Fast Analysis of Hydrocarbons in Natural Gas

Application Note
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Abstract

The effect of column length, oven temperature, and sample loading on analysis time and resolution was evaluated to determine the optimized conditions for C_1–C_6 hydrocarbons in natural gas samples using HP-PLOT/Al_2O_3 columns.

Keywords

Natural gas
HP-PLOT/Al_2O_3 columns
Fast analysis
C_1–C_6 hydrocarbons

Introduction

Routine analyses of natural gas samples require the simultaneous separation of both permanent gases and hydrocarbons. The permanent gases, such as oxygen and nitrogen, can usually be determined within a few minutes at near ambient temperatures using molecular sieve columns. However, separation of C_1 to C_6 hydrocarbons using alumina PLOT columns under similar GC conditions usually requires an analysis time longer than 20 minutes. Fast PLOT column analyses of both permanent gases and hydrocarbons can be achieved by reducing column length and film thickness, increasing carrier flow, optimizing oven temperature, or varying combinations of these parameters.

However, shortening analysis time often results in loss of resolution and, sometimes, decreased sample loading capacity. This is especially true when alumina PLOT columns are used to determine hydrocarbons in natural gas. This is because the alumina PLOT columns have limited sample loading capacity for light hydrocarbons, such as methane and ethane. Therefore, it is important to optimize analytical parameters to improve the loading capacity and resolution as well as to shorten the run time.

The effects of both column length and oven temperature programs on the analysis time for widebore (0.53 mm id) alumina PLOT columns were evaluated. In addition, GC conditions were optimized for fast and efficient analysis of hydrocarbons in natural gas for both high and low sample loadings.

Experimental

Two HP-PLOT/Al_2O_3 "S" type widebore (0.53 mm id) columns, 15 m and 50 m, were evaluated for their effectiveness in separating methane and ethane in natural gas under various oven temperature programs (**Table 1**). These temperature programs were designed to obtain the best separations with the shortest run times.

All analyses were done using a 5890 Series II GC with electronic pressure control (EPC) and a flame ionization detector (FID). Samples were introduced manually using gas-tight syringes. Other GC parameters are listed in **Table 1**.

A natural gas sample was prepared by spiking the natural gas standard (part no. 5080-8756) with 1,3-butadiene, propylene, and isobutylene. **Table 2** lists the hydrocarbon components in the sample.

Results and Discussion

Methane and ethane are the major hydrocarbon components and the target compounds in natural gas analyses. Because they elute very closely to each other on alumina PLOT columns, it is important to select a column that possesses both large loading capacity and high separation efficiency. Wide-bore (0.53 mm id)

HP-PLOT/Al_2O_3 columns were used because of their large loading capacity and ability to handle large carrier flows. **Table 3** lists the results of resolution (methane/ethane) and run times using various oven temperature programs and sample loadings. These temperature programs were designed to achieve the best separation for the shortest run time.

Analysis Using Short Column Length

Using a 10 µl injection and a 15 m HP-PLOT/Al_2O_3 column, baseline separation for methane and ethane in natural gas was not achieved at an initial oven temperature of 110°C (peaks 1 and 2, **Figure 1**), although the run time was within 4.3 minutes. When the initial oven temperature was lowered to 100°C on the same 15 m column, baseline separation was achieved and resolution was improved as shown in **Figure 2A** (see **Table 3**).

Further lowering of the initial temperature (35°C) resulted in increased resolution as well as improved loading capacity (**Figure 2B**). In the 35°C initial temperature run (**Figure 2B**), sample size was increased to 500 µl. This represents the volume of sample (0.5 to 2.0 ml) commonly introduced during natural gas analyses using gas sampling valves.

Effects of Increasing Column Length

Figure 3A shows the analysis of the natural gas sample using a 10 µl injection and a 50 m HP-PLOT/Al_2O_3 column. At a high initial oven temperature (above 100°C), this longer column improved resolution slightly but increased the run time significantly (see **Table 3**). Specifically, the resolution of methane and ethane increased by 8% (from 4.22 to 4.56)

Figure 1. Analysis of hydrocarbons in natural gas on a 15 m x 0.53 mm HP-PLOT/Al_2O_3 column (baseline separation of methane and ethane not achieved).

