Carrier Gas as a new factor affecting the Separation Efficiency of Gas Chromatography: I-Using natural gas as a probe

A.Y. El-Naggar[1, 2*], A. M. El-Fadly[1], A. A. Salem[1**] and M. A. Ebaid[1]

[1-]Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt.
[2-]Chemistry Department, Faculty of Science, Taif University, KSA.
*aynaggar361@yahoo.com

Abstract: Different carrier gases markedly affect retention times and separation efficiency of eluted gases in both gas liquid chromatography (GSC) and gas solid chromatography (GLC), the carrier gases have a pronounced effect on the retention times and efficiency of natural gas separation. In solid chromatography, carrier gases which are adsorbed to any extent occupy more active adsorption sites, reducing the net heat of adsorption of the eluted zone. The efficiency of separation of a light gas mixture is shown to depend markedly on the type and pressure of carrier gas in addition to the column temperatures. Hydrogen and helium are the preferred mobile phases in GSC giving higher efficiency of separation because of their higher thermal conductivity. Helium is the best one because of its safety to handle than hydrogen. Nitrogen is the preferred mobile phase used in FID giving high efficiency of heavy components of natural gas separation. For all different mobile phases, it is preferred to use lower sample capacity in order to obtain high efficiency of gas chromatographic separation.

1. Introduction

The main goal of gas chromatography is separation of multi-component mixtures, to achieve high efficiency of separation, one usually has to optimize the separation process by varying stationary phase, carrier gas flow, column temperature, etc.[1-3] The opinion of many chromatographers about the role of carrier gas is limited only to transporting analyzed compounds along the column. However, carrier gas dramatically affects relative retention values. Various carrier gases have been used in gas liquid chromate-graphy (GLC) and gas solid chromatography (GSC). Nitrogen, helium, hydrogen, and carbon dioxide have been reported to give good results as far as detector stability and sensitivity are concerned [4]. The use of different carrier gases has also been found to have a pronounced effect on the selectivity of eluted gases in both GSC [5] and GLC [6, 7].

The line of this research is the selection of three different carrier gases, helium, hydrogen and nitrogen and investigate their effect on the retention times and separation efficiency of natural gases using Plot Q and DC 200 columns. The composition of the studied natural gas is C1, CO2, C2, C3, iso-C4, n-C4, iso-C5 and n-C5 and there are many standard methods [8-11] dealing with the quantitative analysis of these mixed gases. The efficiency of separation of gas mixture, using the studied carrier gases is shown to depend markedly on the carrier gas type and flow, as do the retention times of components [12].

In other study, water vapor was added to the carrier gas to study the effect of moisture on the retention properties of a poly (ethylene glycol) GC stationary phase [13], the result of this study, a dramatic increase in hydrogen bonding was observed toward alcohols and carboxylic acids, also the Kovats index [14] for methanol was found to increase by 351 units.

The dependence of retention of hydrocarbon gases on nature and pressure of carrier gas in capillary adsorption chromatography was evaluated [15]. Equations were developed to predict the retention times, column efficiency, and resolution for eight p-hydroxybenzoic esters as a function of flow rate and temperature [16, 17]. The influence on retention from pressure and carrier gas have been described and modeled and should be useful for continued refinements on predictive capabilities [18].

This study includes the effect of nature and pressure of different carrier gases on the efficiency of separation using thermal conductivity detector and flame ionization detector [19]. Also, the effect of sample capacity and column temperatures on the efficiency of natural gas separation using the three different carrier gases is shown.

2. Experimental

The NGPA natural gas reference standard (C1, CO2, C2, C3, iso-C4, n-C4, iso-C5 and n-C5) was provided from Phillips Petroleum Company Bartlesville Okiaahoma 74004.

Gas Chromatographic Analysis

The mixed gases C1, CO2, C2, C3, iso-C4, n-C4, iso-C5 and n-C5 were analyzed using Agilent 6890 plus HP gas chromatograph, equipped with thermal conductivity detector (TCD) and flame ionization detector (FID), using the fused silica plot Q capillary column 15 meter in length and 0.35 mm internal diameter, attachment with the TCD. Also using the packed column DC 200 of stainless steel in type, 10 feet in length and 1/8 inch in diameter, attachment with the FID. The elution of the studied gas mixtures was achieved with temperature programming from 60 to 200 $^{\circ}$C at a rate 10 $^{\circ}$C min-1. The different mobile phases used are nitrogen, hydrogen and helium gases, these all gases are Oxygen-free. Flow rates were measured from the end of the column with a soap bubble flow rate. Methane as an unretained marker was used to correct the dead volume in the column in the case of FID, and air used as marker in the case of TCD.

