

Analysis of Natural Gas Using Single Capillary Column and a Pulsed Discharge Helium Ionization Detector

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Precise analysis of natural gas is important for determining the price due to calorific value, identification of source and gas quality. In natural gas, there are lots of components from C₁ to C₁₀ hydrocarbons including isomers. Their physical properties are similar and the composition ratio of major against minor components is great. Therefore, good quantification is not easy in ordinarily analytical means.

The gas chromatographic separation with high resolution capability and versatility has been used to characterize all the components of natural gas. The most recommended method is ASTM D-1945 and GPA standard 2261 multi-column technique, which consists of one ten-port valve, two six-port valves and several columns. Recently, an simpler technique using an alternative system with two GCs and three efficient columns, two capillary columns (PoraPLOT Q and FSOT) and one packed column (Hayesep Q), has been introduced.¹ In this system, the first GC is equipped with a thermal conductivity detector (TCD) and a flame-ionization detector (FID), and the second chromatograph is equipped with a TCD and a flame photometric detector (FPD). Using these techniques, the complex mixture of C₁ to C₁₀ hydrocarbons are well characterized with good resolution and repeatability.^{1,2} However, they require complicated equipments and sophisticated experimental skills and long analysis time. They do not seem to be suitable for industrial usage, such as distributor, small gas station, and dealer. The ratio of the major against the minor components in natural gas is almost third order. The amount of C₆ to C₁₀ hydrocarbons is extremely small enough to be negligible in practical view. A simple analytical technique for C₁ to C₅ hydrocarbons might be appropriate economically for the suppliers.

In 1992, the pulsed discharge helium ionization detector (PDHID) was introduced by Wentworth *et al.*⁴ Attention has been paid to its advantages with simple configuration, convenience, high sensitivity and good versatility. The source of PDHID is a pulsed discharge in helium and responds to the helium ionization detector. As helium gas passes through the ionization chamber, analytes emanating the GC capillary are ionized by the helium metastables and photons, and transfer the signal to the electrometer. Since the ionization potential of the metastable helium is higher than that of all species except with argon ion, it can ionize all other compounds.⁵ Therefore, PDHID has become a universal detector capable of detecting H₂, O₂, CO₂, H₂O as well as organic compounds ranging from light hydrocarbons to high molecular weight pesticides and metal complexes.⁶⁻⁹ Its sensitivity for hydro-

carbons is the order of 1 pg/s.¹⁰

This paper reports on the results of analysis for C₁ to C₅ hydrocarbons in natural gas. The experiment was developed, based on an economic and inexpensive structure which consisted of single column and single detector of PDHID in a gas chromatographic system with a Y-piece split throttling port. This split port was employed for the measurement of the major components. Only small part of them flows to the column to prevent the sensitive detector from being overloaded as they are analyzed at the detector. Most is vented. We introduce a practical skill of measuring, in turn, the major and the minor in the single capillary column.

Experimental

Materials. Standard natural gas was purchased from Matheson(USA). The composition is given in Table 1.

Instrumentation. The experimental system is depicted in Figure 1. A gas chromatograph (DS 6200, Donam Systems, Inc, Korea) equipped with a PDHI detector and a GS-Q capillary column (J&W Scientific, USA) of 30 m length with I.D. 0.5 mm were used for this study. Before the natural gas was launched into the six-port sampling valve (Valco, USA), helium and natural gases were mixed at the preparation unit by the mass flow controllers (Brooks, Japan, flow range; 10-100 mL/min), and then the mixture gas was introduced into the GC column by the six-port valve equipped with 100 μ L sampling loop to inject a constant amount of sample. For the major components (methane, ethane, and propane), a Y-piece split throttling port was set between the six-port valve and the column inlet. The split ratio was adjusted by a 1/16" micro needle valve on the Y-piece port,