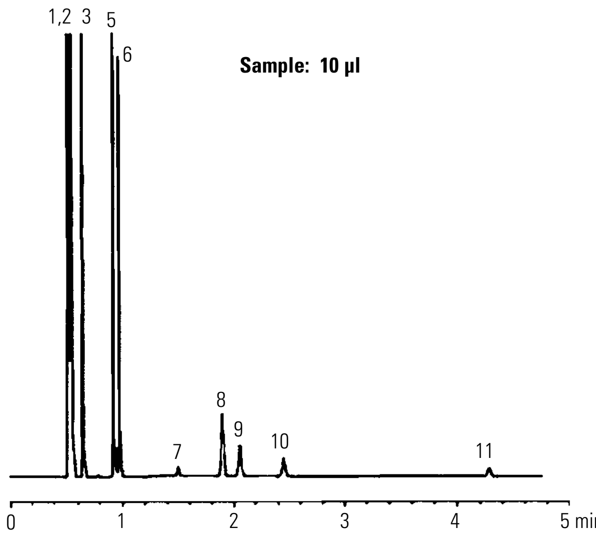


Table 1. Experimental

Gas Chromatograph:	Agilent 5890 Series II GC with EPC
Column:	HP-PLOT/Al_2O_3 S-Deactivated
	1. 15 m x 0.53 mm (Part no. 19095P S21)
	2. 50 m x 0.53 mm (Part no. 19095P-S25)
Carrier:	He, 6 ml/min constant flow
Injector:	Split (split ratio 20:1), inlet 250°C
Detector:	FID (250°C)

Figure	Column	Oven Temperature Program	Injection Volume
1	15 m	110°C (1.5 min) to 180°C at 30°C/min	10 µl
2A	15 m	100°C (1.2 min) to 180°C at 30°C/min	10 µl
2B	15 m	35°C (1 min) to 180°C at 30°C/min	500 µl
3A	50 m	150°C (4 min) to 200°C at 15°C/min	10 µl
3B	50 m	35°C (4 min) to 180°C (3 min) a 30°C/min	1000 µl

Table 2. Hydrocarbons in Natural Gas Sample

1. Methane	5. iso-butane	9. n-Pentane
2. Ethane	6. n-Butane	10. 1,3-Butadiende (spiked)
3. Propane	7. iso-butylene (spiked)	11. Hexane
4. Propylene (spiked)	8. iso-pentane	

Table 3. Resolution and Run Time

Figure	Column	Sample Volume	Resolution (C1/C2)	Run Time
1	15 m	10 µl	3.04	4.3 min
2A	15 m	10 µl	4.22	3.8 min
2B	15 m	500 µl	4.97	5.8 min
3A	50 m	10 µl	4.56	6.4 min
3B	50 m	1000 µl	9.62	11.5 min

and the run time increased by 68% (from 3.8 minutes to 6.4 minutes) with this over three-fold increase in column length (comparing **Figure 2A** with **Figure 3A** in **Table 3**). At the low initial temperature of 35°C, tripling the column length (15 m vs 50 m) nearly doubled resolution (4.97 vs 9.62) and run time (5.8 vs 11.5 minutes).

Effects on Column Capacity

Temperature programming showed a pronounced effect on sample loading capacity. Sample loading capacity increased by 50- to 100-fold (from 10 µl to the 500- or 1000 µl level) when the initial oven temperature was lowered to 35°C. This was true when both short and long columns were used (**Table 3**). On the other hand, resolution improved by twofold when the column length was tripled. Therefore, low initial oven temperature has a greater role than column length in increasing sample loading capacity, analysis speed, and separation efficiency.

Figure 2. Analysis of hydrocarbons in natural gas on a 15-m x 0.53-mm HP-PLOT/Al_2O_3 column (2A—improved resolution of ethane and methane, 2B—improved loading capacity).

