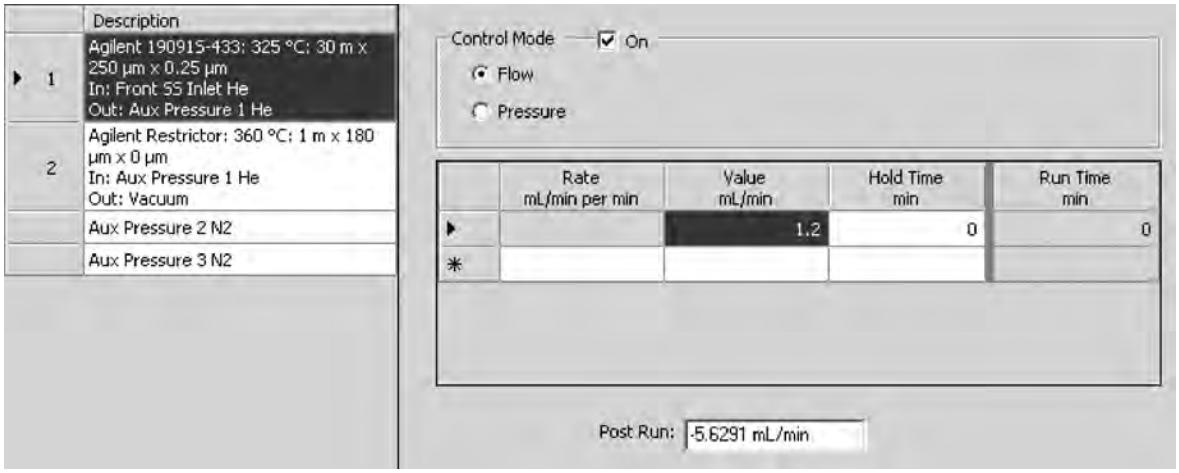

Figure 2. Software setpoints for the analytical column.

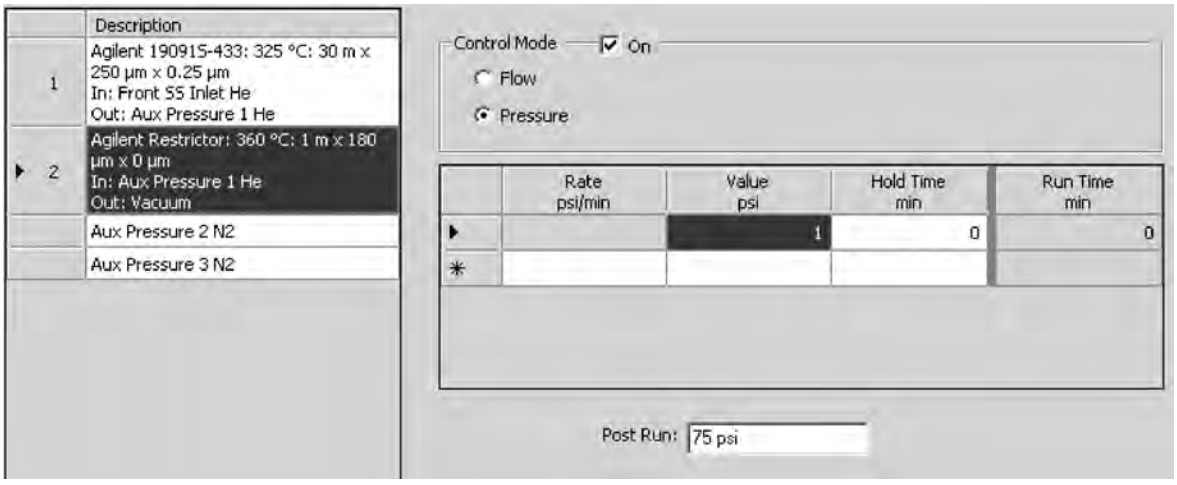

Figure 3. Software setpoints for the restrictor to the MSD.

	Description
▶ 1	Agilent 19091S-433: 325 °C: 30 m x 250 µm x 0.25 µm In: Front SS Inlet He Out: Aux Pressure 1 He
2	Agilent Restrictor: 360 °C: 1 m x 180 µm x 0 µm In: Aux Pressure 1 He Out: Vacuum

Figure 4. Column inlet and outlet conditions.

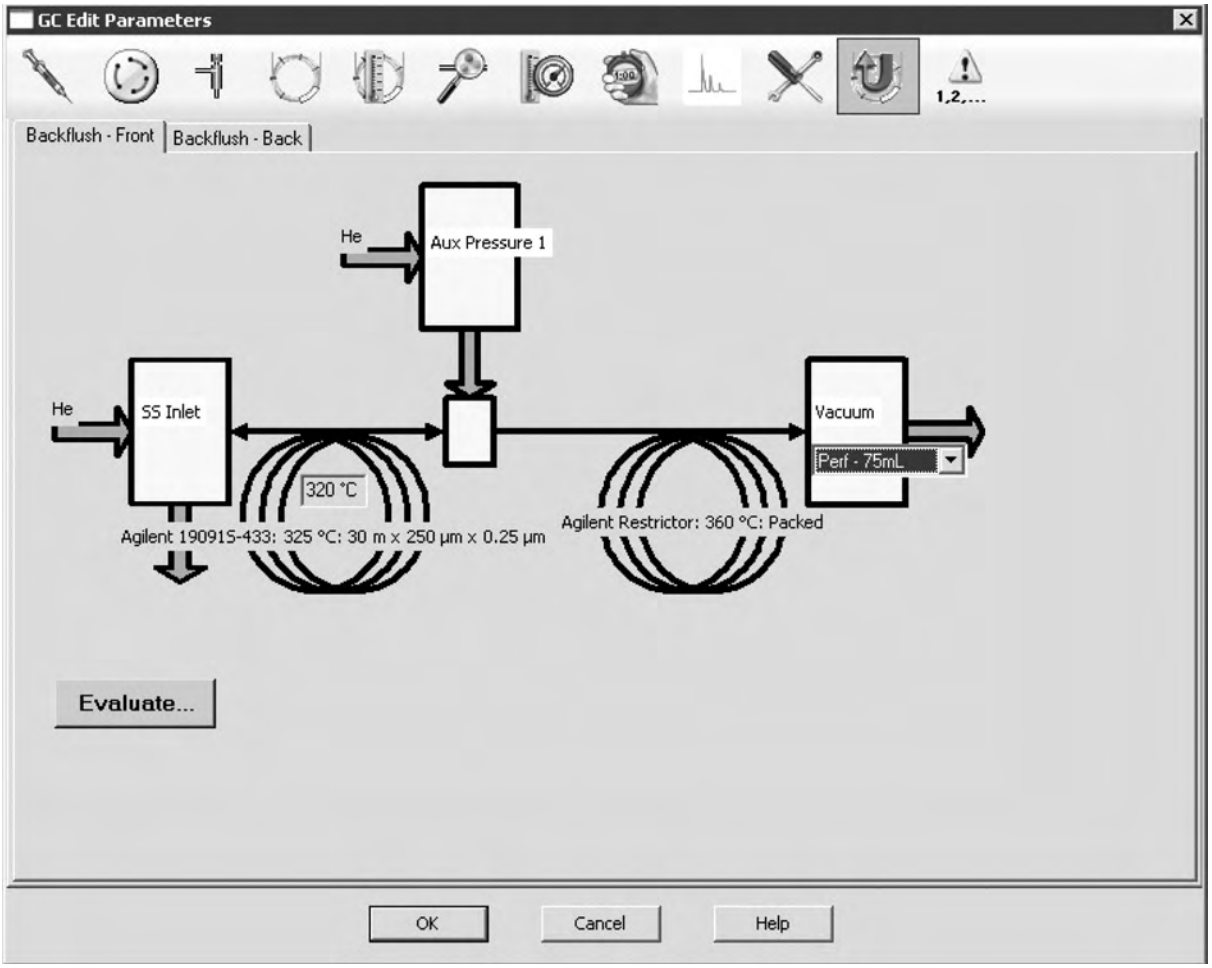

Figure 5. Interactive setup for backflush conditions in ChemStation.

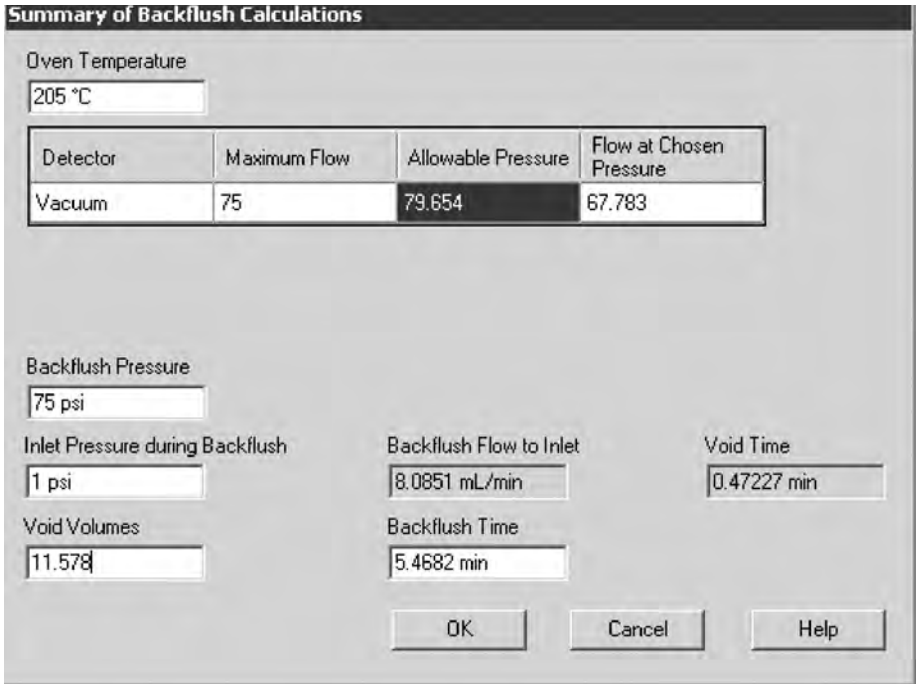

Figure 6. Conditions uploaded to method setpoints.

Results and Discussion

The profile seen in Figure 9 is typical of many crude oils with complex distribution over a large boiling point range, with a large number of unresolved components. Another feature is the long tail of high-boiling components that must be eluted after the compounds of interest. Figure 10 illustrates the three components of interest: a series of three methylbenzothiophenes through an extracted ion chromatogram (EIC) of *m/z* 198.

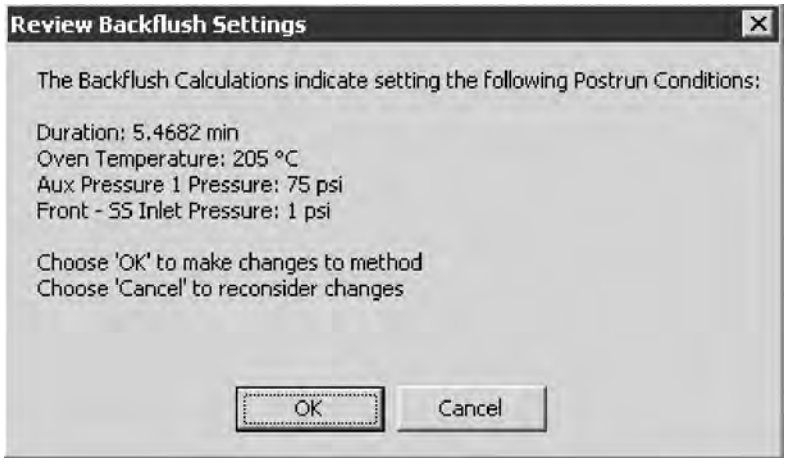

Figure 7. Conditions uploaded to method setpoints.

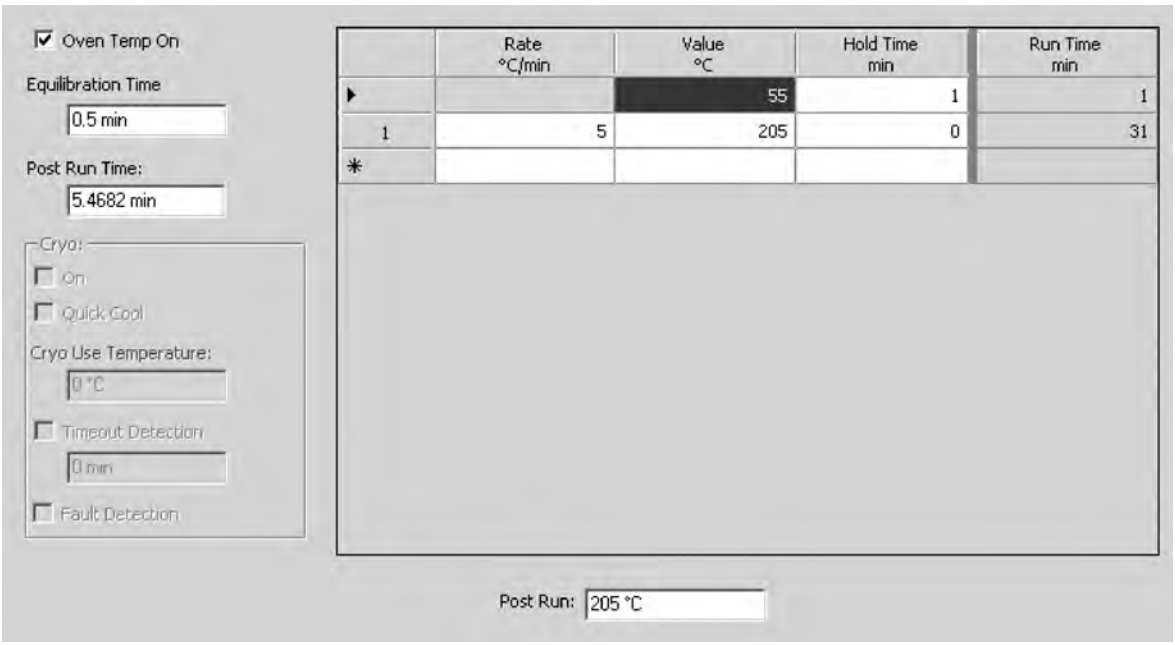

Figure 8. Note that the post-run time has been updated automatically.

Figure 11 shows the chromatogram from another run that includes a backflush immediately after the benzothiophenes had eluted.

In order to validate the efficacy of the backflush, a full-length analysis was undertaken with pure solvent immediately after the backflush run. It

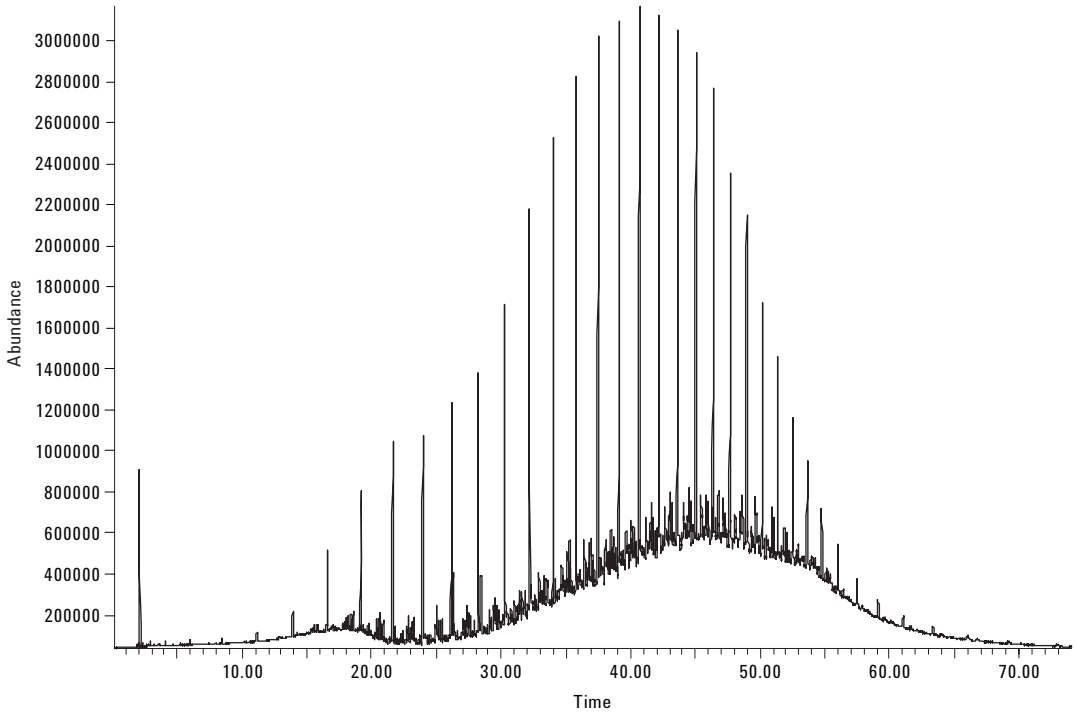

Figure 9. Total ion chromatogram (TIC) of normal analysis. Peaks of interest (benzothiophenes) are obscured by the high concentration of hydrocarbons.

can be seen from Figure 12 that no residual high-boiling components remained in the capillary column after the backflush from this blank solvent injection. Also, there are no residual biomarkers at *m/z* 198. All material (representing over 50% of the sample introduced into the column) eluting after 31 minutes was effectively backflushed.

