The Effects of Carrier Gas Viscosity on Column Efficiency in Capillary Gas Chromatography

By

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(ABSTRACT)

The objective of this study is to determine the effects of carrier gas viscosity of hydrogen and helium on column efficiency; particularly when employing thin films. When using thin films, mass transfer in the stationary phase becomes negligible and mass transfer in the mobile phase predominates. It was envisioned that when employing thin films hydrogen would be the carrier gas of choice due to its higher diffusivity and lower viscosity. The combination of the previous factors should lead to faster analyses (isothermal) and higher column efficiency with hydrogen.

Viscosity is the resistance of a liquid or gas to flow. The viscosity of a gas is determined by two factors: (1) the molecular weight of the gas; and (2) its temperature. When the temperature or molecular weight of the gas is increased its viscosity is also increased. In a chromatographic system, with a constant pressure drop, an increase in viscosity results in a decrease in the linear velocity of the carrier gas, ultimately resulting in lower column efficiency.

The most detrimental effect of increasing viscosity is that the target analyte has more difficulty partitioning through the mobile phase to the surface of the stationary phase and vice versa. This phenomena results in

slow mass transfer of the analyte and increased band broadening. However, it was observed that the diffusivity increases more with temperature than the viscosity. Which is responsible for the faster rate of mass transfer in the mobile phase at higher temperatures and increased column efficiency at higher temperatures.

The results of this research clearly illustrate that the diffusivity is the most important property of a carrier gas. And when using hydrogen as the carrier gas, there is faster mass transfer in the mobile phase due to hydrogens higher diffusivity and lower viscosity.

Dedication

I would like to dedicate this work to my father Charles Henry Armstrong, and to my sisters Carol Ann Linton, Charlene Yvette Armstrong and Victoria Joesy Friend as a small token of appreciation for all the financial and personal sacrifices they have made for me over the years. To the memory of Candice Terresse Williams (1976-1995) who understood the pain of alienation. And to my nephews Lawrence Walter Linton and Johnathan William Linton; always remember the Lily of the Valley!

Acknowledgments

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Also, I would like to acknowledge my research group members who have made graduate school exciting and fun. Personally, I would like to thank Dr. Yuri Kazakevich and Dr. Markus Lymann for their technical expertise and scientific dialogue. Also, I would like to thank Erik Baltussen and Karen Baker for being nice distractions at work!

I would be remised if I did not take time to acknowledge members of my family who supported me through this and all endeavors. Again, I would like to acknowledge my sisters and their spouses Carol (Paul), Vicki (James), and Charlene who have been a constant source of strength. Thank you for showing me the power of our family. To my father Charles Henry Armstrong, Jr., thank you for your tough love; which I am understanding more and more each day. Last but definitely not least, I would like to thank my best friend Daria Lawson for your friendship.

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General Introduction

For the last forty-years, there has been a continuous quest to develop Gas Chromatography to its maximum potential. Scientists have focused on improving almost every instrumental parameter related to gas chromatography. Moreover, great efforts have been directed at attempting to understand every aspect of gas chromatography applications; from how temperature gradients can be used as a means of improving complex separations to the analysis of trace biological compounds.

Certainly, the simple instrumentation and ease of operation are responsible for some of the popularity and the longevity of gas chromatography. In 1994, the estimated world wide sales of gas chromatographs was close to 1 billion dollars. Modern gas chromatographs require little maintenance and can be connected with constant support gases. Gas Chromatographs require a carrier gas which usually is hydrogen, or helium, or nitrogen. Helium is the most commonly used carrier gas. However, hydrogen produces the greatest efficiency due to its higher diffusivity. However, due to the flammability of hydrogen; most chromatographers choose helium over hydrogen for safety considerations.

Gas Chromatography is a physical method of separation based upon a volitilized analyte partitioning between two phases; one being a stationary phase and the other being a mobile phase. Gas Chromatography was first introduced in 1952 by Martin and James (1). This causes one to wonder whether they envisioned that this technique would establish itself as one of the world's most powerful and diverse analytical techniques. Significant strengths of gas chromatography lies in its ability to provide fast and highly sensitive separations. Modern gas chromatographic detectors have minimal detectable quantities on the order of 10^{-11} grams or ppb levels.