Table 1. Composition of the standard natural gas

Component	Concentration ^a (mol %)
N ₂	0.022
CO ₂	0.000
CH ₄	91.743
C ₂ H ₆	4.190
C ₃ H ₈	2.710
<i>i</i> -C ₄ H ₁₀	0.655
<i>n</i> -C ₄ H ₁₀	0.603
<i>i</i> -C ₅ H ₁₂	0.067
<i>n</i> -C ₅ H ₁₂	0.010

^a Data from Matheson Gas Products

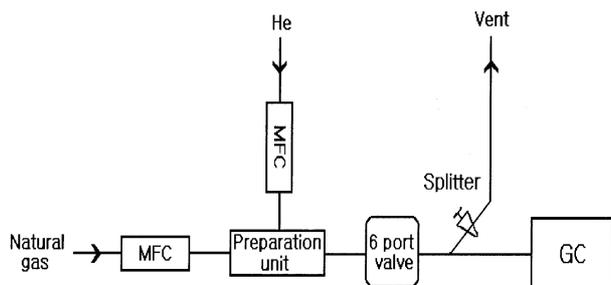


Figure 1. Schematic diagram of an injection system MFC: mass flow controller.

in order that the major components may not be saturated on the sensitive detector. There are two modes, split injection mode for the major and splittless injection mode for the minor. For the split injection mode, only a small amount is sent to the detector through the capillary column and most part is vented. For the splittless injection mode, no vent occurs and all the gas flows into the column. This skill allowed the major and the minor to be measured in the single capillary column, independently. 99.999% pure helium (Praxair, Korea) was used as carrier gas. For analysis of the major components the flow rate of the carrier gas was 27 mL/min, and the oven temperature was held initially at 160 °C for 2 min, then programmed to 240 °C at the increase rate of 40 °C/min. For the minor components (*i*-butane, *n*-butane, *i*-pentane, and *n*-pentane), the flow rate was 8 mL/min, and the oven temperature was held initially at 60 °C for 2 min, then programmed to 80 °C at the rate of 20 °C/min, and to 230 °C at the rate of 30 °C/min. The flow rate of helium gas for discharge was 30 mL/min.

Results and Discussion

Chromatogram in the split injection mode is illustrated in Figure 2. Each component exhibits the excellent peak shape. The retention time of methane, ethane, propane, *i*-butane, and *n*-butane (1.61, 1.71, 1.99, 2.47, and 2.68 min) shows good separation. Concentration of each component is 91.8 (methane), 4.2 (ethane), 2.7 (propane), 0.7 (*i*-butane), and

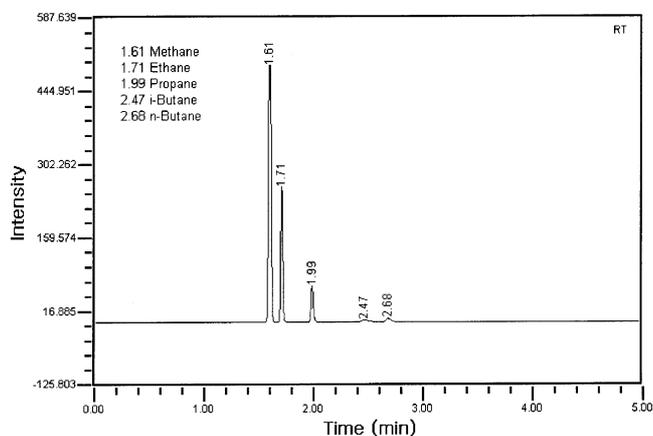


Figure 2. Chromatogram of the major components. GC conditions are in the text.