Figure 13 shows the EIC (*m/z* = 198) for both the normal run and the backflushed runs, showing that no material was lost and retention times were not changed by implementing the backflush.

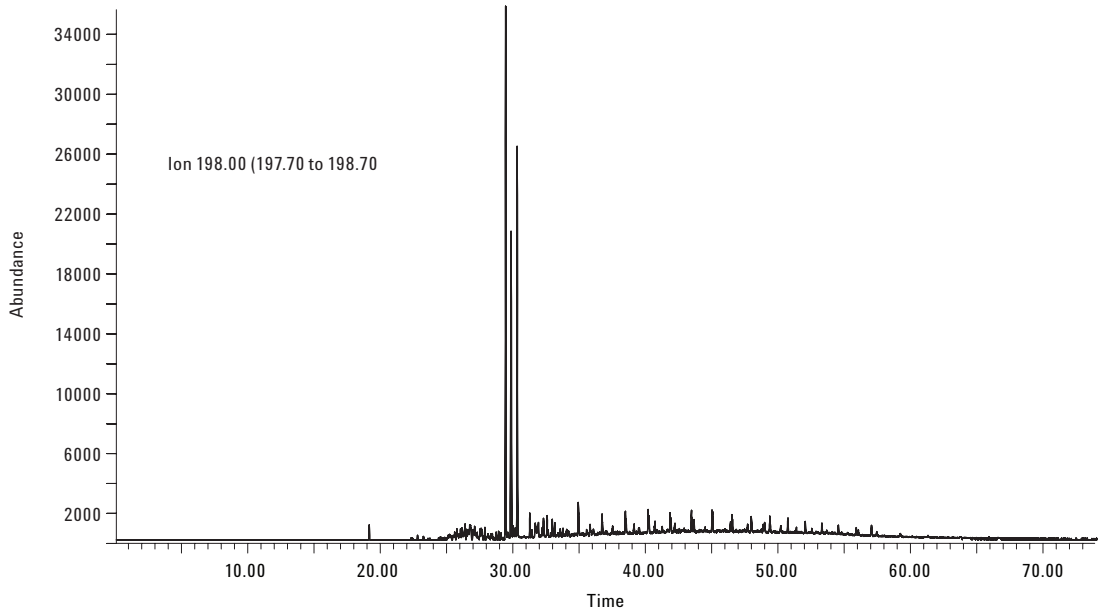

Figure 10. EIC of *m/z* 198 ion. The three methylbenzothiophene peaks of interest at approximately 30 minutes are easily visualized.

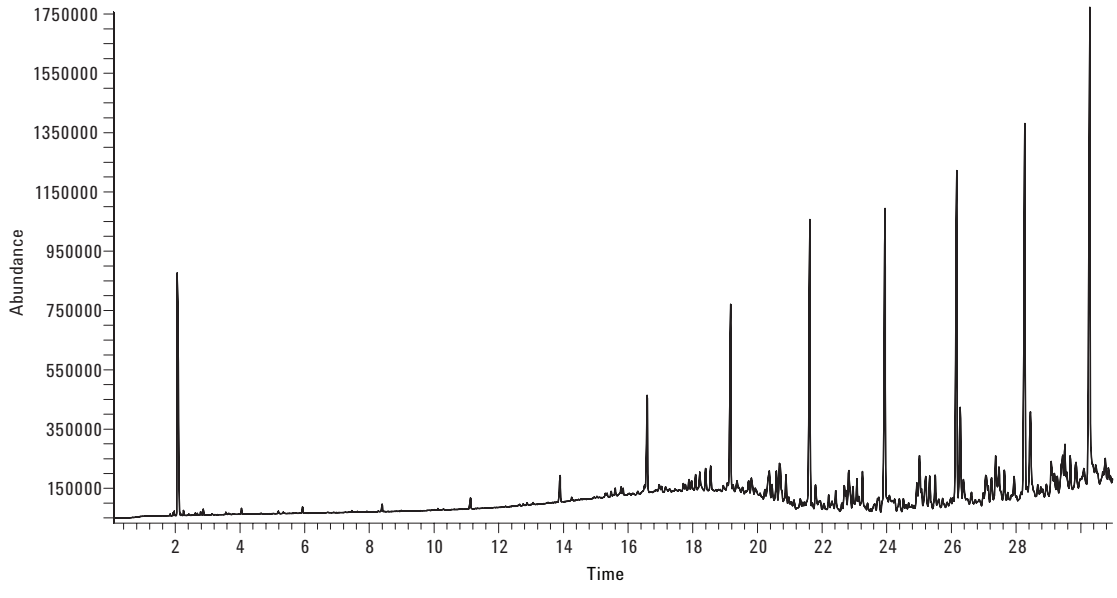

Figure 11. TIC of backflush run; run switched to backflush mode at 31 minutes.

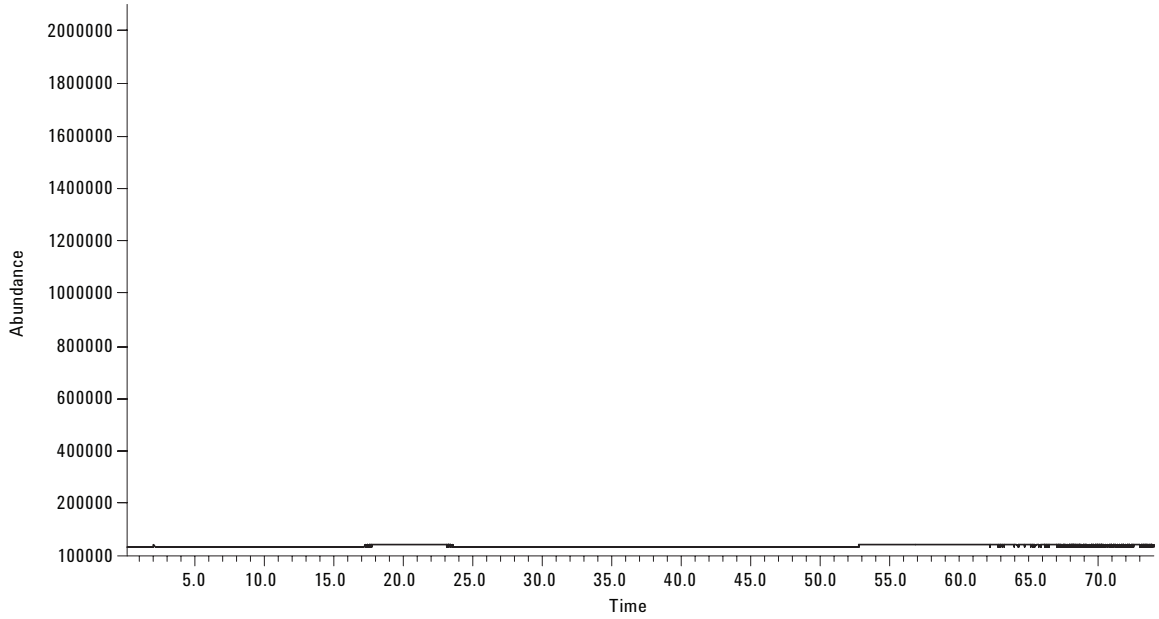

Figure 12. TIC of full run after the backflush with inset of the EIC of *m/z* 198.

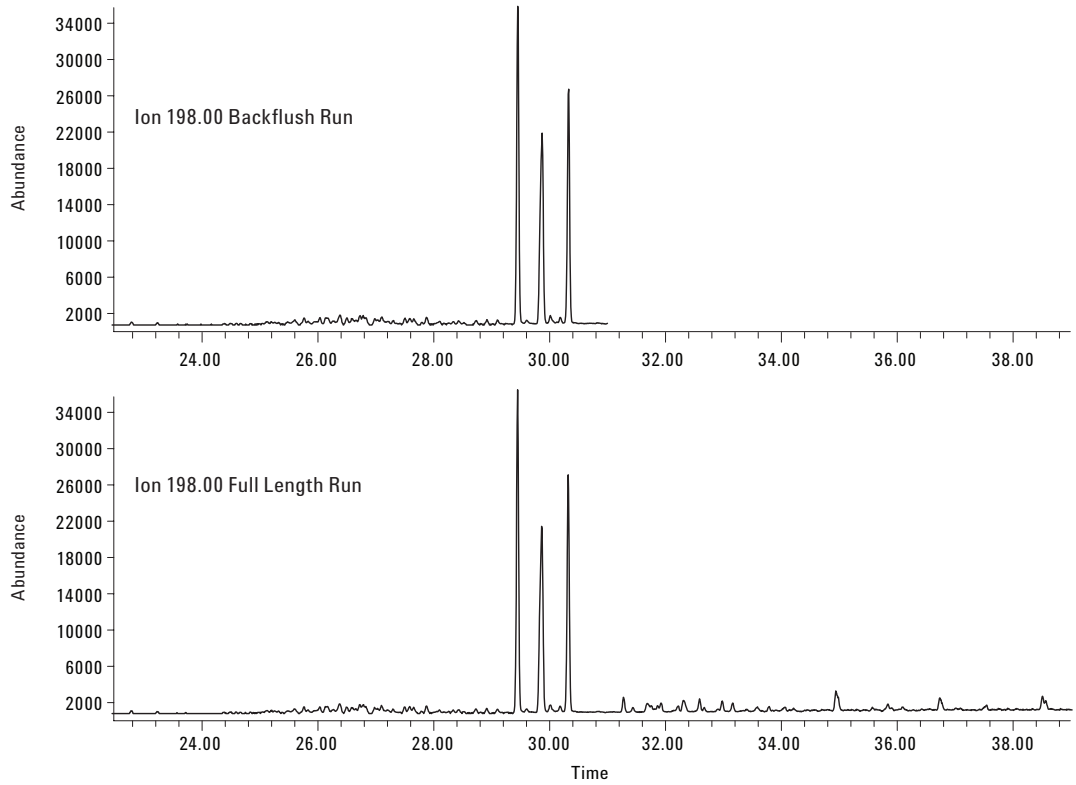

Figure 13. Overlay of EIC of *m/z* 198 from full run and backflush run, showing the exact matching of the analytical portion of each run for the three methylbenzothiophene biomarkers.

Conclusions

This application demonstrates the ease with which backflush can be set up and executed with the 7890A/5975A GC-MS system with EA 01.00 MSD ChemStation. In this example, a total run time saving of 37.5 minutes effectively halved the run time of the original run while ensuring that the analytical column was free from sample carryover. A confirmatory blank run following backflushing substantiates the efficacy of the backflush, verifying removal of all remaining sample components.

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Investigation of the Unique Selectivity and Stability of Agilent GS-OxyPLOT Columns

Application

Gas Chromatography

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Abstract

The stationary phase of a GS-OxyPLOT column is a proprietary, salt deactivated adsorbent. GS-OxyPLOT columns show unique selectivity to oxygenated hydrocarbons, excellent stability and reproducibility, long column lifetime, and a wide application range.

Introduction

The determination of oxygenated hydrocarbons in different sample matrices is very important for the petrochemical industry, because oxygenates directly influence product quality. Presence of such oxygenates may cause the catalysts to be poisoned and deactivated, resulting in more downtime and higher costs. ASTM has developed several methods for analysis of oxygenates, such as ASTM D7059, D4815, and D5599. The oxygenates include ethers, esters, ketones, alcohols, and aldehydes.

Methanol is one of the oxygenates that often present in light hydrocarbon streams. For example, it is added to natural gas and production of crude oil to prevent hydration of hydrocarbons during transportation via pipelines. Therefore, it is important to accurately measure the content of methanol from light hydrocarbons at different concentrations, including at trace levels.

To achieve this, a new porous layer open tubular (PLOT) capillary column, the GS-OxyPLOT column, was used. The stationary phase of the GS-OxyPLOT is a proprietary, salt deactivated adsorbent with a high chromatographic selectivity for low molecular weight oxygenated hydrocarbons, while having virtually no interactions with saturated hydrocarbon solutes [1].

Using Capillary Flow Technology, such as backflush or Deans switch, GS-OxyPLOT columns can provide a turnkey solution for the analysis of trace level oxygenate impurities in complex matrices, such as motor fuels, crude oil, and gaseous hydrocarbon [2]. Meanwhile, a GS-OxyPLOT column can be used as a single analytical column to separate oxygenates for some samples. In this application, methanol was set as an example to investigate the performance of the GS-OxyPLOT column.

Experimental

The experiments were performed on an Agilent 7890A GC system and a 6890N GC system equipped with split/splitless capillary inlet, flame ionization detector (FID), and Agilent 7683 Automatic Liquid Sampler (ALS). The split/splitless inlets were fitted with long-lifetime septa (Agilent p/n 5183-4761) and spilt/splitless injection liners (Agilent p/n 5183-4711). Injections were done using 10-µL syringes (Agilent p/n 9301-0714). A glass indicating moisture trap (Agilent p/n LGMT-2-HP), an oxygen trap (Agilent p/n BOT-2), and a

hydrocarbon trap (Agilent p/n 5060-9096) were installed. Agilent ChemStation was used for all instrument control, data acquisition, and data analysis.

Results and Discussion

Analysis of Normal Hydrocarbons and Methanol

A mixture of normal hydrocarbons and methanol was prepared with the following approximate concentrations %(w/w): 34.8% n-pentane, 12.8% n-hexane, 1.8% n-heptane, 1.9% n-octane, 2.1% n-nonane, 3.9% n-decane, 2.1% n-undecane, 9.8% n-dodecane, 11.8% n-tridecane, 4.7% n-tetradecane, 2.4% n-pentadecane, 4.5% n-hexadecane, 2.4% n-heptadecane, 1.0% n-octadecane, 0.9% n-eicosane, 0.9% n-docosane, 1.1% n-tetracosane, and 0.8% methanol.

The analytical conditions are summarized in Table 1. The normal hydrocarbons and methanol analysis was performed on a GS-OxyPLOT column (Agilent p/n 115-4912). The GC chromatogram is shown in Figure 1.

Table 1. Conditions for Normal Hydrocarbons and Methanol Analysis

Column	GS-OxyPLOT, 10 m × 0.53 mm × 10 µm (Agilent p/n 115-4912)
Carrier gas	Helium, constant flow mode, 40 cm/s @ 50 °C
Inlet	Split/splitless at 325 °C
Split ratio	80:1
Oven temperature	50 °C (2 min); 10 °C/min to 290 °C (2 min)
Post-run	300 °C (2 min)
Detector	FID at 325 °C
Injection size	0.2 µL

In Figure 1, the GS-OxyPLOT column shows unique retention characteristics for methanol. The lower boiling point hydrocarbons were not strongly retained on the stationary phase and eluted through the FID very rapidly. The methanol eluted after n-C14, allowing it to be quantified without any interference from the hydrocarbon matrix, and making it feasible for trace-level methanol analysis in a range of hydrocarbon streams.