The number of theoretical plates achieved during a separation determines the "quality" of the analysis. In 1956 Van Deemter derived an equation that relates the column efficiency of packed columns to three factors. They are as follows: eddy diffusion, longitudinal diffusion, and mass transfer in the stationary phase. This equation was later modified by Golay to apply to open tubular columns in 1958. The major differences in the Golay and Van Deemter equations are that the eddy diffusion or multiple path term was eliminated for open tubular columns, and a new term, mass transfer in the mobile phase was added.

The significance of the Van Deemter/Golay equations is that they offer direct knowledge of how to maximize column efficiency. This study focused simply on minimizing those factors which result in low column efficiency. Particularly, those factors related to the mobile phase. The terms in the Van Deemter/Golay equation suggest using a carrier gas with a high diffusivity and low viscosity to increase the rate of mass transfer in the mobile phase. This technique is only useful when employing thin film capillaries, where mass transfer in the mobile is the predominate factor. By comparing hydrogen and helium, we are able to understand how the viscosity of the carrier gas effects column efficiency.

It was noted from previous research that there is a significant increase in column efficiency when using hydrogen (2). However, what was most curious is that the difference in the efficiency of hydrogen and helium seemed to increase as the temperature increased. We attributed this phenomena to the fact that the viscosity of helium increases more dramatically with temperature than does the viscosity of hydrogen (see figure 1). This causes slow mass transfer in the mobile phase and lower column efficiency when using helium.

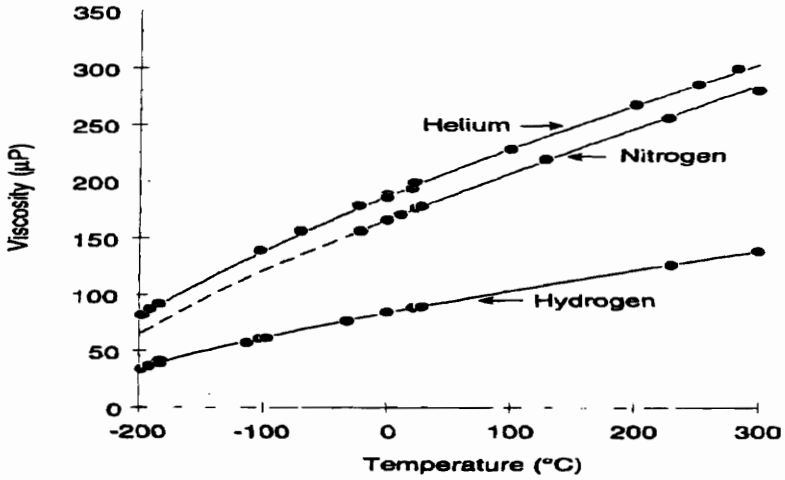

Figure 1: Shows the Viscosity (poise) of Hydrogen, Helium, and Nitrogen as a function of temperature (3).

The objective of this research is to experimentally show that mass transfer in the mobile phase is a dominant term for thin film columns, and that hydrogen is the best carrier gas for thin film columns.

Historical Review

The versatility of gas chromatography resides mainly in its ability to be coupled with many different detectors and columns types with little to no adaptation. The beauty of modern gas chromatographs is that they may be simultaneously coupled with a wide variety of detectors such as Thermal Conductivity (**TCD**), Flame Ionization (**FID**), Mass Spectrometer (**MS**) or the Electron-Capture (**ECD**). Each detector has distinct advantages.

With improving detector technology and the development of high efficiency capillary columns several changes had to be made to the rest of the chromatographic system. To prevent column overloading and to stay within the linear operating conditions of the detectors new injection techniques had to be developed.

