

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

Application Note
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Author

Zhenghua Ji
Agilent Technologies
2850 Centerville Road
Wilmington, DE 19808

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Abstract

An Agilent 6890 series gas chromatograph (GC) equipped with a TCD (thermal conductivity detector) was used with an 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 Al₂O₃

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, CO₂, 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 C₇ 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



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achieved on these two kinds of PLOT columns. Additionally, water, CO₂, and odorants deactivate Al₂O₃ 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 Al₂O₃ PLOT and molesieve PLOT columns when separating features of the Al₂O₃ PLOT and molesieve PLOT columns when separating alkanes and fixed gases. The PLOT-Q coating overcomes the reproducibility problem caused by polar compounds deactivating Al₂O₃ and molesieve absorbent coatings in natural gas samples.

Additionally, PLOT-Q columns can separate CO₂, 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 C₇ 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 method 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**.

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 loop |
| Split flow | 150 ml/min |
| Valve | Valco 6-port valve, 0.25 cc sampling loop |
| Detector | TCD |
| Reference flow | Helium, 30 ml/min |
| Auxiliary gas flow | Helium, 3 ml/min |

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 num-

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 |

ber 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.

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 C₁₄ as well as some polar compounds. Their upper isothermal and programming temperature limits are 270°C and 290°C, respectively.

The separation of the constituents 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 dioxide 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)

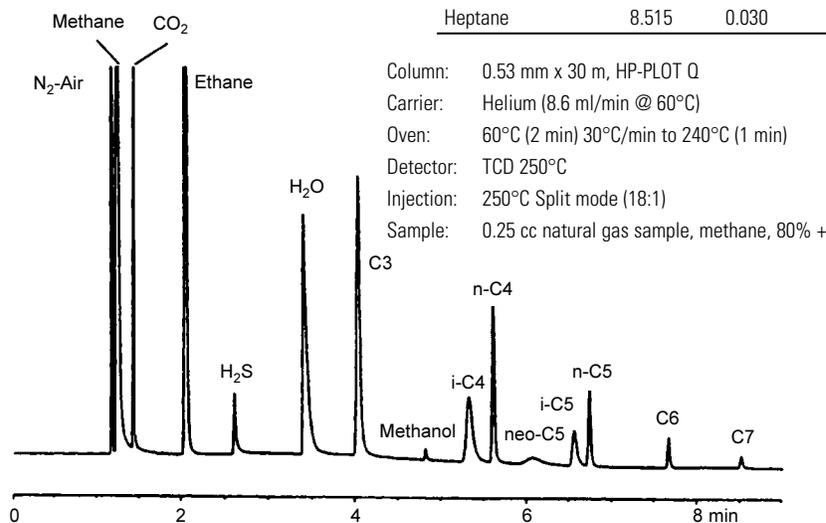
| Resolution R _S | HP-PLOT Q | Brand X | Brand Y |
|--|-----------|---------|---------|
| R _S (N ₂ -Air/Methane, 40°C) | 2.560 | 2.380 | 1.760 |
| R _S (N ₂ -Air/Methane, 60°C) | 1.760 | 1.600 | 1.340 |
| R _S (CO ₂ /Methane, 40°C) | 11.200 | 8.100 | 10.100 |
| R _S (CO ₂ /Methane, 60°C) | 7.200 | 5.100 | 5.300 |

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

Peak resolution for N₂-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

Figure 1. Separation of Natural Gas



column absorbants from sample components such as water and CO₂ 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 |

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 C₁₄ 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 C₁₄, 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