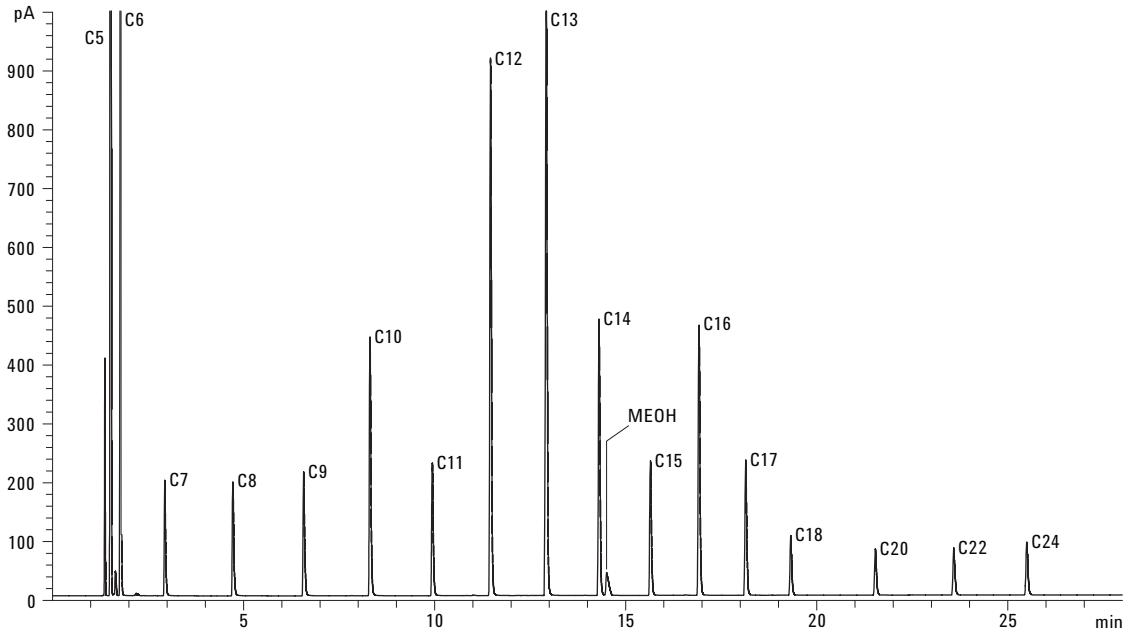

Figure1. Analysis of methanol and normal hydrocarbons on a GS-OxyPLOT column, 10 m × 0.53 mm × 10 µm.

In addition, the baseline was quite smooth, even when the oven temperature was up to 290 °C. GS-OxyPLOT has an upper temperature limit of 350 °C and exhibits virtually no bleed, making it widely applicable for long-term reliable analysis.

Analysis of Alcohols

A mixture containing a range of primary alcohols from methanol to lauryl alcohol was analyzed on a GS-OxyPLOT column using a temperature-programmed method. Table 2 lists conditions for alcohols separation, and the resulting chromatogram is shown in Figure 2.

Sample

The sample had an approximate concentration (v/v) of 1% methanol, ethanol, propanol, butanol, amyl-alcohol, heptanol, octanol, nonanol, decyl alcohol, and lauryl alcohol in toluene.

As can be seen in Figure 2, all of the alcohols are separated and eluted with good peak shape within an analysis time of 15 min. In this experiment, oven temperature was set up to 300 °C. Thanks to its advanced dynamic coating process, Agilent's GS-OxyPLOT stationary phase exhibits virtually no detector spiking due to particle generation from the phase coating [3].

Due to the high viscosity of alcohols, especially decyl alcohol and lauryl alcohol, it is necessary to wash the needle after each injection in case of carryover problems.

Table 2. Conditions for Alcohols Analysis

Column	GS-OxyPLOT, 10 m × 0.53 mm × 10 µm
Carrier Gas	Helium, constant flow mode, 40 cm/s at 150 °C
Inlet	Split/splitless at 325 °C
Split ratio	50:1
Oven temperature	150 °C (0 min); 10 °C/min to 300 °C (5 min)
Detector	FID at 325 °C
Injection size	0.2 µL

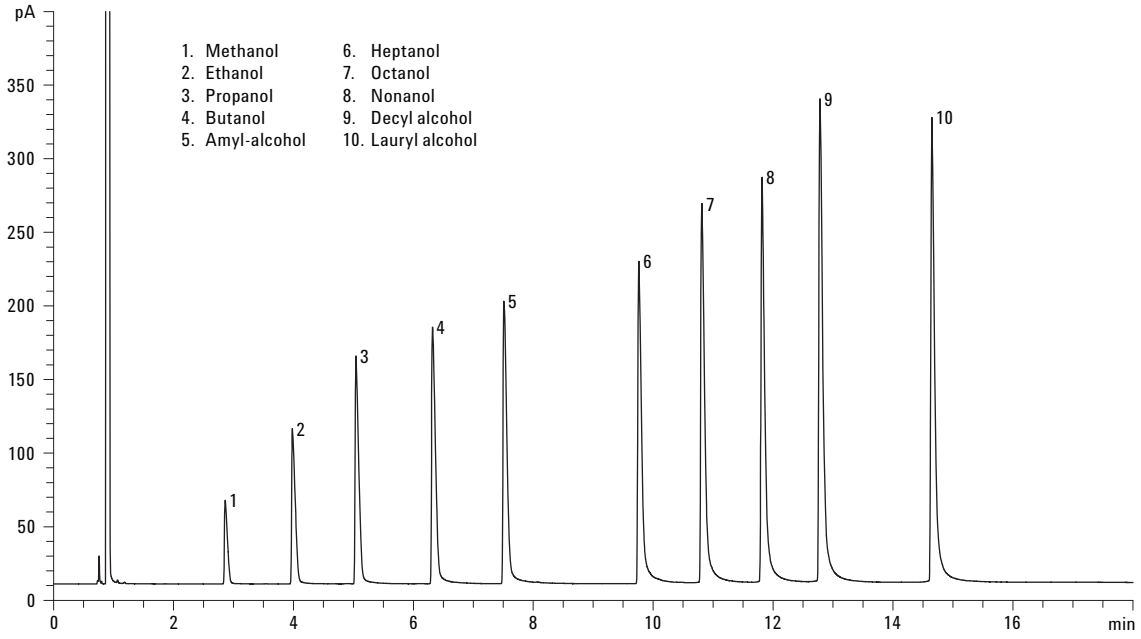

Figure 2. Separation of alcohols using GS-OxyPLOT, 10 m × 0.53 mm × 10 µm.

Influence of Temperature on the Selectivity of GS-OxyPLOT

To polar stationary phases, the temperature has a direct influence on the selectivity. GS-OxyPLOT offers extremely high polarity. The analysis of normal hydrocarbons and methanol demonstrated that methanol elutes after n-C14. Using a mixture containing methanol, n-tetradecane, and n-pentadecane, isothermal Kovats retention indices were tested at isothermal oven temperatures of 150, 200, 220 and 250 °C, respectively (Table 3). The relationship between Kovats retention indices and oven temperature is shown in Table 4.

Table 3. Conditions for Kovats Retention Indices Test

Column	GS-OxyPLOT, 10 m × 0.53 mm × 10 µm
Carrier gas	Helium, constant flow mode, 30 cm/s at 150 °C
Inlet	Split/splitless at 250 °C 100:1 split ratio
Oven temperature	150, 200, 220, and 250 °C, respectively; isothermal
Detector	FID at 250 °C
Injection size	0.2 µL

Table 4. Kovats Retention Indices and Oven Temperature (n > 3)

Oven temp.	150 °C	200 °C	220 °C	250 °C
LOT1	1419	1418	1418	1413
LOT2	1420	1421	1419	1417

Retention index, Ix, was calculated using the following equation:

$$Ix = 100n + 100[\log(t_x) - \log(t_n)]/[\log(t_{n+1}) - \log(t_n)]$$

Where t_n and t_{n+1} are retention times of the reference n-alkane hydrocarbons eluting immediately before and after chemical compound X; t_x is the retention time of compound X. Here compound X is methanol, the reference n-alkane hydrocarbons are n-tetradecane and n-pentadecane, respectively.

Table 4 shows good repeatability of Kovats rentention indices for two different lots of GS-OxyPLOT columns. The retention index for methanol only changed by less than 10 index units over 100 °C temperature difference. Therefore, when the oven temperature changes from 150 to 250 °C, it has little influence on the selectivity of GS-OxyPLOT.

Influence of Moisture on GS-OxyPLOT

Some PLOT columns can adsorb water, which can lead to changes in retention times and selectivity for analytes. Therefore, column performance will be influenced greatly in the presence of water. Although cumbersome solvent-extraction procedures can be performed before injection, injecting sample that contains water is, in some cases, unavoidable.

From a GC point of view, water is a less-than-ideal solvent. The problems associated with water include large vapor expansion volume, poor wet ability and solubility in many stationary phases, detector problems, and perceived chemical damage to the stationary phase. In order to test the effect of water, a GS-OxyPLOT column that had gone through about 1,500 runs was tested before and after injecting 100% aqueous samples.

Water has a large vapor expansion volume; the vapor volume of water (assuming a 1-µL injection) can easily exceed the physical volume of the injection liner (typically 200 to 900 µL). The volume for the liner used in this experiment (Agilent p/n 5183-4711) is 870 µL, so the injection volume was set as 0.2 µL. Table 5 lists the conditions for the moisture testing, and the resulting chromatograms are shown in Figure 3.

Table 5. Conditions for Moisture Test

Column	GS-OxyPLOT, 10 m × 0.53 mm × 10 µm
Carrier gas	Helium, constant flow mode, 38 cm/s at 150 °C
Inlet	Split/splitless at 300 °C 15:1 split ratio
Oven temperature	150 °C isothermal, post-run: 300 °C (5 min)
Detector	FID at 300 °C, H2:45mL/min, air: 400 mL/min, makeup: 30 mL/min
Injection size	0.2 µL
Sample	0.1% n-Dodecane, Methyl tert-butyl ether, n-Tridecane, Iso-Butyraldehyde, n-Tetradecane, Methanol, Acetone, and n-Pentadecane

As shown in Figure 3, the area of n-pentadecane remained the same before and after 100 injections of water. However, compared with the area before injecting water, the area of methanol (peak 6) decreased by 50%, and the area of acetone (peak 7) decreased by14.4% after 100 injections of water (see Table 6). It demonstrated that water can affect the activity of GS-OxyPLOT, especially for the analysis of those relatively low molecular weight oxygenated compounds, such as methanol and acetone.

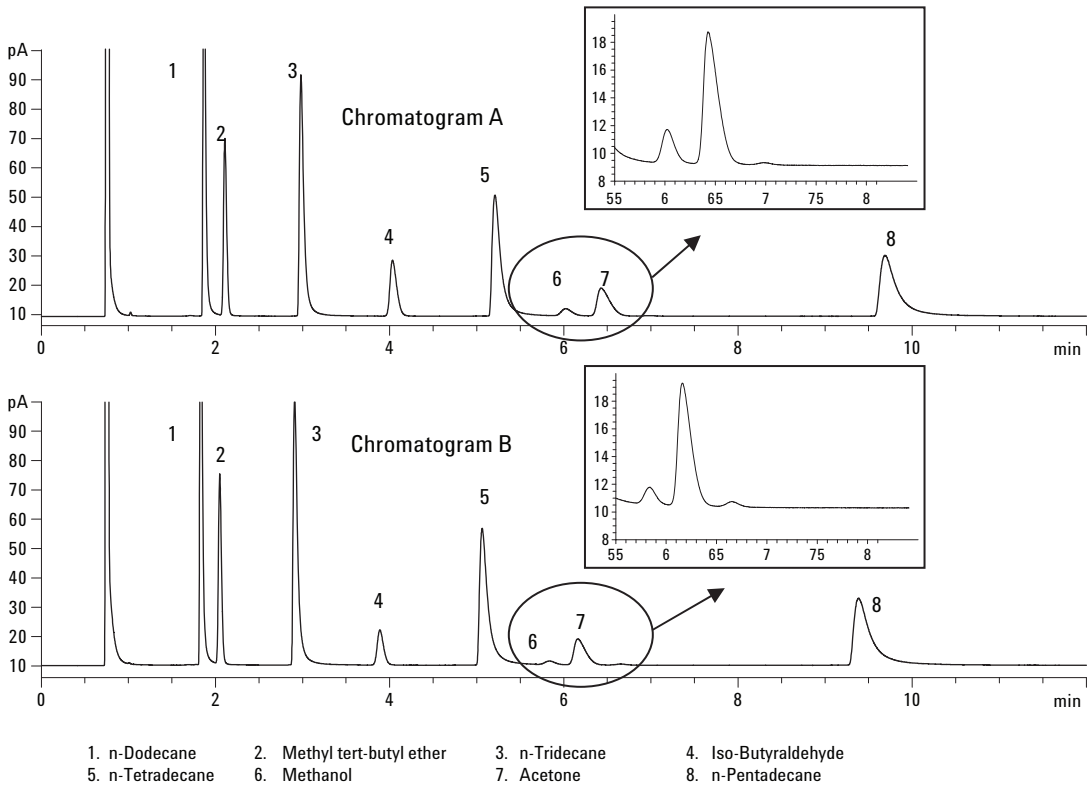

Figure 3. Comparison of test mixture separation before (A) and after (B) 100 injections of water.

As for retention times and column efficiency, they are not strongly influenced. After 100 injections of water, the retention time of C15 changed from 9.689 min to 9.384 min, and the column efficiency of C15 changed from 14,792 to 14,781.

Condition the column at 300 °C for two hours, followed by 12 hours at 250 °C. As shown in Figure 4 and Table 6, it is obvious that GS-OxyPLOT phase can be regenerated by conditioning.

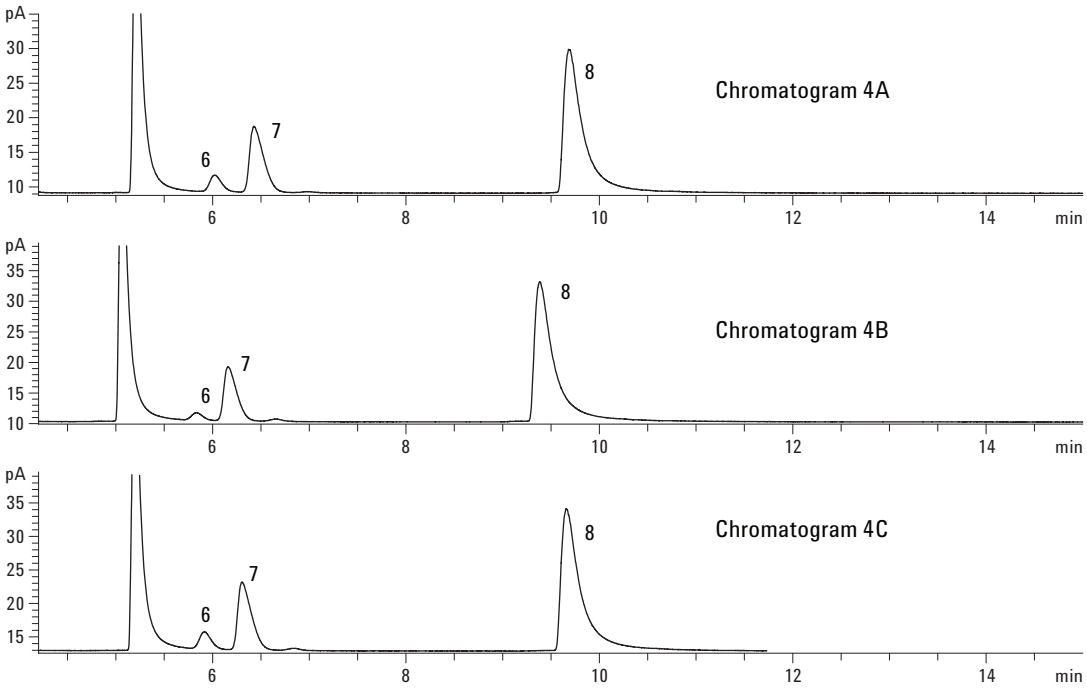

Figure 4. Expanded view shows comparison of test mixture separation on GS-OxyPLOT.
4A. Before injection of water. 4B. After 100 injections of water. 4C. After conditioning the column.