The first was split injection. This injection technique requires that 99% of the sample be purged through the split valve and only 1% be delivered onto the column. The split injection technique is very reproducible and easy to use. However, higher molecular weight compounds experience more discrimination because they are less volatile. These less volatile compounds seem to be purged through the split flow before they are completely vaporized. However, split injections have proven to be quite satisfactory for most applications. Split injections are the most widely used injection technique. The popularity of the split injection probably resides in its simplicity.

Splitless injection is a better sample introduction technique for trace analysis. It provides a high dynamic range sensitivity but it requires more time for optimizing injection conditions (3). With splitless injections 95% of the sample is actually delivered onto the column. The purge valve is closed during the initial injection period and then is opened after 30 to 60 seconds to clean out the injection liner. Again, splitless injections are great

for dilute samples and for trace analysis. Successful splitless injections require experience and perhaps trial and error to determine optimum splitless times, sample solvents, and initial column temperature.

The major disadvantage to splitless injections is that the introduction of large solvent volumes may cause solvent peak broadening due to overloading of the column. This is particularly a problem when using narrow-bore capillary columns with thin films. Also, solvent impurities may affect the resolution of the target analytes in the mixture. Similar in nature to the cold on-column injection the initial column temperature must be set below the boiling point of the sample solvent. This is to promote solvent focusing. Solvent focusing increases the sensitivity and the resolution of the solutes.

Cold on-column injections allow deposition of the liquid sample directly into the column. The most impressive feature of this injection technique is that no discrimination occurs between the solutes because everything is delivered directly onto the column. Of the three major injection techniques, cold on-column injections are the most technically complex and the most limited. In order to perform ultra trace analysis using cold on-column injections, the solvents have to be 99.99% free from impurities. This is to minimize matrix interferences. Also, most components experience peak broadening when performing on-column injections due to column overloading. The previous factor establishes that there is a compromise between sample capacity and efficiency.

The on-column injection technique is limited in that it normally requires wide-bore capillary columns for direct analyte transfer. The phenomena of depositing the sample directly onto the column may minimize errors in quantitative analysis (3). Also, the columns used must be coated with a thick film stationary phase. Increasing the film thickness, automatically results in a decrease in column efficiency. This decrease in efficiency is caused by the slow mass transfer in the stationary phase and because the diameter is larger there is slow mass transfer in the mobile

phase. Both of these factors result in peak broadening and decreased resolution.

Any one of the afore-mentioned injection techniques can be used when employing any of the detectors previously mentioned; one can perform trace analysis, qualitative analysis, or quantitative analysis.

Much of modern chromatographic theory focuses on understanding what characteristics make columns more efficient. This area of study has almost become a science within itself. Chromatography has moved from using exclusively packed columns to the almost exclusive use of capillary columns. The range of diameters for the capillary columns are from 50 μm to 530 μm. It is no secret that the use of capillary column seems to be more advantageous than packed columns due solely to the increase in column efficiency and the higher resolution achieved.

The "heart" of a chromatographic system is the column. The column is the site at which separation occurs via selective interactions with the stationary phase. In the beginning, the only columns used in chromatography were packed columns. Packed columns consist of small irregularly shaped particles coated with thin layers of stationary phases. These particles are then packed into 1/8" and 1/4" columns usually made of stainless steel. Again, the major benefits of employing packed columns are their rugged nature and the ability to inject large volumes without affecting the column efficiency. Also, packed columns are excellent for environmental analysis where the samples often contain particulate matter. Mainly because one does not have to be concerned with particulates plugging the column due to it larger diameter as you do with capillary columns. Disadvantages of packed columns have lower resolution and slower analysis times.

In short, packed columns worked great initially but the growing need to separate more complex mixtures required an increase in resolution that packed columns could not produce. In the late 1950's Golay proved that

capillary columns coated with a thin-uniform layer of stationary phase could be used to enhance the resolution and speed of analysis of gas chromatography (4).