The injector and detector temperatures are 200 $^{\circ}$C and 250 $^{\circ}$C respectively. The data was estimated by integration of the area under the resolved chromatographic profile, using the HP computer of software chemstation.

3. Results and Discussions
I- Effect of sample capacity on the separation efficiency
1-Using thermal conductivity detector (catharometer)

Thermal conductivity detector was used for the analysis of light gases and inorganic gases. The relation between the different sample size and height equivalent to theoretical plates (HETP) for the three different carrier gases was show in Fig. (1), it has been found that it is preferred to inject small sample capacity in order to obtain separation of light gases with high efficiency.

2-Using flame ionization detector (FID)

The relation between the different sample size and height equivalent to theoretical plates (HETP) for the studied three carrier gases was show in Fig. (2), it has been found that generally, the small sample capacity results in small value for HETP and hence high efficiency of natural gas Separation. In the case of nitrogen as carrier gas, the HETP shows the lowest value for any component in the gas mixture than the other two carrier gases, this reflect that in the case of flame ionization detector the high efficiency of separation was achieved by using

nitrogen as carrier gas, this may be attributed to when the carrier gas is nitrogen, the probe molecules can diffuse maximally in the stationary liquid phase than in mobile phase.

The HETP is inversely proportional to the molecular weight of the components of natural gas, in other words the efficiency of separation is proportional to the molecular weight of the probe molecules this may be attributed to the higher molecular weight will diffuse largely in stationary liquid phase. Using catharometer, the HETP take the opposite character of flame ionization detector that it is directly proportional to the molecular weight of the light paraffins, this proved that the catharometer is highly efficient in the detection of lighter paraffins than the heavier one.
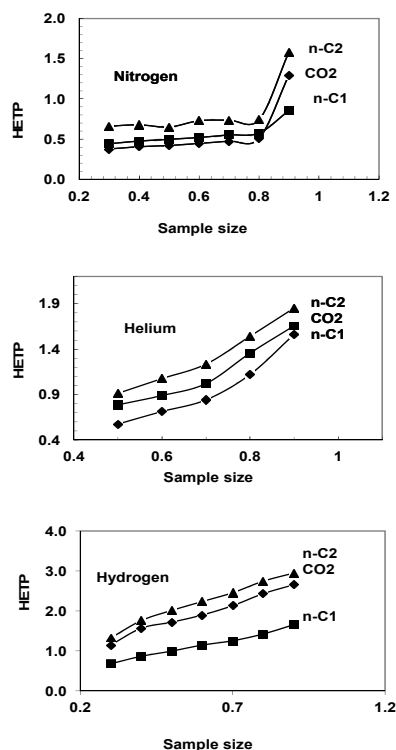

Fig.(1): Effect of sample size on the separation efficiency of light gases using thermal conductivity detector

II-Effect of temperature on the separation efficiency
1- Using thermal conductivity detector (catharometer)

The relation between different temperatures and No. of theoretical plates for each studied carrier gas was shown in Fig. (3). It has been found that for the three studied carrier gases, increasing the temperature will increase the separation efficiency of the selected

probe (ethane). Also, it is clear that at any temperature degree helium and hydrogen are the preferred carrier gases in catharometer, this may be due to their higher thermal conductivity compared with that of nitrogen.