Table 6. Comparison of Test Mixture Separation

	Methanol			Acetone			n-Pentadecane		
	Before injection of water	After 100 injections of water	After conditioning column	Before injection of water	After 100 injections of water	After conditioning column	Before injection of water	After 100 injections of water	After conditioning column
RT (min)	6.022	5.835	5.915	6.429	6.160	6.305	9.689	9.384	9.658
Area	20.23	9.18	20.88	94.53	80.92	98.07	277.79	287.7	287.9
Plates	11887	12920	11616	9532	10357	9573	14792	14781	15100

After conditioning the GS-OxyPLOT column, the peak area and retention time reproducibility were determined. Figure 5 and Table 7 show excellent RT precision, lower than 0.6% over five test mixture runs on this GS-OxyPLOT column. The peak area has a relative standard deviation (RSD%) below 2.5%. It proved that column performance can be restored via conditioning.

Determination of Methanol

The following analysis of methanol followed ASTM D7059 [4]: "Standard Test Method for Determination of Methanol in Crude Oils by Multidimensional Gas Chromatography." Methanol was determined by gas chromatography with FID using internal standard method with GS-OxyPLOT column.

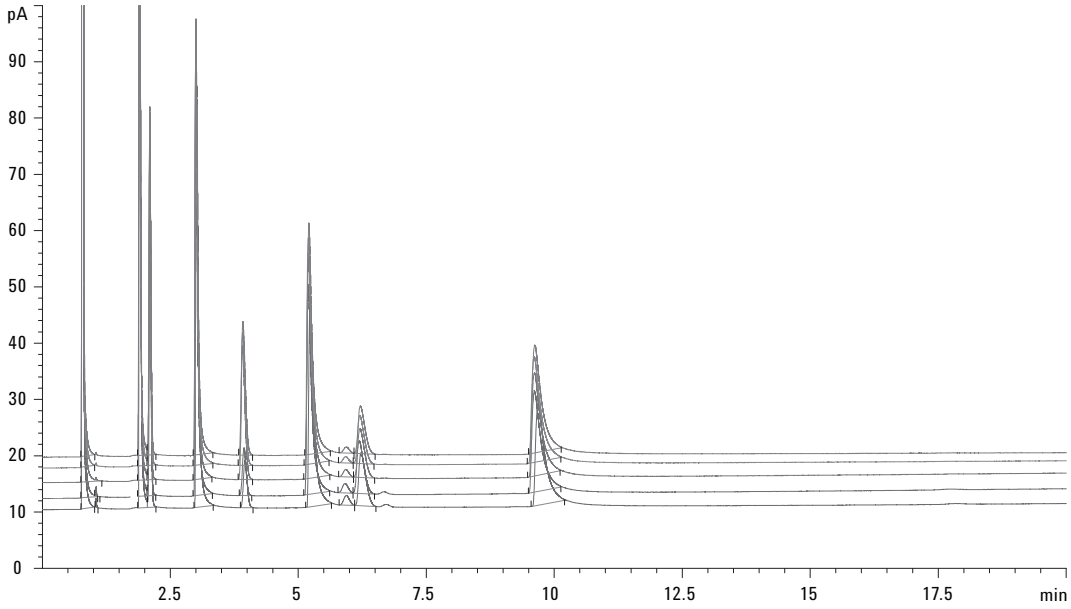

Figure 5. Fifth run overlaid using GS-OxyPLOT (after conditioning column).

Table 7. Peak Area Reproducibility and Retention Time Reproducibility on GS-OxyPLOT (after conditioning column)

Compound (by eluted order)	Dodecane	MTBE	Tridecane	Iso-Butyraldehyde	Tetradecane	MeOH	Acetone	n-C15
Area RSD% (N = 5)	1.18	1.58	1.59	2.49	1.15	2.12	1.98	1.82
RT RSD% (N = 5)	0.18	0.12	0.26	0.55	0.29	0.16	0.19	0.33

Reagents and Materials

Carrier gas, Helium, > 99.95% purity
Methanol, > 99.9% purity
1-propanol, > 99.9% purity, and containing < 500 ppm methanol
Toluene, > 99.9% purity, and containing < 0.5 ppm methanol

A set of calibration standards 5, 25, 125, 250, 500, 1,000 and 1,500 ppm (m/m) of methanol, and each containing 500 ppm (m/m) of 1-propanol internal standard, were prepared in toluene.

The calibration standard solutions should be stored in tightly sealed bottles in a dark place below 5 °C.

Linearity

Under the conditions listed in Table 8, the methanol calibration standards were analyzed. The linearity is shown by plotting the response ratio of methanol and internal standard 1-propanol against their amount ratio (see Figure 6). For methanol, good linearity was gained ranging from 5 to 1,500 ppm. The correlation r^2 value for the calibration curve is higher than 0.999.

Figure 7 and Figure 8 are chromatograms of methanol at a level of 5 ppm and 1500 ppm, respectively. At a relatively high concentration of 1500 ppm, methanol still could get a sharp peak. The limit of quantification (LOQ) was calculated to be 1 ppm using the chromatogram of 5 ppm methanol.

Table 8. System Settings for the Calibration Curve

Column	GS-OxyPLOT, 10 m × 0.53 mm × 10 µm
Carrier gas	Helium, constant flow mode, 50 cm/s at 150 °C
Inlet	Split/splitless at 250 °C 10:1 split ratio
Oven temperature	150 °C (3 min); 20/min to 300 °C (5 min)
Detector	FID at 325 °C
Injection size	1 µL

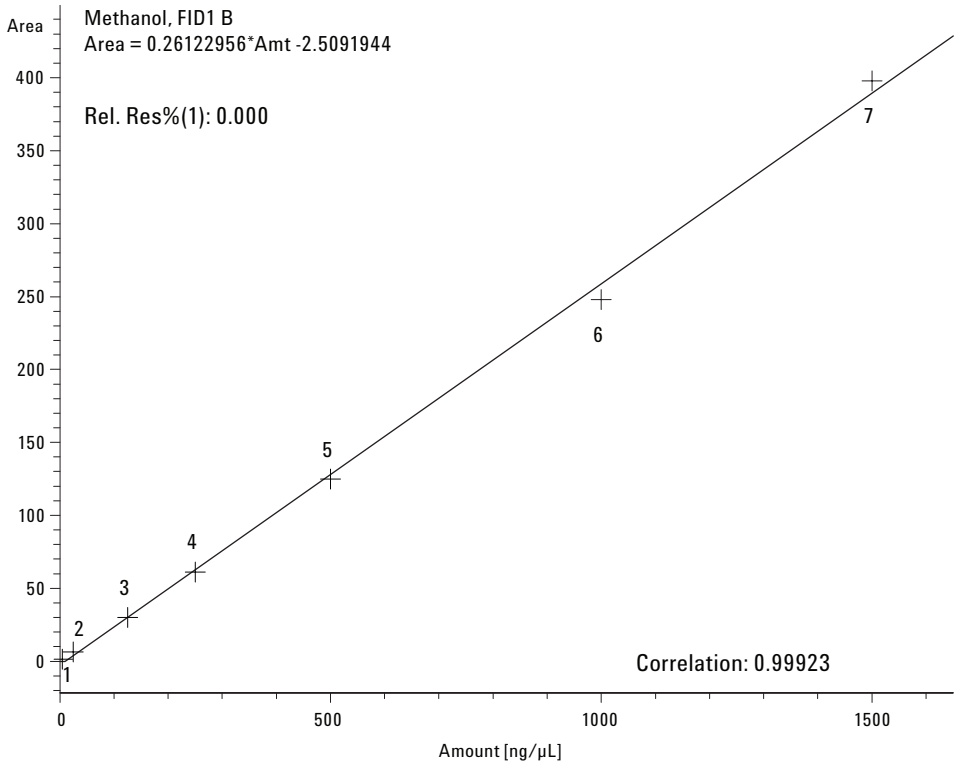

Figure 6. The calibration curve of methanol in toluene.

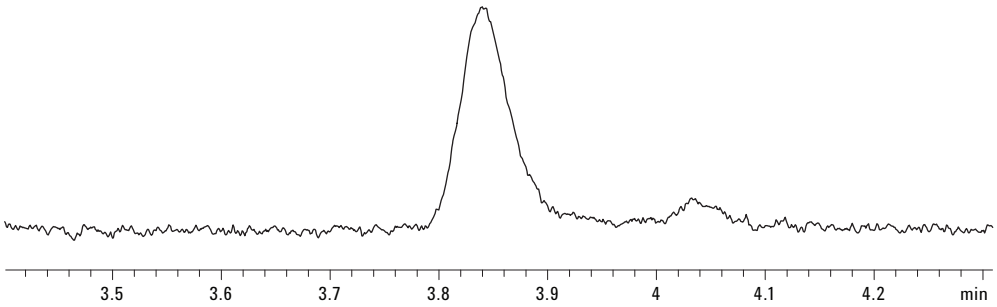

Figure 7. Test mixture of 5 ppm methanol in toluene.

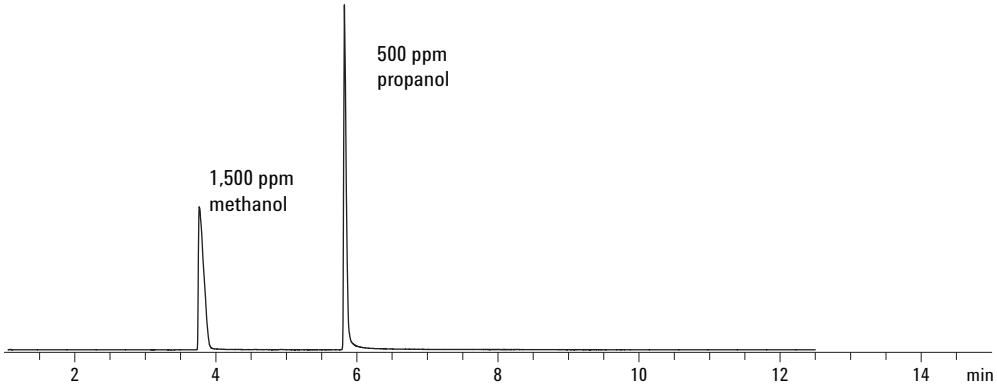

Figure 8. Test mixture of 1,500 ppm methanol in toluene.

Repeatability

The reproducibility of the GS-OxyPLOT is given in Table 9. Those values were obtained by the replicate analysis of different methanol levels (25, 125, and 1,500 ppm) in different days. The injection was done by ALS with RSD no less than 3% either intraday or interday analysis, which was very low for this type of determination.

Life Span

Under the conditions in Table 5, a mixture was analyzed with a GS-OxyPLOT column which went through 1,500 injections of methanol. It shows that the column has a long lifetime. The GS-OxyPLOT column still has good resolution for each compound and high efficiency of 1,482 plates per meter for n-pentadecane (see Figure 9).

Table 9. Relative Standard Deviations Intraday and Interday at Different Levels (25, 125, and 1,500 ppm) of Methanol

Day	25 ppm (average)	RSD (%)	125 ppm (average)	RSD (%)	1,500 ppm (average)	RSD (%)
D 1	25.2	0.46	123.9	0.45	1507.3	0.55
D 2	25.3	1.53	123.2	0.79	1494.4	0.45
D 3	24.4	0.36	125.4	1.71	1523.5	0.35
D 4	25.9	1.06	123.0	0.90	1537.8	0.51
D 5	23.9	0.44	121.1	0.76	1502.4	1.03
Stand. dev.	0.7		1.70		17.4	
Average	24.97		123.6		1513.1	
RSD (%)	2.8		1.37		1.15	

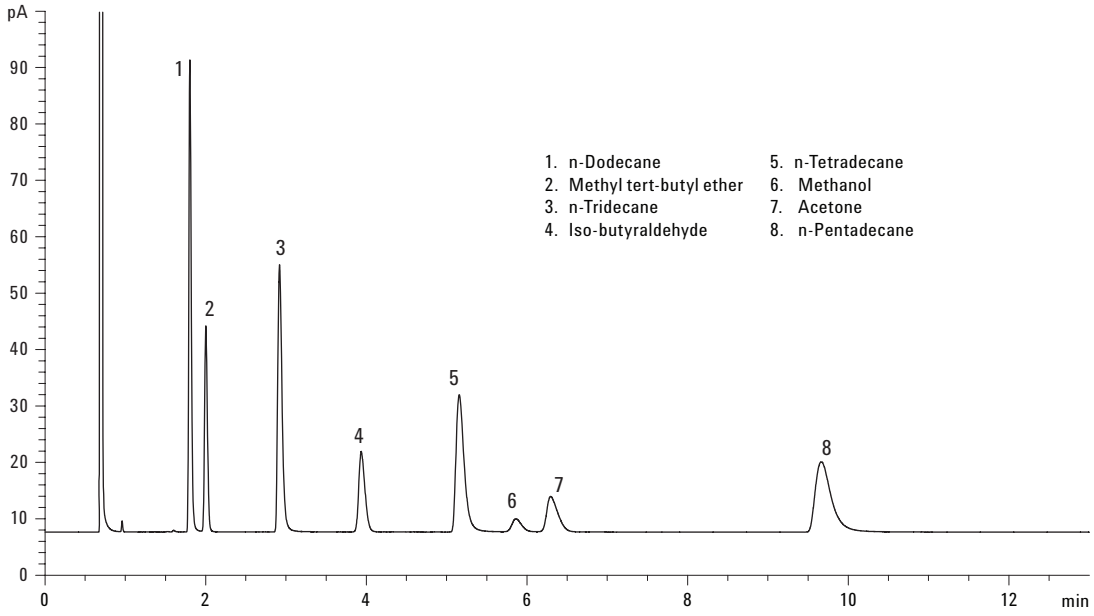

Figure 9. Chromatogram of performance mixture after 1,500 injections.

Conclusions

GS-OxyPLOT provides good retention and selectivity for oxygenated compounds. Normal alkanes up to C24 and primary alcohols up to lauryl alcohol can elute from GS-OxyPLOT within its program temperature maximum limit of 350 °C. Methanol elutes after n-C14 with retention index higher than 1,400; the retention index is quite stable from 150 to 250 °C, allowing methanol to be measured at low levels in a wide range of hydrocarbon streams.

Methanol has to be measured usually at specs as low as 5 ppm. From 5 to 1,500 ppm, it shows good linearity on GS-OxyPLOT. And the column has proven extremely stable with long lifetime.

GS-OxyPLOT can tolerate a little amount of water in samples, and column performance can be restored via conditioning.

GS-OxyPLOT can be used for a single-column system or in multidimensional GC systems. It offers a unique solution for the analysis of oxygenates in the chemical and petrochemical industries.

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Analysis of Permanent Gases and Light Hydrocarbons Using Agilent 7820A GC With 3-Valve System

Application Note

HPI

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Highlights

- Agilent 7820A GC 3-valve system provides a low-cost but powerful platform for analysis of permanent gases and light hydrocarbons.
- Full electronic pneumatics control (EPC) provides an easy-to-use operation for the end user and ensures excellent repeatability for both retention time and peak area.
- This application work can also be used as a reference in the analysis of natural gas, petroleum gas, synthesis gas, purified gas, water gas, blast furnace gas, stack gas, and so on.

Abstract

A new economical solution is provided to test permanent gases and light hydrocarbons. An Agilent 7820A Gas Chromatograph equipped with three valves, a flame ionization detector (FID), and a thermal conductivity detector (TCD), is configured for analysis of permanent gases and light hydrocarbons. The TCD channel with packed columns is used to measure H_2,CO_2,O_2, N_2,CH_4 and CO. A capillary column (Al_2O_3 PLOT: 50 m × 0.53 mm) is used to measure all hydrocarbons (C1~C6) including CH_4.