Capillary columns are simply open tubular columns with a uniformly thin layer of stationary phase coated on the wall surface. Modern capillary columns are usually made of fused silica glass with a polyimide exterior coating. Capillary columns are usually made of fused silica glass because of the flexibility and high-temperature capabilities. The purpose of the polyimide coating is to give the column added strength. The stationary phase may be cross-linked or bonded. Cross-linking increases the lifetime of the column by reducing column bleed at high temperatures. Also, it is postulated that the viscosity of the stationary phase is increased due to cross-linking. It was suggested that it is more difficult for the analyte to diffuse through the inner network of the cross-linked film.

Compounds that could not previously be separated with packed columns such as isomers have been resolved easily using capillary columns. A theoretical plate is one solute equilibrium between the stationary and the mobile phases. The more theoretical plates achieved the better the separation. The maximum number of theoretical plates for a packed column is approximately 10,000. Whereas, capillary columns generate up to 500,000 plates easily. Moreover, separations using capillary columns are faster than their packed counterparts due to the fact that higher flow rates can be used. A detailed discussion of capillary theory will be presented in Chapter 2.

Today, capillary columns are manufactured in a wide range of column diameters and film thicknesses. The diameter range from 50μm to 530μm. Due to their large sample capacity wide diameter columns are better for trace analysis. Unfortunately, as the diameter of the column is increased; mass transfer in the mobile is increased which results in peak broadening.

Conversely, the practical advantages of narrow-bore columns is that they produce faster and more efficient separations than their wide-bore counterparts. An added benefit of narrow-bore columns is that they can achieve superb resolution of isomers. The disadvantage of using narrow-bore columns is that very small samples sizes must be injected.

Sample volume is a critical factor in capillary gas chromatography. The larger the sample volume the fewer theoretical plates achieved. This phenomena is true for both wide or narrow diameter columns. In an attempt to overcome this factor columns with thick films were developed. As the stationary phase thickness is increased the capacity of the column is also increased. The stationary phases are classified into three major flavors and they are as follows: polar, semi-polar, and non-polar. The functionality of the analyte and its volatility determines the type of stationary phase and film thickness to be used (5). There is one basic rule to remember when selecting a stationary phase; that is "like dissolves like".

According to Ettre, there are three main reasons for employing columns with thick films (6). The first, as one increases the films thickness the capacity factor is also increases which mean less plates are required to resolve any given peak pair when compared to thin films (6). Moreover, capillary columns are already limited in their sample capacity. By increasing the film thickness the sample capacity increases. Also, the solutes interaction with the inner surface of the column is reduced. It has been argued that the solute does not completely partition through thick films. So this results in less column activity. Disadvantages of increasing film thickness are higher column bleed when performing high temperature analysis and mass transfer in the stationary is increased which leads to band broadening.

Unfortunately, it is not possible to analyze high-boiling compounds at lower temperatures. Many industrial firms, such as petroleum companies, have the need for high-temperature analyses. However, due to the substantial amount of column bleed it is not practical to employ thick

films when performing high-temperature analysis. As a result , thin film columns became popular for high temperature work. The major advantages of using thin films are that they can withstand high temperatures with experiencing very little column bleed and their analysis times are shorter. Also, mass transfer in the stationary phase is minimized; which results in higher column efficiency. However, when using thin film columns the solutes have more possibility for interactions with the column surface.

When using thin films the mass transfer term in the stationary phase becomes negligible and the mass transfer term in the mobile phase dominates. It was envisioned that when using thin films at high temperatures the column efficiency could be improved by using hydrogen. Due to the higher diffusivity of hydrogen, it was also envisioned that using hydrogen would maximize the column efficiency because there would be faster mass transfer in the mobile phase.

The object of this study is to explore the role of carrier gas viscosity on column efficiency particularly when employing thin films. For most gases, the viscosity increases sharply with temperature. Of all the carrier gases used in capillary gas chromatography, hydrogen is the least viscous followed by nitrogen and then helium. We expect due to hydrogen's lower viscosity and higher diffusivity it should be the carrier gas of choice. Especially, when column parameters such as thin films and larger diameters dictate that mass transfer in the mobile is the dominate property. Hydrogen is less expensive than helium and can reduce laboratory operating cost by thousands of dollars per year.