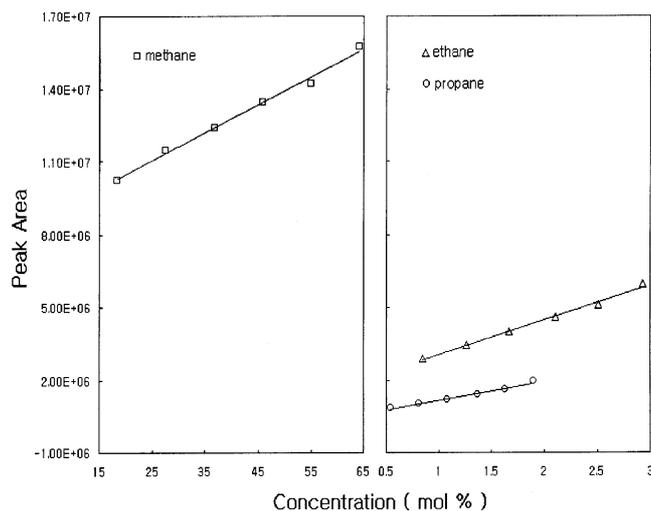


Figure 3. Calibration curves of the major components.

0.6 mol % (*n*-butane), respectively. The calibration curve for each component in the natural gas was obtained by changing the flow rates in the column but the total flow rate of helium and the natural gas was kept constant (50 mL/min). The flow rates of the natural gas were increased with 10, 15, 20, 25, 30, and 35 mL/min as the flow rates of helium were decreased with 40, 35, 30, 25, 20, and 15 mL/min, respectively. Keeping the total constant during GC temperature programming is important for good reproducible results of the gas analysis. The resulting chromatogram is illustrated in Figure 3. Good linearity (0.98-0.99 of correlation coefficient) for methane, ethane, propane was obtained.

The condition of analysis for the minor was the same as for the major except that the mode is splittless injection mode. The chromatogram of the minor components is shown in Figure 4. The major components were saturated as seen in the figure. Retention times of *i*-butane, *n*-butane are different from those in Figure 1, because the flow rate in the column inlet is changed by the splitter. The calibration curves (Figure 5) for *i*-butane, *n*-butane, *n*-pentane, *i*-pentane are linear (0.98-0.99 of correlation coefficients).

To investigate the precision of the analysis, relative stan-

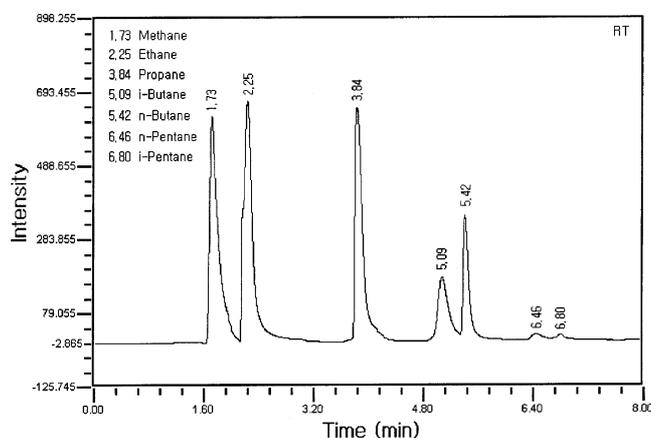


Figure 4. Chromatogram of the minor components. GC conditions are in the text.