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Introduction

Analysis of permanent gases and light hydrocarbons has been widely employed in the petrochemical, chemical and energy industries. These permanent gases, such as O_2, N_2, CH_4, CO, and CO_2 are the common target compounds in natural gas, petroleum gas, synthesis gas, purified gas, water gas, blast furnace gas, stack gas, and so on. Understanding the concentrations of these components is important for petrochemical, chemical and energy industrial processes. The 7820A 3-valve system offers an easy-to-use and powerful platform for the analysis of these kinds of samples.

This work illustrates one typical application of the 7820A 3-valve system for the analysis of permanent gases and light hydrocarbons.

Experimental

Three valves were used in this 7820A system: six-port gas sampling, ten-port gas sampling with back-flush to vent, and another six-port column isolation. The valve diagram and columns configuration are shown in Figure 1. Normally, the valve sample loops are connected in series for simultaneous dual-channel injection. Valve control is handled by EZChrom Elite compact software. Chromatographic conditions and valve time events are listed in Tables 1 and 2.

Table 1. Gas Chromatographic Conditions

Sample loop size	0.25 mL
FID channel flow	5 mL/min
FID temp	300 °C
FID channel carrier	N_2
Capillary splitter temp	200 °C
Split ratio	25:1
TCD channel flow	30 mL/min
TCD temp	250 °C
TCD channel carrier	He
Valve box temp	120 °C
Oven program	45 °C (6 min) >180 °C (2.25 min) at 20 °C/min

Table 2. Time Events

Events	**Time (min)**
Valve 1 ON*	0.01
TCD Negative Polarity ON	0.6
TCD Negative Polarity OFF	1.4
Valve 2 ON	1.7
Valve 1 OFF*	2.5
Valve 2 OFF	3.2

*Time events of valve 3 are the same as valve 1.

A fixed gas mix standard, (Jiliang Standard Gas Inc., Shanghai), was used in this application test. The components and concentrations are listed in Table 3.

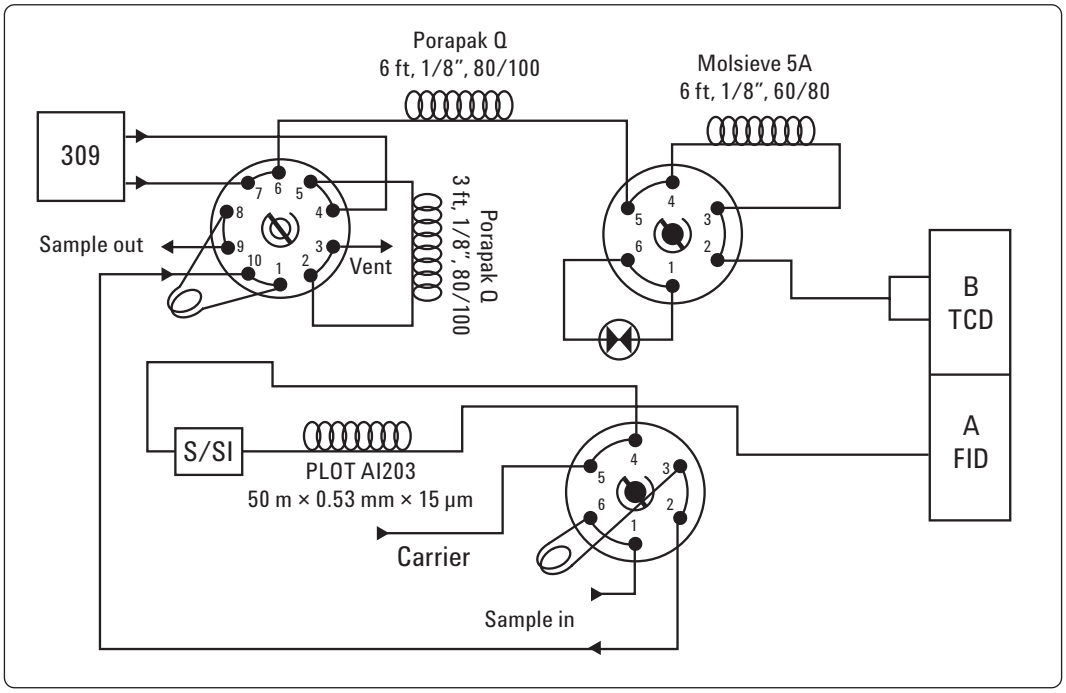

Figure 1. Valve diagram for dual-channel natural gas analysis.

Table 3. Concentrations of the Standard Gases

Components	H_2	O_2	N_2	CO	CO_2	CH_4	C_2H_6	C_3H_8	iC_4	nC_4	iC_5	nC_5	nC_6
Conc. (%)	6.09	3.00	9.97	1.99	3.48	71.92	2.00	0.99	0.11	0.10	0.12	0.12	0.11

Results

Chromatograms

Chromatograms for the FID and TCD channels of standard gas are shown in Figures 2 and 3. Hydrocarbons from C1 to C6 are separated by a PLOT Al_2O_3 column in approximately 15 minutes. For natural gas samples containing hydrocarbons higher than C6, the final temperatures of the oven program can be modified to 220 °C for the elution of hydrocarbons up to C11.

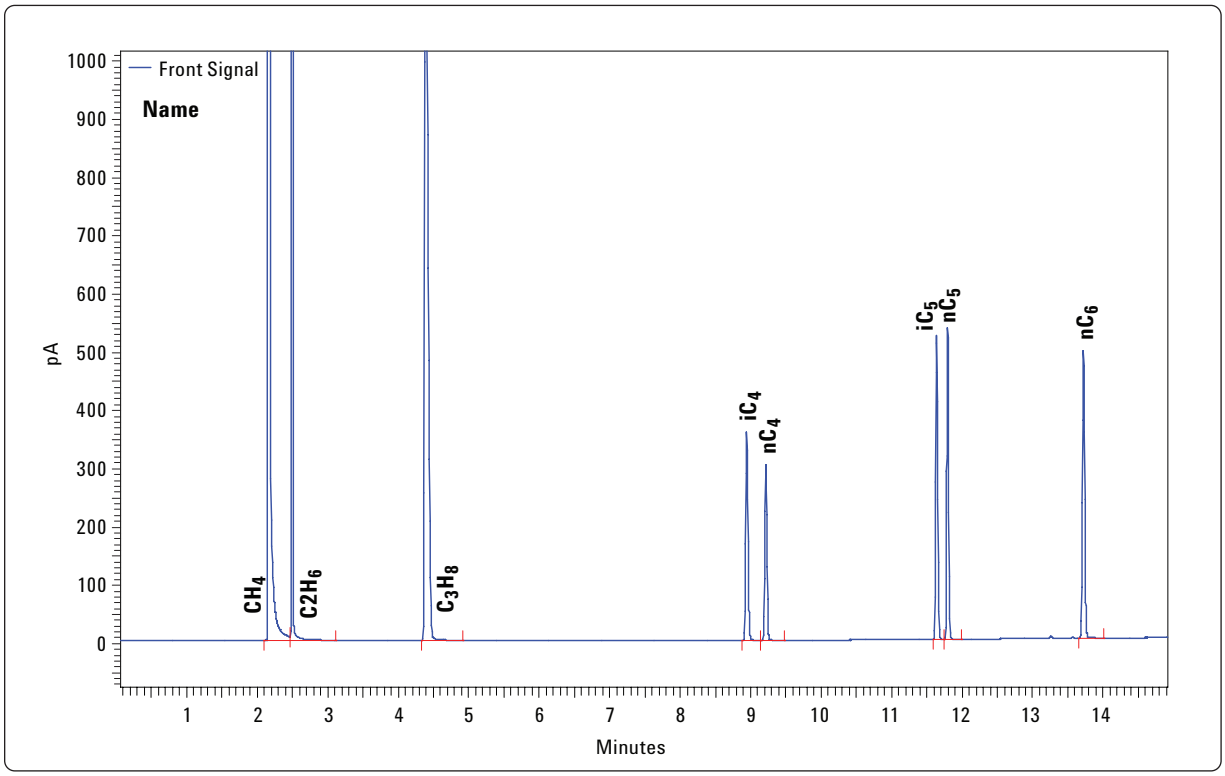

Figure 2. FID Channel chromatogram of CH_4, C_2H_6, C_3H_8, iC_4, nC_4, iC_5, nC_5, and nC_6.

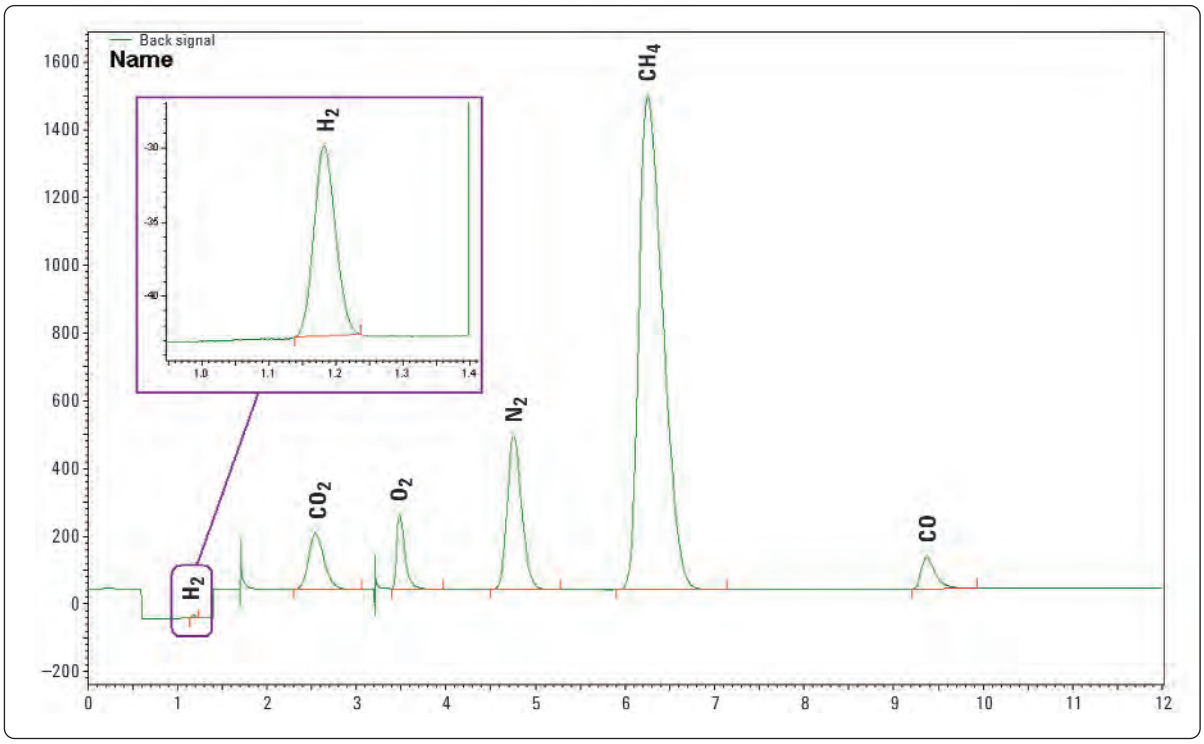

Figure 3. TCD Channel chromatogram of H_2, O_2, CO_2, N_2, CH_4, CO.

Linearity

The mixed standard was dynamically diluted to five different lower-concentration levels for calibration. The linearity results of all the permanent gas components are listed in Table 4.

Table 4. Linearity Results of TCD Channel

%	H_2	CO_2	O_2	N_2	CH_4	CO
Level 1	0.305	0.174	0.150	0.500	3.596	0.100
Level 2	0.609	0.348	0.300	0.997	7.192	0.199
Level 3	1.523	0.870	0.750	2.493	17.98	0.498
Level 4	3.045	1.740	1.500	4.985	35.96	0.995
Level 5	6.090	3.480	3.000	9.970	71.92	1.990
R^2	0.999	0.999	0.998	1.000	0.999	0.999

Repeatability

The relative standard deviations (RSD) for all hydrocarbon components were lower than 0.8% by using split injection on the FID channel. This was due to the full electronic pneumatics control (EPC) from injector to detector on 7820A. Results of the TCD channel also show excellent repeatability (Table 5). Component concentrations were 0.305%, 0.174%, 0.15%, 0.5%, 3.596%, and 0.1%, respectively for H_2, CO_2, O_2, N_2, CH_4, and CO.

Table 5. TCD Channel Repeatability

Runs	H_2	CO_2	O_2	N_2	CH_4	CO
1	10389	753601	137865	2180997	10904896	370250
2	10630	750304	142332	2191591	10947696	378184
3	10498	749748	140281	2156911	10926314	379868
4	10595	745289	139133	2168986	10822886	374996
5	10358	744909	140300	2172639	10826691	371749
RSD%	1.15	0.49	1.18	0.6	0.53	1.09

Low Level Permanent Gases

Another standard gas cylinder (Jiliang Standard Gas Inc., Shanghai) was tested by the 7820A 3-valve system to check low level response and repeatability. Figure 4 shows the chromatogram of the low level permanent gas mix and Figure 5 shows the overlapped chromatograms of five runs. Chromatogram conditions and concentrations of each compound are listed as follows:

Carrier gas:	He	
Sample loop:	1 mL	
Oven:	45 °C (6 min) >180 °C (2.25 min) at 20°C/min	
TCD:	250 °C	
1.	CO_2	200 ppm
2.	O_2	176 ppm
3.	N_2	Balance gas
4.	CH_4	810 ppm
*	Signal of valve switching	

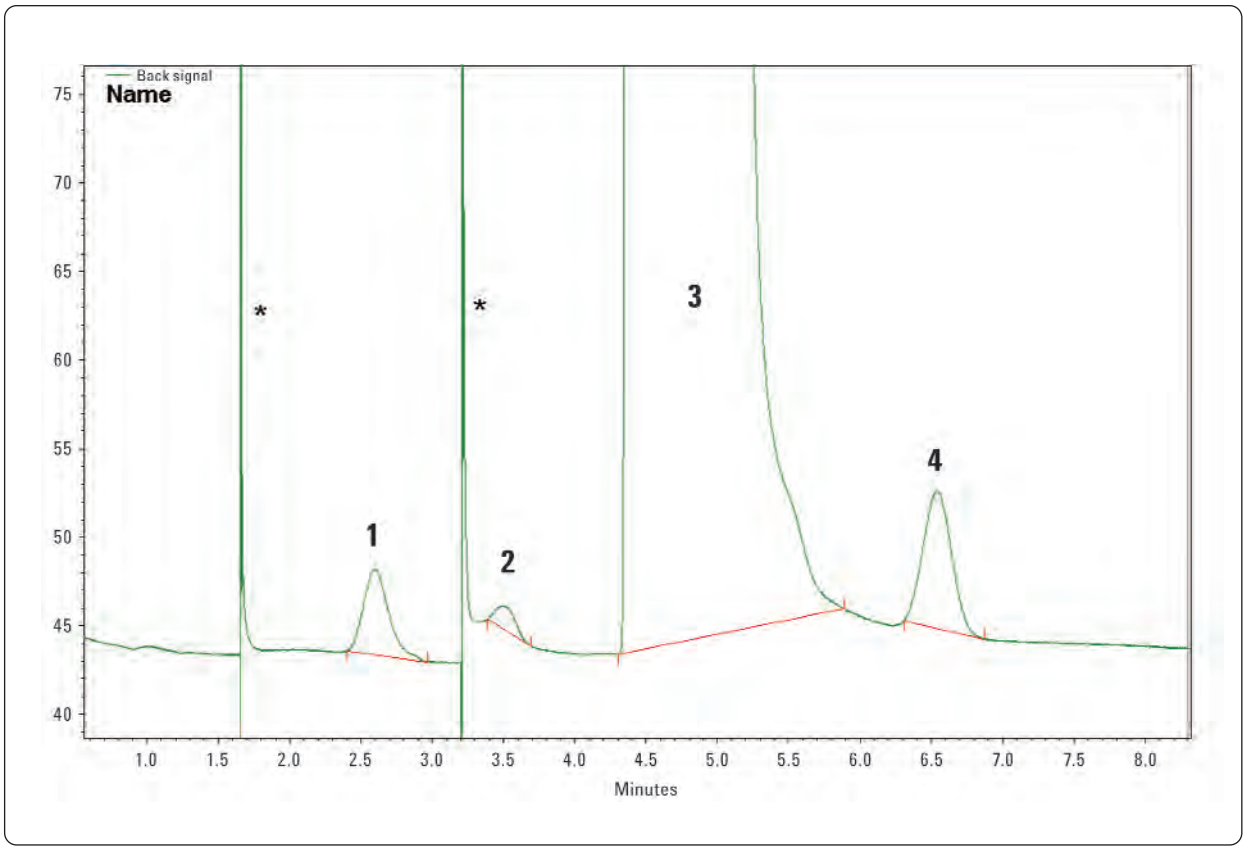

Figure 4. Chromatogram of low level permanent gas standard mix.