Theory

An important fact to remember when using gas chromatography is that a wealth of information can be extracted from a single chromatogram. Data such as retention time, capacity factor, and the number of theoretical plates of a solute may be readily calculated.

The retention time describes the solutes interaction with the stationary phase and the mobile phase. The retention is the sum of the adjusted retention time and the dead time of the column. The equation for the retention time is shown below

$$t_r \equiv t'_r + t_m \qquad \textbf{eq. 1}$$

Where, t_r= retention time
t'_r= adjusted retention time
t_m= dead time

The adjusted retention time is represented by t'_r. The adjusted retention time represents the amount of time the solute spends in the stationary phase and the dead time is the amount of time the solute spends in the mobile phase. It is important to remember that every analyte spends the same amount of time in the mobile phase. However, the difference is the time spent in the liquid phase and this is what makes the adjusted retention time an important parameter in gas chromatography. The adjusted retention time is used in most chromatographic calculations with the exception of the efficiency calculations. An example of how to calculate the t_r, t'_r and t_m from raw chromatographic data is shown in figure 2.

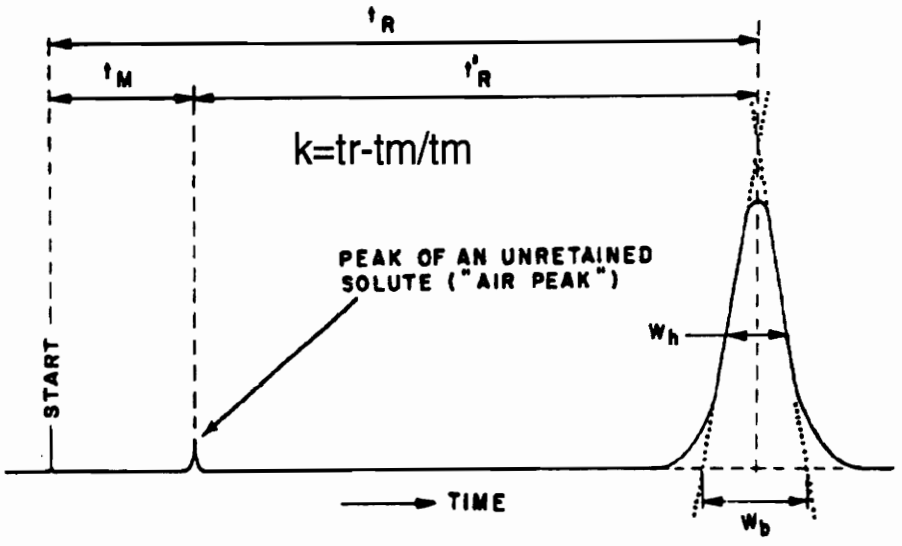

Figure 2: Calculation of retention data from a chromatogram (7)

Precise dead time measurements are very important in capillary gas chromatography because most experimental calculations require the dead time, for example, the capacity factor, the linear gas velocity, and mass transfers terms in the Van Deemter/Golay equation just to mention a few. When the dead time calculations are incorrect it causes systematic error in these calculations.

The two most popular ways of determining the dead time are: (1) injecting an unretained substance such as methane and (2) mathematical extrapolation. Injecting methane is a very accurate means of determining dead time. Past experiments have shown that this method produces an experimental error of less than 2%. The mathematical extrapolation technique is also precise, however, this technique is time consuming and the result are not much better than the simpler method.

One important parameter in gas chromatography is to operate the column at the highest possible linear velocity without sacrificing column efficiency. This results in the shortest possible analysis time, which is

important when analyzing large number of samples. Again, the dead tine is used to calculate the linear velocity because it gives information about how fast the flow is through the column. The equation for calculating the linear gas velocity is shown below

$$\mu \equiv \frac{L}{t_m} \qquad \textbf{eq. 2}$$

Where, μ= linear velocity
L= column length
t_m= dead time

In order to have the highest possible column efficiency the linear velocity should be at the optimal linear velocity for the carrier gas. The optimum linear velocity for hydrogen is approximately 40-45 cm/sec, helium 30-35 cm/sec, and nitrogen 20-30 cm/sec. Obviously, the analysis time when using hydrogen is faster due to the higher flow rate capabilities and larger optimum range.