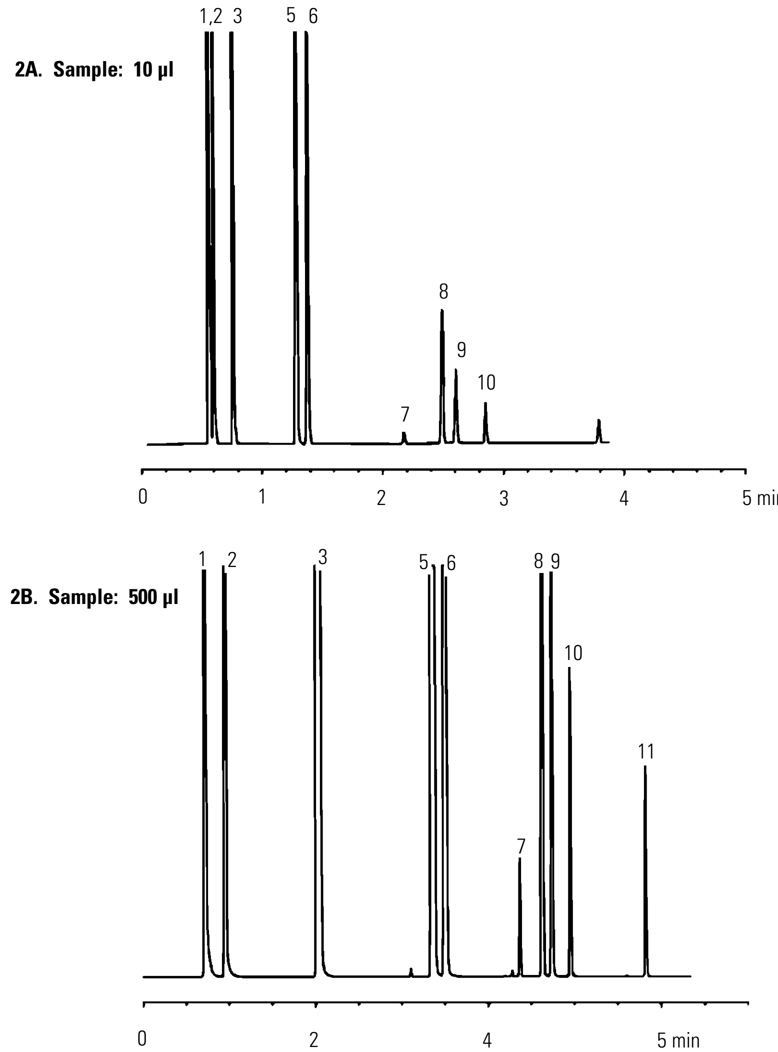
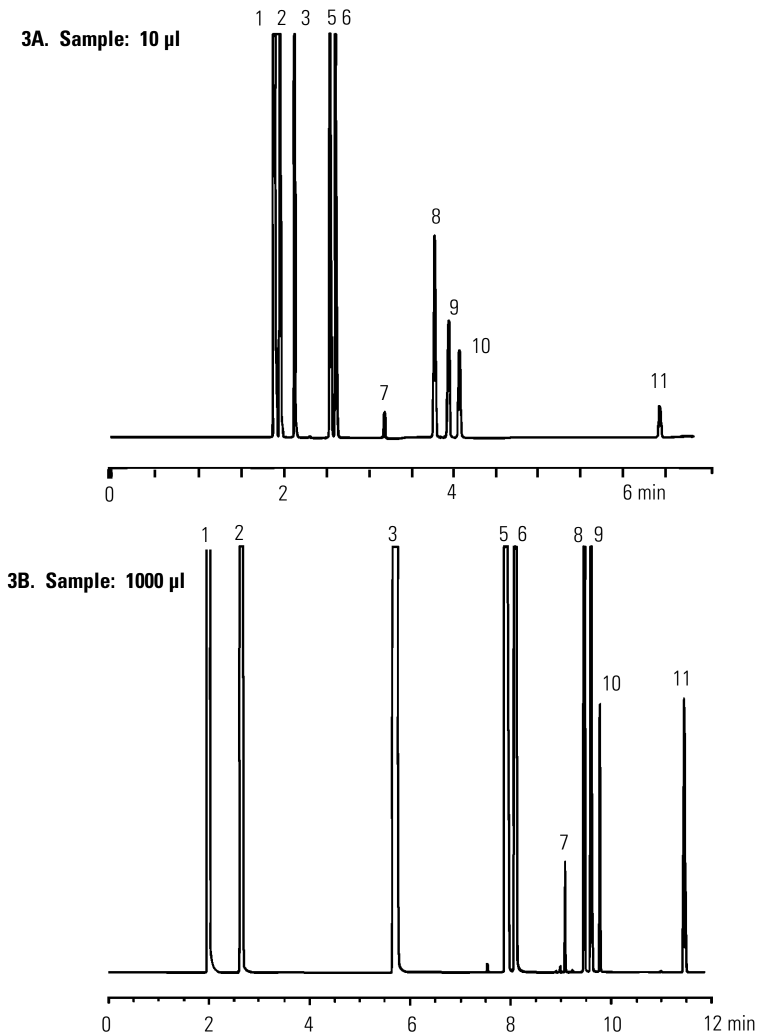


Figure 3. Analysis of hydrocarbons in natural gas on a 50 m x 0.53 mm HP-PLOT/Al_2O_3 column (3A—baseline separation of methane and ethane, 3B—improved loading capacity).



Conclusion

Separation of methane and ethane in natural gas requires high-capacity and high-efficiency columns. To shorten analysis time, the column length, oven temperature program, and sample loading capacity must be optimized. The 15 m HP-PLOT/Al_2O_3 column provides fast and effective analysis of natural gas (C_1 to C_6 hydrocarbons) in 6 minutes under an optimized oven temperature program (initial oven temperature at 35°C).

References

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