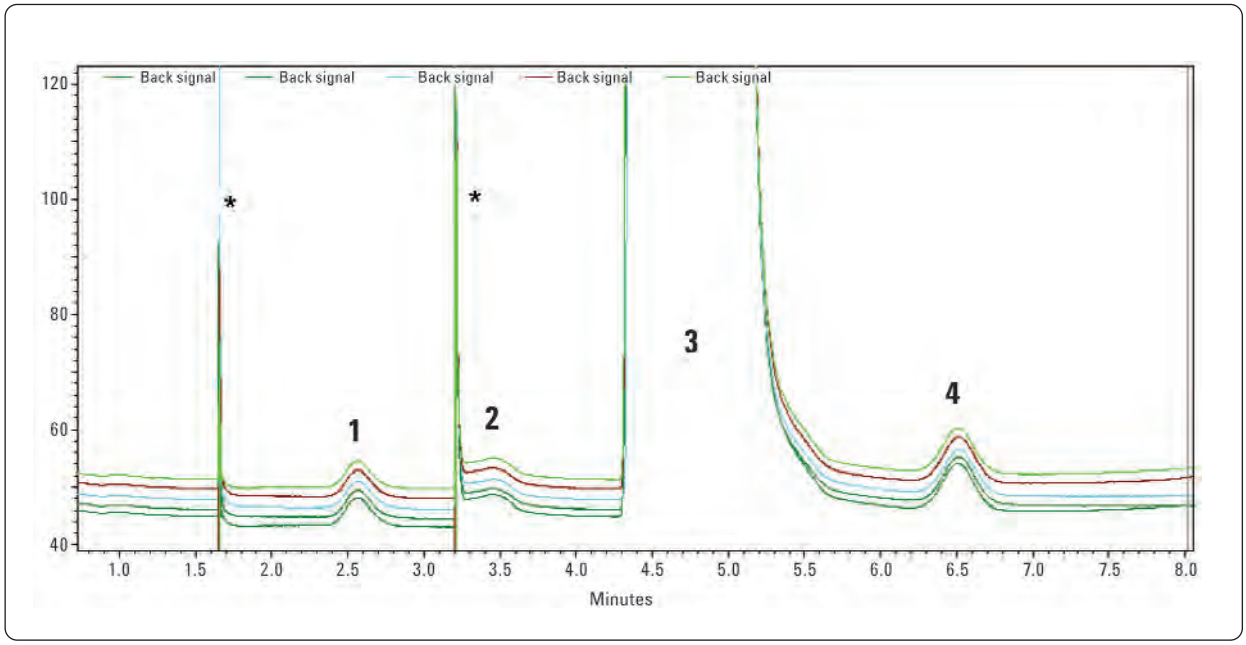

Figure 5. Overlapped chromatograms of five runs.

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Enhanced Sensitivity for Biomarker Characterization in Petroleum Using Triple Quadrupole GC/MS and Backflushing

Application Note

Environmental

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Abstract

A rapid, reliable method for the routine detection and quantification of biomarkers in petroleum was developed using the Agilent 7890A/7000A Series Triple Quadrupole GC/MS with backflushing using a Pressure Controlled Tee configuration. In a single run, diverse biomarkers from several transitions can be detected, confirmed, and quantified at levels as low as 2 ppm, with RSDs well below 5%. This method is suitable for "fingerprinting" of petroleum samples and the deconvolution of oil mixtures in complex, multisource petroleum systems.

Agilent Technologies

Introduction

Petroleum biomarkers are complex molecular fossils derived from once living organisms [1]. These compounds provide unique clues to the identity of source rocks from which petroleum samples are derived. This information includes the biological source organisms which generated the organic matter, the environmental conditions that prevailed in the water column and sediment at the time, the thermal history of both the rock and the oil, and the degree of microbial biodegradation. Biomarkers are used in conjunction with other geochemical parameters to help solve oil exploration, development, and production problems. They provide much more detailed information about petroleum source and history than nonbiomarker analysis (bulk isotopes, elemental analysis, and so forth) alone.

High resolution mass spectrometry (HRMS) is often used to analyze biomarkers in petroleum, due to its ability to provide quantitative data for compounds present in complex mixtures. However, HRMS requires a significant financial investment as well as highly trained operators to assure valid results. Triple Quadrupole GC/MS offers a viable alternative for the rapid, routine analysis of biomarkers in petroleum, providing excellent precision, sensitivity, selectivity, and dynamic range. Implementing GC backflushing in the acquisition method improves data quality robustness, due to the very complex and varied nature of petroleum samples.

Experimental

Standards and Samples

STANFORD-1 is a new external standard for quantitative biomarker analysis. It is a mixture of pure biomarker standards and paraffin-free saturate fractions from Paleozoic, Mesozoic, Cenozoic, biodegraded, terrestrially-influenced, carbonate/evaporate-sourced, and open-marine sourced petroleum samples. It contains known quantities of most, if not all, commonly used biomarkers and two internal standards, BTI-6 and 5-β cholane, which are useful for quantifying hopane and sterane biomarkers across diverse GC/MS systems.

C30 sterane fractions were prepared using standard normal phase liquid chromatography techniques, n-alkane removal, and proprietary molecular sieve and HPLC techniques for the final enrichment of target compounds. Two compounds which coelute with n-propylcholestane (4-methylstigmastane and hopane) were completely removed from the sample to avoid known interference with the *m/z* 414→217 transition.

Instruments

The experiments were performed on an Agilent 7890A gas chromatograph equipped with a split/splitless inlet, an Agilent 7000A Triple Quadrupole GC/MS with Triple-Axis Detector, and an Agilent 7683B automatic liquid sampler (ALS). The split/splitless inlet is fitted with a deactivated, helical double taper injection liner (p/n 5188-5398). Injections were made using a 10-µL syringe (p/n 9301-0713). A variety of configurations was explored to examine possible improvements in analysis time. Ultimately, two configurations were used for the experiments, and the instrument conditions and specific configurations are listed in Table 1.

MS SRM Parameters

The MS/MS parameters used in the analysis of the petroleum samples are shown in Tables 2 and 3 and in the Figure 6 legend. Experience with HRMS metastable transitions was used to select these precursor and product ions, and an extensive study of product ions was not performed.

Table 1. Gas Chromatograph and Mass Spectrometer Conditions

GC Run Conditions	60 m Configuration	40 m Configuration
Column	Two 30 m x 0.25 mm x 0.25 µm DB-1MS Ultra Inert columns (p/n123-0132UI)	Two 20 m x 0.18 mm x 0.18 µm DB-1MS Ultra Inert columns (p/n 121-0122UI)
Inlet temperature	325 °C	325 °C
Inlet pressure	19.197 psi	17.13 psi
Carrier gas	Helium, constant flow mode	Hydrogen, constant flow mode
Flow rate	Column 1: 1.15 mL/min; Column 2: 1.20 mL/min	Column 1: 0.95 mL/min; Column 2: 1.0 mL/min
Injection mode	Pulsed splitless (50 psi until 1 min)	Pulsed splitless (50 psi until 0.75 min)
Oven program	50 °C (1 min hold), then 40 °C/min to 140 °C for 0 min, then 2 °C/min to 313.5 °C for 0 min	40 °C (0.6 min hold), then 40 °C/min to 140 °C for 0.5 min, then 3.4 °C/min to 300 °C for 1 min
Column velocity	Column 1: 27.636; Column 2: 39.923 cm/s	Column 1: 45.449; Column 2: 65.944 cm/s
Injection volume	1 µL	1 µL
Transfer line temperature	325 °C	325 °C
GC Post-Run Conditions		
Backflush device	Purged Ultimate Union (p/n G3186-60580) controlled by a Electronic Pneumatic Control (EPC) (p/n G3470A)	Purged Ultimate Union (p/n G3186-60580) controlled by a Electronic Pneumatic Control (EPC) (p/n G3471A)
Backflush conditions	–4 mL/min at 325 °C for 7 min	–4 mL/min at 325 °C for 5 min
MS Conditions		
Tune	Autotune	Autotune
Delta EMV	70 eV	70 eV
Acquisition parameters	EI; selected reaction monitoring	EI; selected reaction monitoring
Solvent delay	5 min	3 min
MS temperatures	Source 250 °C; Quadrupoles 150 °C	Source 250°C; Quadrupoles 150 °C

Table 2. Analysis Parameters for Precision Experiments*

Compound	Transition (*m/z*)
Stigmastane	400.4 → 217.2
Homohopane (22S)	426.4 → 191.2
n-propylcholestane	414.4 → 217.2
27-nordiacholestane (13β,17α(H),20S)	358.4 → 217.2
27-norcholestane	358.4 → 217.2
4-methylstigmastane	414.4 → 231.2
Dinosterane	414.4 → 98.1
Hopane	412.4 → 369.4
5β-Cholane (ISTD)	330.3 → 217.2

*The method contained 17 transitions in total. The dwell time and collision energy used for each transition was 50 msec and 5 eV, respectively, using the 60 m configuration.

Results and Discussion

Backflushing with a Pressure Controlled Tee Configuration

Backflushing was used to remove higher boiling substances from the column prior to each subsequent run. Using this technique, late eluting peaks are flushed out of the inlet split flow vent instead of driving them through the entire length of column and into the mass spectrometer. Backflushing reduces accumulated chemical noise due to carryover (which can be observed even in SRM mode as a rising baseline) and the cycle time of the analysis, thus increasing throughput. System uptime is also increased, due to reduced maintenance of the columns and MS detector. The suite of Agilent Capillary

Flow Technology modules comprises a proprietary solution that enables easy and rapid backflushing with minimal dead volumes for maintaining chromatographic resolution. It also uses ferrules and fittings that eliminate leaks. All Capillary Flow Technology modules require the use of an Auxiliary Electronic Pneumatic Control (EPC) module or a Pneumatic Control Module (PCM) to provide a precisely-controlled second source of gas that directs the column flow to the appropriate column or detector. During analysis, the EPC module supplies a pressure slightly above the pressure of the carrier gas through the column. When backflushing, the inlet pressure is dropped and the EPC module pressure is increased, forcing the flow to reverse through the column and out the split vent.

A quick and simple approach to backflushing is to use a Capillary Flow Technology device in the middle of the analytical column [2–4]. As an example employed here, instead of using a 40-m column, two 20-m columns are used and connected by an ultralow dead volume Purged Ultimate Union in a Pressure Controlled Tee (PCT) configuration (Figure 1). The EPC module adds just enough makeup gas to match that from the first column, so there is very little flow addition and subsequent decrease in sensitivity due to suboptimal carrier gas flows into the mass spectrometer. As a general rule, the flow for column 2 is set to be 0.02 to 0.05 mL/min greater than that for column 1. Backflushing in this configuration is accomplished simply by reducing the flow or pressure in the first column and increasing it in the second column.

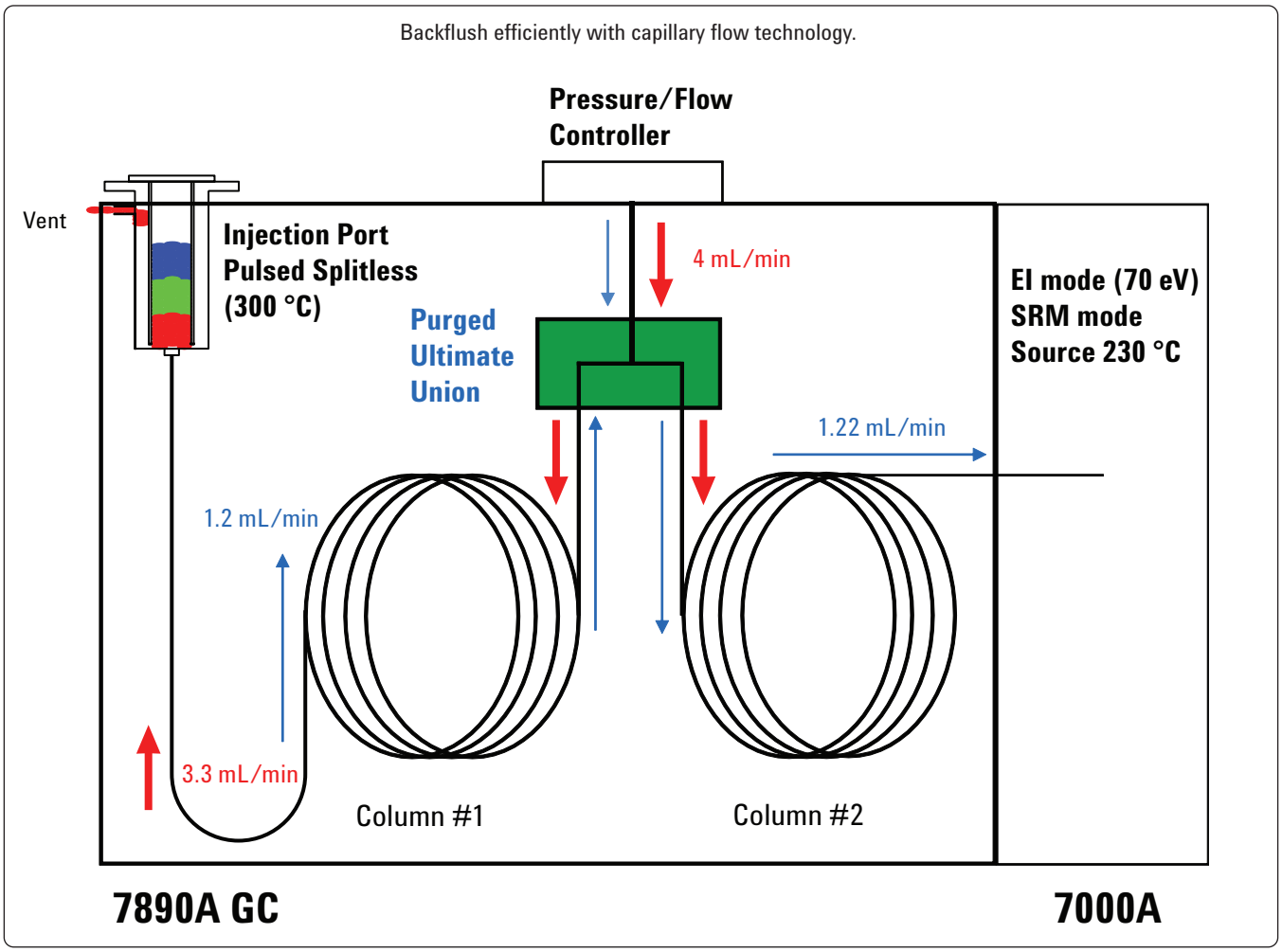

Figure 1. Schematic of the Pressure Controlled Tee GC/MS configuration. The narrower (blue) lines indicate the forward flow during analysis and the thicker (red) lines indicate the backflushing post-run state.

Figure 2 illustrates the advantages of backflushing with the PCT configuration. Typical hydrocarbon GC/MS analysis requires long cycle times due to long hold times at high oven temperatures to avoid contaminating subsequent analyses with carryover of high-boiling components (top chromatogram). Using backflush, targeted volatile components, in this case those eluting within 25 minutes, can be analyzed with significantly shorter cycle times, eliminating the need for column baking and extended GC run times (bottom chromatogram). High boiling hydrocarbons are not retained and column degradation by "permanently" absorbed components and high temperature hold times is decreased. In the example shown, cycle times are reduced from over 100 minutes to less than 30 minutes, and a blank injection after backflushing reveals no high-boiling components and only the baseline rise associated with column bleed.