 2-Using flame ionization detector (FID)

Fig. (4) shows the effect of temperatures on the number of theoretical plates and hence on the separation efficiency of n- pentane, it is shown that the efficiency of separation using any carrier gas will increase with increasing the temperature tell reached to 100 °C after this point there is a slight increase in separation efficiency with temperature.
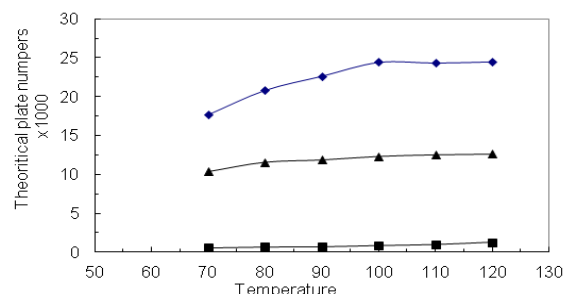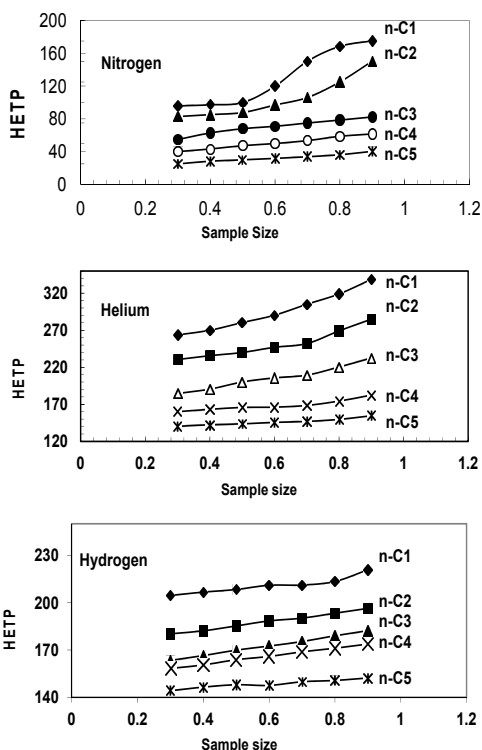

Fig. (2): Effect of sample size on the separation efficiency of natural gas using flam ionization detector.

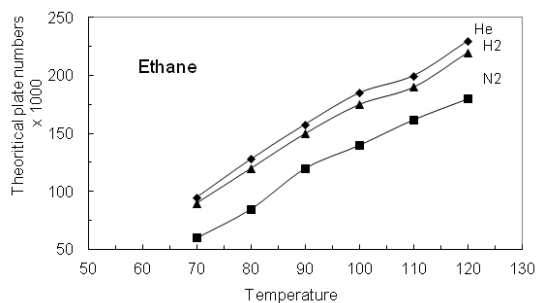Fig.(3) Effect of temperature on the separation efficiency using catharometer

Fig.(4) Effect of temperature on the separation efficiency Using flame ionization detector

In the case of flame ionization detector, nitrogen is the best-used mobile phase giving high theoretical plate numbers at any point of temperature and hence high separation efficiency.

The effect of temperature on the detector sensitivity is different according to the used mobile phase. Hydrogen and helium are the best mobile phases used in thermal conductivity detector and nitrogen is the preferred one in FID.

III- Effect of gas velocity on the separation efficiency

Fig. (5) Shows the relation between gas flow rate and height equivalent to theoretical plates using nitrogen as carrier gas, it has been observed that the flame ionization detector gives optimum gas velocity at 12 ml min-1 for heavy gases (C3, C4 and C5). This means that this flow rate was preferred for obtaining high efficiency of heavy gases.

Fig.(6) Shows the same relation using thermal conductivity detector and hydrogen as carrier gas, it has been found that the optimum gas velocity for C1, C2 and CO2 was 3 ml min-1.
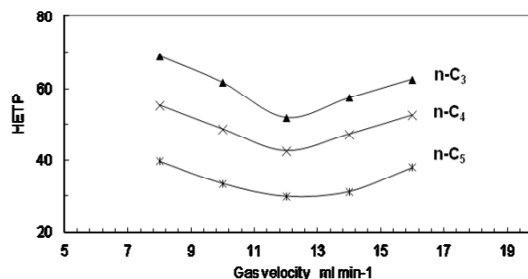

Fig. (5) Effect of gas velocity on the separation efficiency of FID using DC-200 column and nitrogen as carrier gas
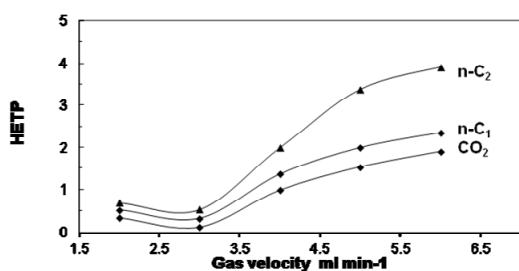
Fig. (6) Effect of gas velocity on the separation efficiency of TCD using plot-Q column and hydrogen as carrier gas

IV-Application of the studied carrier gases
1-Using thermal conductivity detector (catharometer)
Gas chromatographic analysis of light gases (C1, C2, C3) and inorganic gas (CO2) on Plot Q as solid stationary phase, using thermal conductivity detector at three different carrier gases and at the same conditions (sample size, flow rate and temperature) was shown in Fig. (7).