As the Golay plots illustrate, the highest efficiency can be attained when using nitrogen (lower HETP). However, the optimum linear velocity for nitrogen is very low. So, the analysis times when using nitrogen will always be longer than with hydrogen or helium. Hydrogen is the better carrier gas because high flow rates can be used with a minimal loss in column efficiency. This results in faster analysis times when using hydrogen.

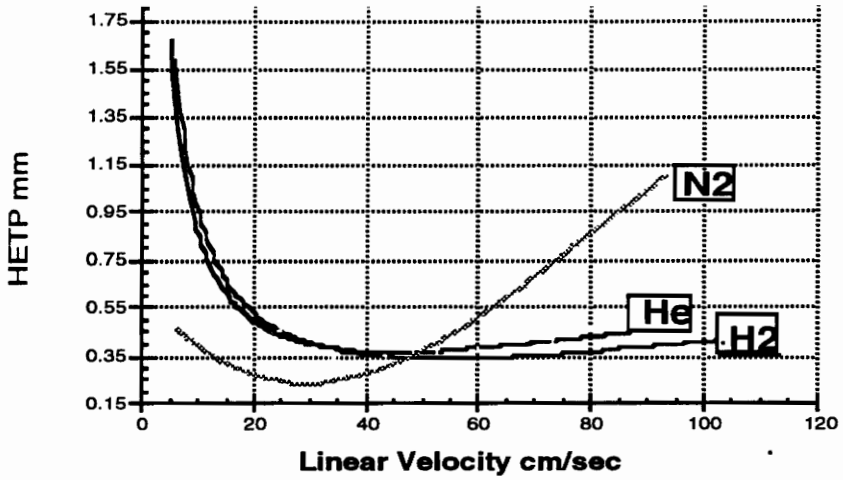

Figure 3: Golay plots for Hydrogen, Helium and Nitrogen

The adjusted retention time and the dead time are used to calculate the capacity factor. The capacity factors represents the distribution of the solute between the stationary phase and the mobile phase. The theory of separation in gas chromatography is that some analytes will be retarded longer by the stationary phase thereby having larger capacity factors. The longer a solute is retained by the stationary phase; the larger the capacity factor. The equation for the capacity factor is:

$$k' \equiv \frac{t_r - t_m}{t_m} \qquad \textbf{eq. 3}$$

If the capacity factor is large then the solute is greatly retarded by the stationary phase. The capacity factor changes when the temperature of the system changes, or the film thickness of the stationary phase is changed, or when the type of stationary phase used for the analysis is changed. When the temperature of the column is increased the capacity factor is decreased due to the higher vapor pressure of the analyte. If the film thickness of the column is doubled the capacity factor and the retention time will also double. The functionality's of the analytes will determine the best stationary phase to be used for the separation. The functionality of the

analyte should match that of the stationary phase as closely as possible for good retention. For example, non-polar stationary phases are more selective for non-polar compounds. Polar compounds will not partition well into a non-polar stationary phase.

The selectivity of a liquid phase describes how well it separates two compounds. The selectivity is the ratio of capacity factors for the two compounds. The equation is as follows:

$$\alpha = \frac{k'_2}{k'_1} \qquad \textbf{eq. 4}$$

where k'_1= capacity factor of the first solute

k'_2= capacity factor of the second solute

A large alpha means that the stationary phase is more selective for one compound. When the alpha value is large it means the compounds are easily resolved (8). The only way to change the selectivity is to change the type of stationary phase used, or the column temperature.