Faster Analysis of Biomarkers

Run times can be accelerated 30 minutes per cycle without loss in chromatographic resolution or substantial loss in signal by switching from a 60-m (0.25-mm id) column with helium carrier gas to a 40-m (0.18-mm id) column with hydrogen carrier gas (Figure 3). The speed of the 7000A Triple Quadrupole mass spectrometer in SRM mode required only a change in dwell time from 50 to 20 msec to record the required 17 transitions with the same number of scans over the peaks. Because the 7000A Triple Quadrupole MS allows dwell times as short as 1 msec, even faster analysis is possible. An experimental comparison with an uninterrupted 60-m column (results not shown) demonstrated that the insertion of the PCT configuration results in no degradation in chromatography due to the low dead-volume of the Purged Ultimate Union.

Backflush for rapid and robust analyses.

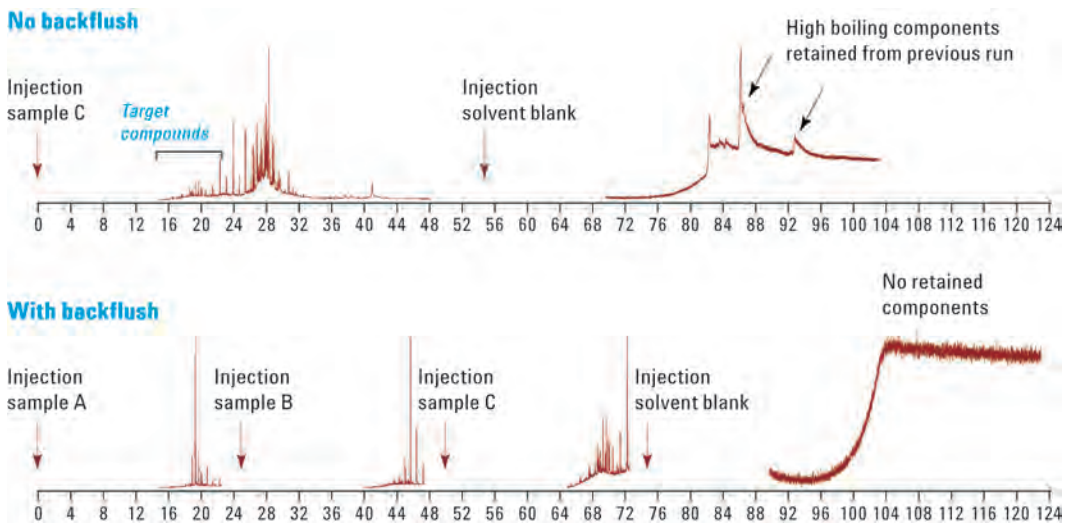

Figure 2. Petroleum samples, including one from Williston Basin source rocks (Sample C) which contains many late eluting, high molecular weight hydrocarbons, were analyzed without (top) and with (bottom) backflushing (40 m configuration). The target compounds comprise a subset of the total number of possible compounds in any injected sample and are indicated by brackets in the top chromatogram. As in a typical analysis, a sequence of samples was analyzed from three sources using the backflushing method in the bottom trace, followed by a solvent blank injection which demonstrated the lack of retained components.

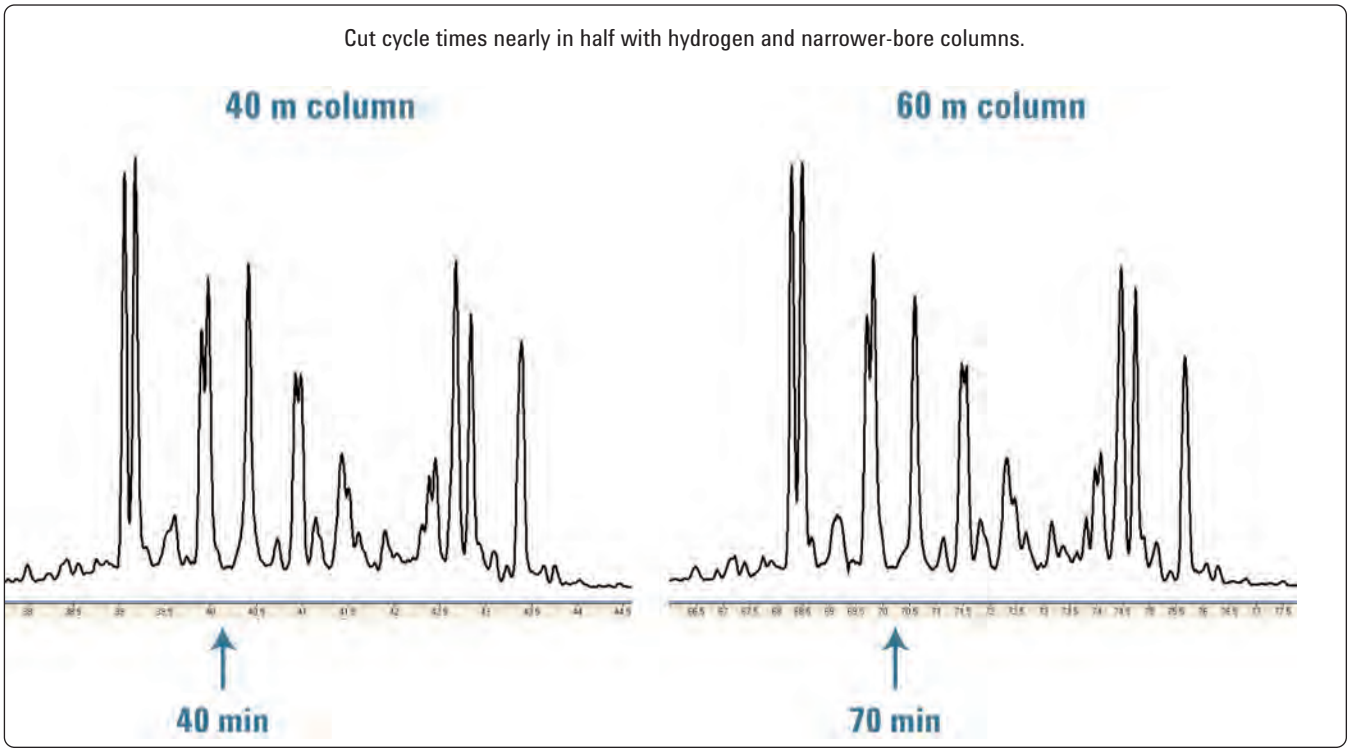

Figure 3. C28 steranes were analyzed using m/z transition 386→217 on either a 60 meter, 0.25 µm column and helium carrier gas, or a 40 meter, 0.18 µm column with hydrogen carrier gas. Employing hydrogen and the smaller bore column reduces analytical time significantly without loss in compound resolution.

Sensitivity, Selectivity and Precision

Routine biomarker analysis in petroleum samples requires precise determination of the abundance of a large number of individual compounds which can vary over a large range of concentrations in these complex mixtures. This precision allows the distinction of differences between petroleum samples with subtly different source or post-generation history. Results for ten sequential runs of the STANFORD-1 standard demonstrate that calculated concentrations of eight different compounds using several different transitions with widely varying concentrations is quite precise (Table 2, Figure 4a).

Most relative standard deviations (RSDs) were well below 5%. The only compound that gave an RSD higher than 5% (dinosterane) was present at a very low concentration (~2 ppm) and required manual integration for quantification. In addition, the calculated concentrations of the compounds were within a few percent of the expected concentration across all ten runs, except for the manually integrated dinosterane (Figure 4b). This precision demonstrates the ability of the Triple Quadrupole GC/MS system to distinguish subtle variations in petroleum composition for traditional biomarker studies, reservoir partitioning studies, and three-dimensional basin modeling.

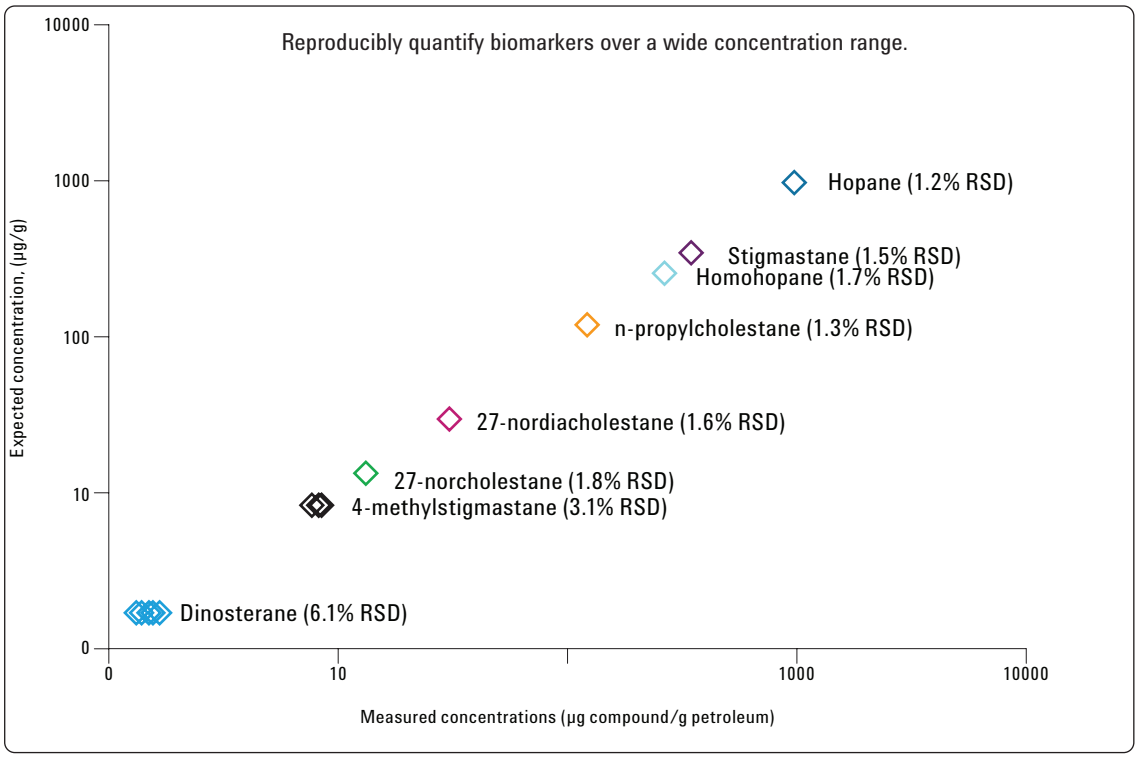

Figure 4a. Precision experiment results for eight biomarkers of widely varying concentrations contained within the STANFORD-1 standard. Ten sequential analyses were performed over a 15 hour period using the 60-m column PCT configuration. See Table 3 for transitions.

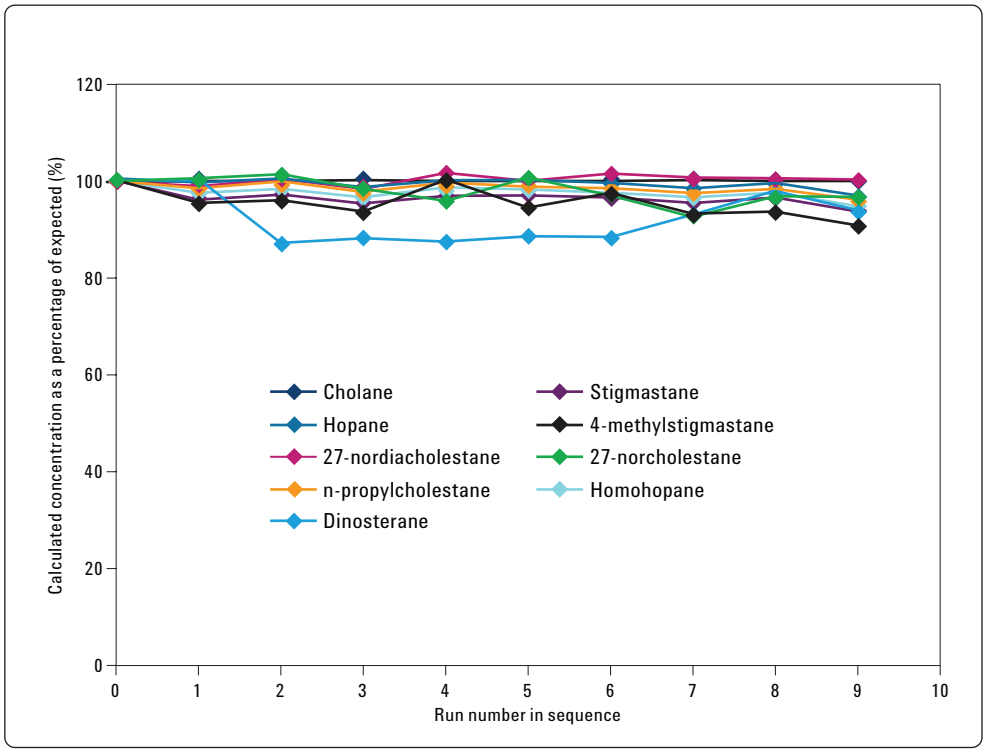

Figure 4b. The data from the analysis described in Figure 4a were plotted as calculated concentration of each biomarker versus the expected concentration over 10 analyses.

Deconvolving Oil Mixtures

A sophisticated understanding of petroleum systems requires the recognition and deconvolution of oil samples derived from more than one source rock. This problem is common where stacked source rocks exist in sedimentary basins (Figure 5). For this work a series of laboratory mixtures consisting of a marine petroleum endmember and a lacustrine endmember were analyzed for stigmastane, a ubiquitous component present in petroleum from both sources, and n-propylcholestane, a compound unique to oil from marine source rock.

As the ubiquitous component must be measured on a different SRM transition and is an order of magnitude more abundant in the marine oil, transition ratio stability and a large instrumental dynamic range are necessary to accurately identify small marine petroleum inputs in lacustrine source rock samples. The data demonstrate that mixtures as low as 0.2% (v/v) in the minor marine component can be accurately determined (Figure 6).

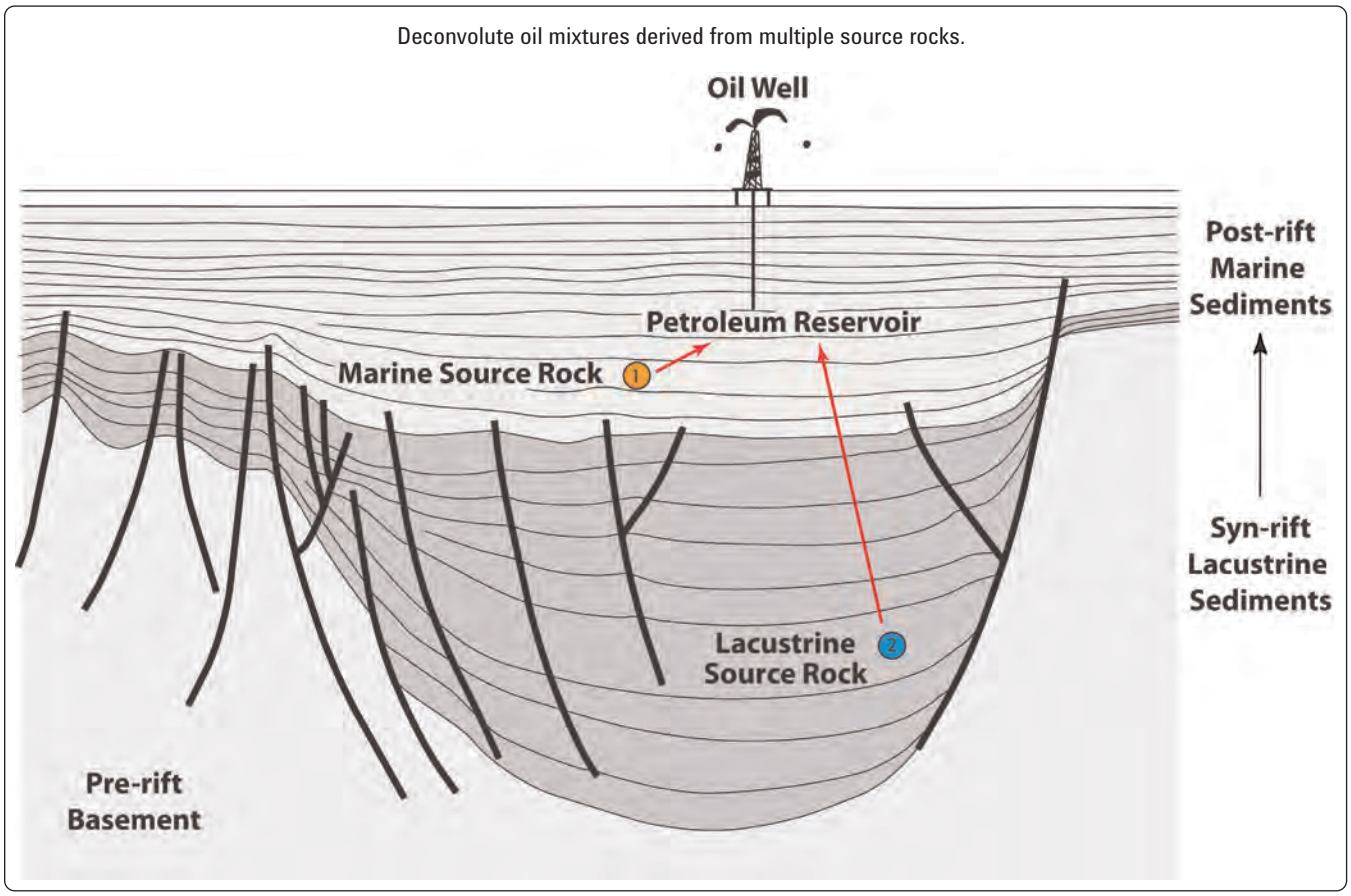

Figure 5. Diagram of an oil deposit containing source rocks from both marine (1) and lacustrine (2) sources.