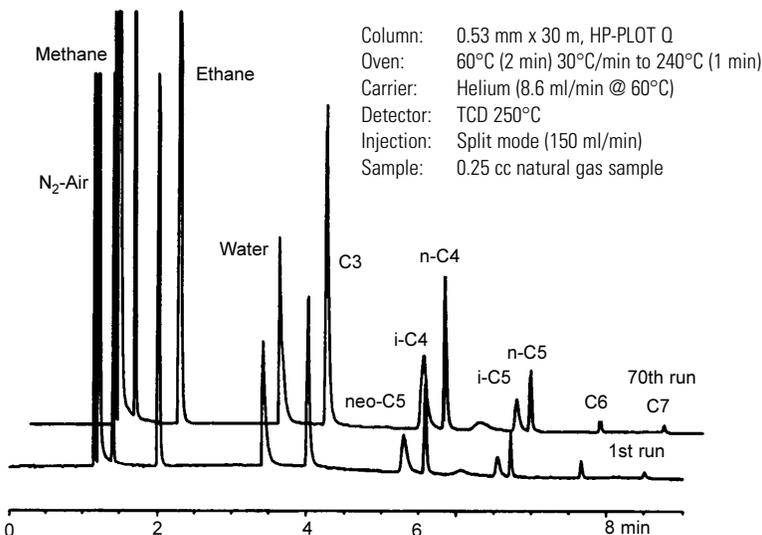


Figure 3. Sulfur Compound Separation

1. Hydrogen sulfide
2. Carbonyl sulfide
3. Ethanethiol
4. iso-Propyl mercaptan
5. n-Propyl mercaptan
6. n-Butyl mercaptan

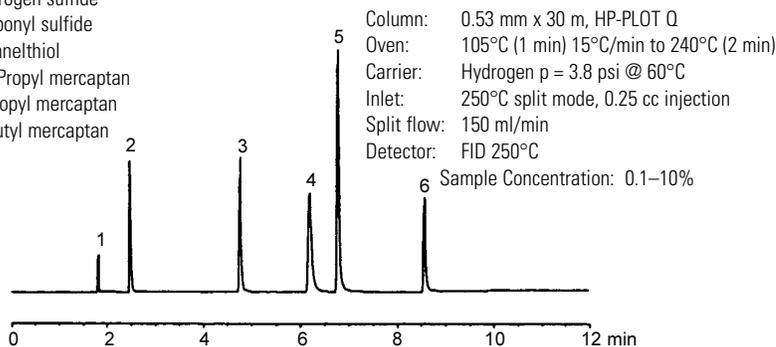
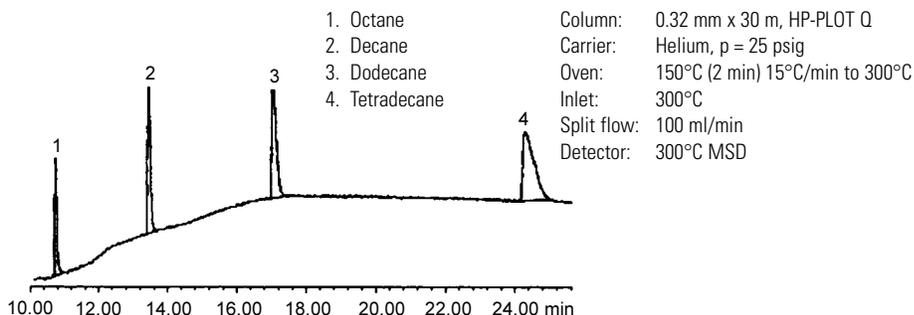


Figure 4. Elution of C8 to C14 on HP-PLOT Q column



References

1. Jane B. Hooper, "Natural Gas and Refined Products", *Analytical Chemistry*, **65**, No. 212, June 15, 1993, p189R-192R.
2. Hai Pham Tuan, Hans-Gerd Janssen, Ellen M. Kuiper-van Loo and Harm Vlap, "Improved Method for the Determination of Sulfur Components in Natural Gas", *HRC*, **18**, Sept. 1995, p525-534.
3. Roger Firor, Hewlett-Packard Company, Application Note, 228-124, 1990.
4. Zhenghua Ji and Imogene Chang, Hewlett-Packard Company, Application Note, 228-286, 1994.

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