The resolution in capillary gas chromatography measures the degree of separation for two peaks (9). The optimum resolution between two peaks is 1.5. If the resolution is larger than 1.5 time is being wasted and this factor can be reduced by increasing the temperature or the mobile phase flow rate. However, if the resolution is less than 1.5 the peaks are overlapping.

$$R = \frac{2(\Delta T_r)}{W_1 + W_2} \qquad \textbf{eq. 5}$$

where

R = resolution

W_1 = width of the first peak

W_2 = width of the second peak

ΔT_r = difference in the retention times of the first and second solute

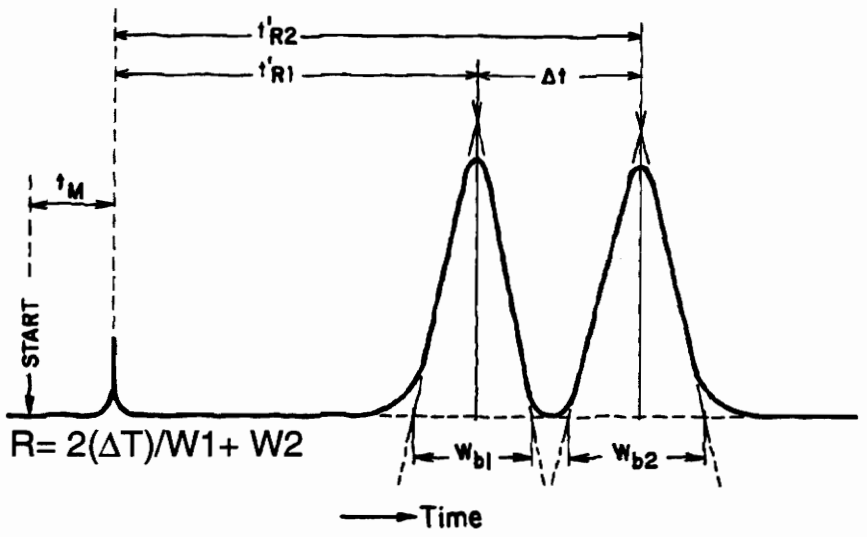

Figure 4: Calculation of the resolution from raw chromatographic data (7)

Several chromatographic factors influence the resolution and they are as follows: capacity factor, selectivity, and the number of theoretical plates. The selectivity is only a function of the type of stationary phase. A capacity factor greater than two is desired for all separations.

The higher the column efficiency; the less band broadening. This results in better separation of the solutes by producing "narrow" peaks. The master resolution equation better illustrates the relationship between column efficiency, capacity factor, and selectivity on resolution of the analytes.

$$R = \left(\frac{k}{1+k}\right)\left(\frac{\alpha-1}{\alpha}\right)\left(\frac{\sqrt{N}}{4}\right) \quad \textbf{eq. 6}$$

Where, k= capacity factor of the last peak
N= number of theoretical plates
α= selectivity

The thrust of this research is to determine the effects of carrier gas viscosity on column efficiency. We expect to prove that using hydrogen as the carrier gas will generate less resistance to mass transfer in the mobile phase. This results in a faster rate of diffusion of the analyte from the center of concentration in the mobile to the surface of the stationary phase. Because we are employing thin films mass transfer in the stationary phase is very fast. A combination of the previous factors should result in higher column efficiency. However, in order to achieve this goal one must possess a thorough understanding of column efficiency.

The efficiency of a GC column is determined by the number of theoretical plates that column is able to generate. The more plates the better the column. As stated previously, a theoretical plate is one solute equilibrium between the stationary phase and the mobile phase. The more theoretical plates achieved during a given separation the better the resolution of the sample components. This is illustrated by the role the column efficiency plays in the master resolution equation (eq. 6). The number of theoretical plates is usually represented by N.