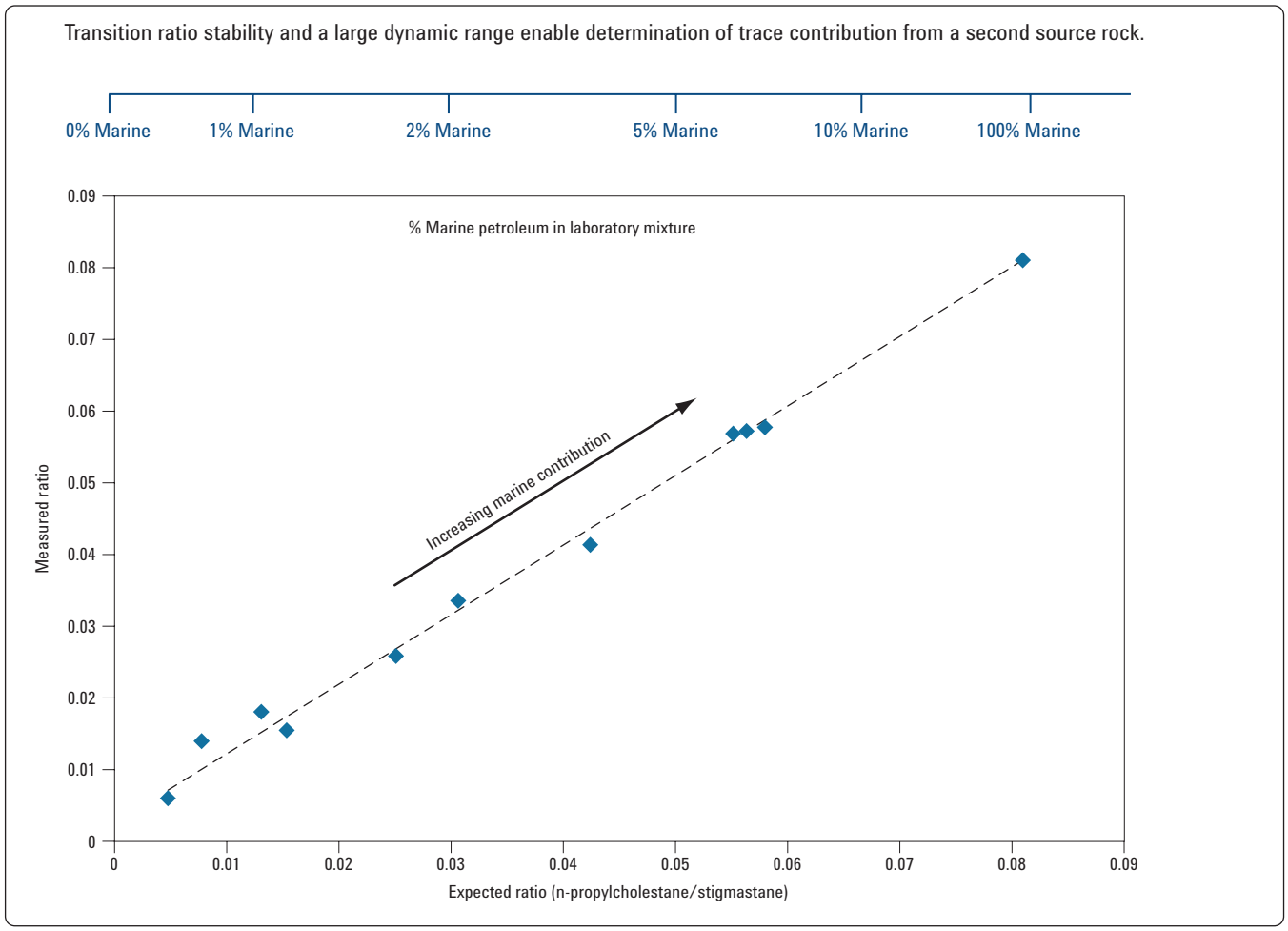

Figure 6. A series of laboratory mixtures consisting of various percentages of a marine petroleum sample in a lacustrine sample were analyzed for stigmastane, a ubiquitous component present in petroleum from both sources, and n-propylcholestane, a compound unique to oil from lacustrine source rock. The measured ratio of the two compounds was then plotted versus the expected ratio. Transitions monitored were: n-propylcholestane, m/z 414.4→217.2; stigmastane, m/z 400.4→217.2.

Conclusions

The Agilent 7000A Triple Quadrupole MS with 7890 GC using backflushing is a viable approach to the routine analysis of petroleum biomarkers, providing increased sensitivity, better selectivity and the potential to greatly reduce analysis time versus traditional GC/MS analysis. Column backflush provides higher sample throughput with lower carryover and source maintenance, and the use of hydrogen carrier gas and narrower bore columns reduces run times nearly two-fold at no significant loss in chromatographic resolution. The SRM speed, linearity, dynamic range and transition ratio stability of the 7000A Triple Quadrupole mass spectrometer enable quantitative characterization for the fingerprinting of petroleum samples and the deconvolution of complex petroleum mixtures.

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Technical Overviews

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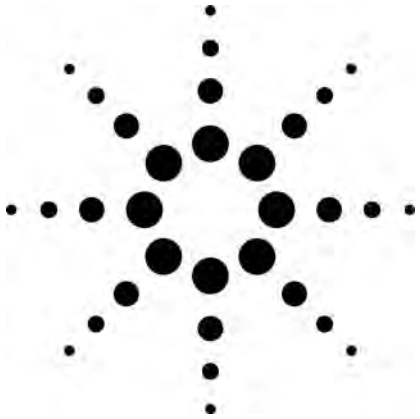
GS-OxyPLOT: A PLOT Column for the GC Analysis of Oxygenated Hydrocarbons

Technical Overview



Allen Vickers

Introduction

GS-OxyPLOT is a porous layer open tubular (PLOT) column. The stationary phase is a proprietary, salt deactivated adsorbent with a high chromatographic selectivity for low molecular weight oxygenated hydrocarbons. It is designed for and ideally suited for application in the ASTM methods listed in Table 1. It is an appropriate replacement for Varian's CP-LowOx column, usually with little to no changes in analytical parameters. This column is particularly useful for the trace analysis of oxygenates such as those listed in Table 2. Other oxygenated hydrocarbons are also suitable for analysis with this column subject to limitations given below.

The column can be used as a single, primary analytical separation column for oxygenated compounds. In complex sample matrices that have high molecular weight species (ca. 300 mol. wt. and higher) and/or species with insufficiently high vapor pressure to migrate through the GS-OxyPLOT, this column can be used in multidimensional GC systems with other columns that have vastly different polarity and lower selectivity toward oxygenated hydrocarbons. For example, a nonpolar DB-1 column can be used as an injection precolumn to retain low volatility solutes, allowing the less retained, polar oxygenated solutes to move into the GS-OxyPLOT. Since the stationary phase of GS-OxyPLOT is an oxygenate adsorbent phase, the oxygenates that enter the column are trapped. As the GC oven temperature is increased, the oxygenates will begin to migrate and are separated in the column prior to detection.

When first installed, the GS-OxyPLOT should be conditioned at 300 °C for at least 3 hours. Experience has shown that this column has an infinite shelf life, but when the column has not been in use for extended periods of time, longer conditioning times of 8 hours or more may be required to obtain retention time stability. The column can be stored with septa placed over the ends of the column, returned to the original column box, and stored at normal ambient temperatures for future use.

GS-OxyPLOT has a minimum temperature limit of 0 °C, an isothermal maximum temperature limit of 300 °C, and an oven program maximum temperature of 350 °C. Because the stationary phase is a strong adsorbent for polar compounds, especially water, it is recommended that when the column is installed in a GC, but idle, that the GC oven be set to an isothermal temperature of 220 °C with normal carrier gas flow, so that the instrument can be brought back into operation quickly when samples are ready to be analyzed. Otherwise, if the column is left at low oven temperatures, it may require reconditioning at 300 °C for several hours to obtain stable retention times.

Saturated hydrocarbon solutes have virtually no interaction with the GS-OxyPLOT and elute from the column so long as the column temperature is hot enough to induce a high enough vapor pressure for the solute to move in the carrier gas. Normal alkanes up to C_{18} will elute from GS-OxyPLOT within the program temperature maximum limit of the column. Because of the highly polar character of the GS-OxyPLOT phase, as would be

expected for oxygenate-selective PLOT column, the column has a relatively low sample load capacity for these nonpolar solutes. The low sample loading capacity is manifested chromatographically as a tailing peaking, indicative of phase overload in GS-OxyPLOT columns. Unsaturated hydrocarbons and aromatic hydrocarbons have relatively high retention. Injection of these organic compound classes should be limited to organic compounds with 11 carbons or less to prevent the column from fouling. As with the normal alkanes, the alkyl benzenes will show phase overloading at relatively low concentrations.

While GS-OxyPLOT is an ideal analytical solution for low molecular weight, oxygenated hydrocarbons, like all other similar oxygenate-selective PLOT columns,it is not recommended for higher molecular weight alkenals (e.g., 1-hexenal and 1-ocetenal). The combined interaction of the unsaturated and carbonyl functional groups can instigate tailing due to strong interactions and in some cases reaction between the phase and solutes.

Table 1. ASTM Standardized Methods for Which GS-OxyPLOT Is Specifically Designed

ASTM Method D7059	Determination of Methanol in Crude Oils by Gas Chromatography with Flame Ionization Detection
Proposed ASTM Method	Determination of C_1 to C_5 Oxygenates at Trace Levels in High Ethanol Content Gasoline Streams by Multidimensional Chromatography with Flame Ionization Detection*
Proposed ASTM Method	Determination of Oxygenates in Ethene, Propene, and C_4 and C_5 Hydrocarbon Matrices by Gas Chromatography and Flame Ionization Detection*

*These are "proposed methods" (i.e., do not have method designation numbers) that are destined for approval by ASTM Committee D2. These methods have already been accepted by, and are being implemented in, petrochemical refineries around the world.

Table 2. Examples of Oxygenated Compounds Suitable for GC Analysis Using the GS-OxyPLOT Column

1. Dimethyl Ether	13. Acetone
2. Diethyl Ether	14. Isovaleraldehyde
3. Acetaldehyde	15. Valeraldehyde
4. Ethyl t-Butyl Ether	16. Methyl Ethyl Ketone
5. Methyl t-Butyl Ether	17. Ethanol
6. Diisopropyl Ether	18. 1-Propanol
7. Propionaldehyde	19. Isopropyl Alcohol
8. tert-Amyl Methyl Ether	20. Allyl Alcohol
9. Propyl Ether	21. Isobutyl Alcohol
10. Isobutraldehyde	22. tert-Butyl Alcohol
11. Butylaldehyde	23. sec-Butyl Alcohol
12. Methanol	24. n-Butyl Alcohol
	25. 2-Methyl-2-Pentanol

Ordering Information for the GS-OxyPLOT Column

ID (mm)	Length (m)	Film Thickness (µm)	Temperature Limit (°C)	Cage Size	Part Number
0.53	10	10	350	7″	115-4912
0.53	10	10	350	5″	115-4912E

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5989-6447EN

Agilent Technologies

Agilent 355 Sulfur Chemiluminescence Detector (355 SCD): Odorants and Other Sulfur Compounds in Liquefied Petroleum and Natural Gases

Technical Overview

Introduction

This technical overview briefly describes the analysis of liquefied petroleum gases as fully defined in ASTM D 5504-95. The method provides for the determination of individual volatile sulfur containing compounds, as well as the determination of total sulfur content in gaseous fuels, including natural gas.

Gas chromatography with sulfur chemiluminescence detection provides a rapid means to identify and quantify various sulfur compounds that may be present in petroleum feeds and products, such as liquefied petroleum gases (LPGs) and natural gas liquids (NGLs). These samples can contain many different amounts and types of sulfur compounds. Many sulfur compounds are corrosive to equipment, inhibit or destroy catalysts employed in downstream processing, and impart other undesirable properties to products. However, odorous sulfur compounds such as ethyl mercaptan, tetrahydrothiophene, and occasionally thiophane are intentionally added to propane as warning agents for detecting LPG leaks. The ability to speciate sulfur compounds in these liquids is useful for quality assurance of odorant addition and for better control of the sulfur compounds in finished products. The following chromatogram illustrates the ability of the Agilent 355 Sulfur Chemiluminescence Detector (SCD) to speciate sulfur compounds in an NGL sample.

This particular NGL sample contained approximately 100 ppm wt total sulfur. The chromatographic conditions for the illustrated analysis were as follows: Agilent 5890 Series II gas chromatograph; Agilent 355 SCD operated according to standard conditions; and 30 m, 0.32 mm id, 4 µm methyl silicone WCOT fused silica column. The temperature program was: –10° C for three minutes to the final required temperature at a rate of 10° C per minute.

Evolving column technology allows for the analysis of liquefied petroleum gases or natural gas liquids with separation of H_2S and COS at ambient temperatures using capillary columns such as the Chrompack CP Sil 5 CB (0.32 mm), Chrompack CP SilicaPLOT (30 m 0.32 mm id), or the Astec Gaspro (15 m 0.32 mm id).

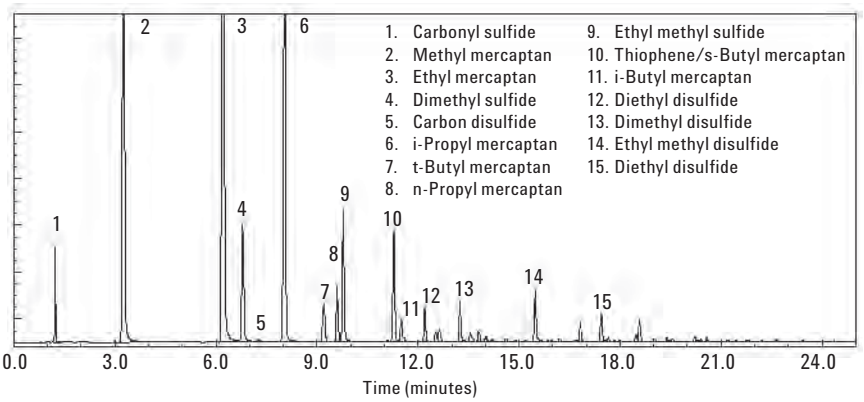

Figure 1. Sulfur compounds in natural gas liquids.

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