All used carrier gases can separate the light gases mentioned above with nearly the same duration of analysis and the same degree of separation but using nitrogen as mobile phase the sensitivity of catharometer must be amplified many times in order to obtain a chromatogram that can be shown although the sample capacity is the same for all studied carrier gases. Using hydrogen and helium as carrier gases results in good elution of the light gas mixtures with high detector (catharometer) sensitivity.

They have thermal conductivities about seven times greater than nitrogen and greater than those of any other gas as given in Table (1), they give symmetric and sharp peaks but the mobile phase hydrogen shows slightly lower duration of analysis. So hydrogen is the preferred one giving high detector sensitivity and high efficiency of separation because of its higher thermal conductivity.

When the thermal conductivity cell is used as the detector, it is advantageous to use a carrier gas that has a thermal conductivity vastly different from any compounds to be determined. Because thermal conductivity is inversely related to the square root of the molecular weight, the molecular weight of as large a response as possible from the detector. The fact that hydrogen and helium have a low molecular weight and can be used as mobile phase in catharometer, in some cases helium is preferred because its safe to handle makes it a suitable choice.

Table (1) Thermal conductivity of the different carrier gases and probes

No.	Carrier gases and probes	Thermal conductivity Unites at 0 ^{o}C
1	H_2	41.6
2	He	34.8
3	N_2	5.8
4	CH_4	7.2
5	C_5H_{12}	3.1
6	C_6H_{14}	3.0

In gas adsorption chromatography, it is proffered usually to use helium and hydrogen, inert carrier gases that are not adsorbed on the surface of solid stationary phase to any great extent. It was thought that the use of a carrier gas that was adsorbed would have some effect on the separation of gaseous mixtures. More active adsorption sites would be occupied to some extent by the carrier gases, and the retention times of eluted gases would be reduced.

2-Using flame ionization detector (FID)
Gas chromatographic analysis of the mixed gases C1, C2, C3, i-C4, n-C4, i-C5 and n-C5 on silicon oil DC-200 as liquid stationary phase using three different carrier gases at the same conditions (sample size, flow rate and temperatures) was shown in Fig. (8). The three different carrier gases can be used in the elution of the mixed gases but with different detector (FID) sensitivity, in the case of nitrogen as carrier gas, the FID shows high sensitivity (about 80000) compared with helium (about 35000) and hydrogen (about 25000).

When flame ionization detector is used in the gas chromatographic process, nitrogen (free oxygen) was the preferred used mobile phase providing maximum detector sensitivity and high efficiency for the separation of the heavy components of the natural gases. The flame ionization detector sensitivity is ten thousands higher than that of thermal conductivity detector, So FID with N2 as carrier gas were used for the elution and quantitative determination of the manure quantities of the heavy components of natural gas.

4. Conclusions
1- The type of carrier gas has been found to have a pronounced effect on the retention times of the eluted gas mixtures and also on the selectivity of the gas-stationary phase chromatographic system.
2-In gas solid chromatography (GSC) and thermal conductivity detector, the carrier gas must be has a thermal conductivity different from any compounds to be analyzed and the greater the difference the greater the sensitivity of the method of detection.

3-Hydrogen and helium are the preferred mobile phases in GSC giving higher efficiency of separation because of their higher thermal conductivity. In some cases hydrogen is the proffered one due to there higher thermal conductivity than helium.

4- In gas liquid chromatography and flame ionization detector, the carrier gas have a pronounced effect on the retention times and on the efficiency of gas chromatographic separation. Nitrogen is the preferred mobile phase used in FID giving high efficiency of heavy components of natural gas separation.

5- In the studied three carrier gases and in both adsorption chromatography and partition chromatography, it is preferred to use small sample capacity in order to obtain high separation efficiency.

6-both adsorption chromatography and partition chromatography show high separation efficiency with increasing temperature.

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