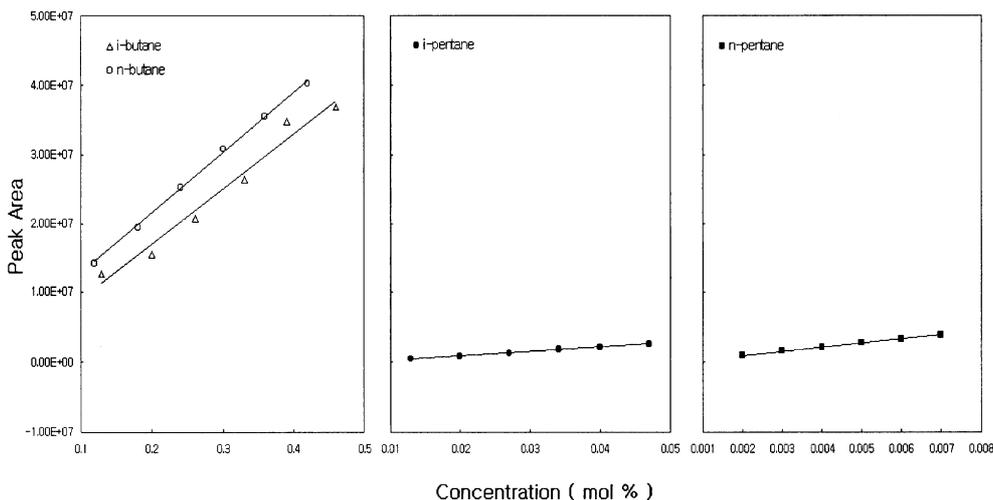


Figure 5. Calibration curves of the minor components.

Table 2. Repeatability of the natural gas analysis

Component	Repeatability (%RSD) ^a
CH ₄	0.05
C ₂ H ₆	0.91
C ₃ H ₈	1.39
<i>i</i> -C ₄ H ₁₀	0.54
<i>n</i> -C ₄ H ₁₀	2.57
<i>i</i> -C ₅ H ₁₂	6.79
<i>n</i> -C ₅ H ₁₂	12.20

^aCalculated from the results of six runs (methane, ethane, propane) and four runs (butane, pentane) within a day

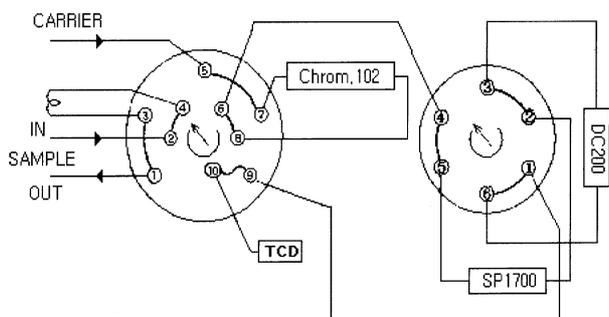


Figure 6. Valve diagram for analysis of natural gas.

standard deviations (RSD) were calculated from the results of six runs (for the major) and four runs (for the minor) within a day. For the RSD of the natural gas analysis, ISO 6568 suggests 0.1% for methane, 0.5-1% for more than 0.5 mol % composition, and 5-20% for less than 0.5 mol % composition. Resulting RSD values are given in Table 2. This method is not precise, but very convenient as compared with multi-column method (Figure 6 and Figure 7).

In conclusion, we can state that the single capillary column and PDHID system furnished with a splitter is convenient for monitoring major and minor components of natural gas. This method may be useful in practical places requiring for analyzing natural gas supplied home or to small factories. The skill is simple and the cost is cheap.

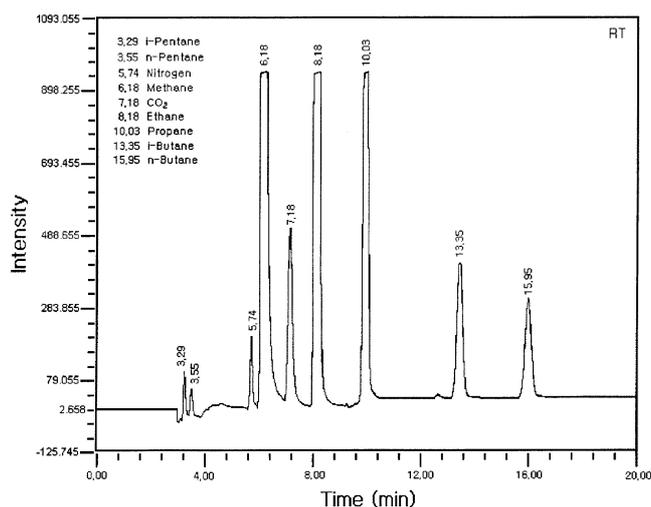


Figure 7. Typical gas chromatogram of natural gas by multi-column method (He carrier gas: 25 mL/min, isothermal at 80 °C, TCD: 100 °C).

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