$$N = 5.545\left(\frac{t_r}{W_{1/2h}}\right)^2 \quad \textbf{eq. 7}$$

$$N = 16\left(\frac{t_r}{W}\right)^2 \quad \textbf{eq. 8}$$

EFFICIENCY- -THEORETICAL PLATES, N

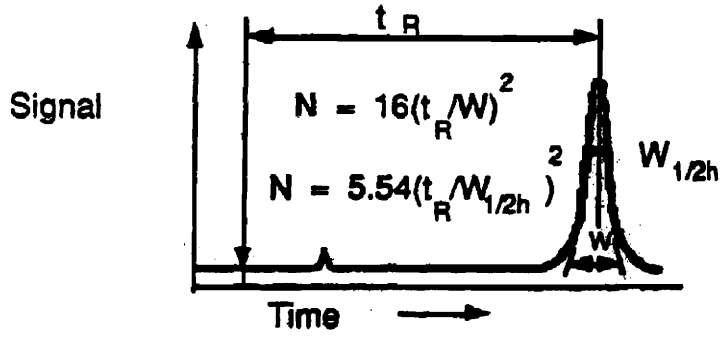

Figure 5: Calculation of efficiency from a chromatogram

There are two commonly used ways of calculating the number of theoretical plates of an analysis. The first is shown equation 7, where the width of the base at half-height is used. When using the width at half height the influence of peak tailing is minimized. Unfortunately, when using the width at the base of the peaks the integrator has several different methods of calculating the width. This causes inconsistencies within the calculation. However, when using the peak width at half-height the data from injection to injection is more consistent because width at half-height is always calculated in the same manner.

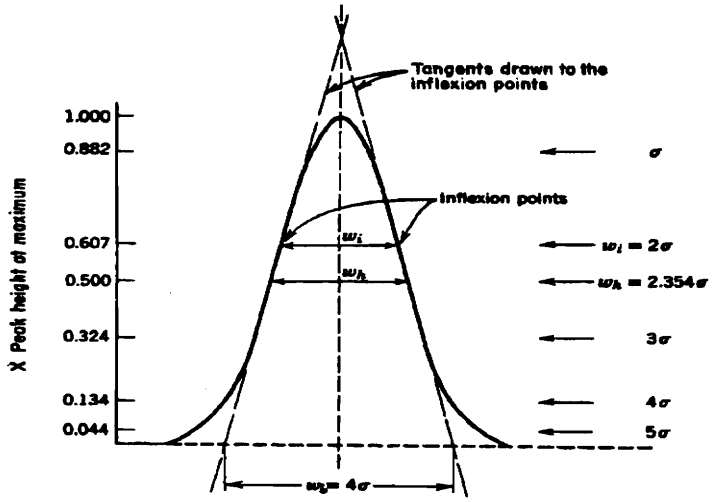

Figure 6: Calculation of the width at base and width at half-height from a chromatogram (2)

Column efficiency is also expressed by the height equivalent to a theoretical plate. HETP is that amount of column required to achieve one solute equilibrium between the stationary and mobile phases. It is calculated by dividing the length of column by the total number to theoretical plates achieved during the separation. For optimal performance the HETP should be minimized.

$$HETP = \frac{2Dm}{\mu} + \frac{11k^2 + 6k + 1}{24(1+k)^2}\frac{r^2\mu}{Dm} + \frac{2K\,d_f^2}{3(1+k)^2}\frac{\mu}{Ds} \qquad \textbf{Eq. 9}$$

Where, μ= linear velocity

D_m= diffusion coefficient in the mobile phase

k= capacity factor

r= radius of the column

d_f= film thickness

D_S= diffusion coefficient in the stationary phase

Increasing the temperature decreases band broadening in the stationary phase and the mobile phase. When the temperature is increased the diffusivity in the stationary phase is increased which reduces resistance to mass transfer. Also, the gas is affected when the temperature is increased due to the fact that it enhances longitudinal diffusion and increases the diffusivity of the carrier gas which results in faster mass transfer in the mobile phase.

Operating at the optimum linear velocity results in the highest possible efficiency. However, when using a multi-component sample the linear velocity is not optimized for each component. The greatest benefit of using hydrogen is that the column efficiency is not drastically affected by changes in the linear velocity. The optimum linear velocity is

determined by plotting the height equivalent to a theoretical plate versus the linear velocity. The minimum of this curve is the optimum linear velocity. Or, as shown below, the optimum linear velocity can be determined by plotting the column efficiency versus the flow rate.

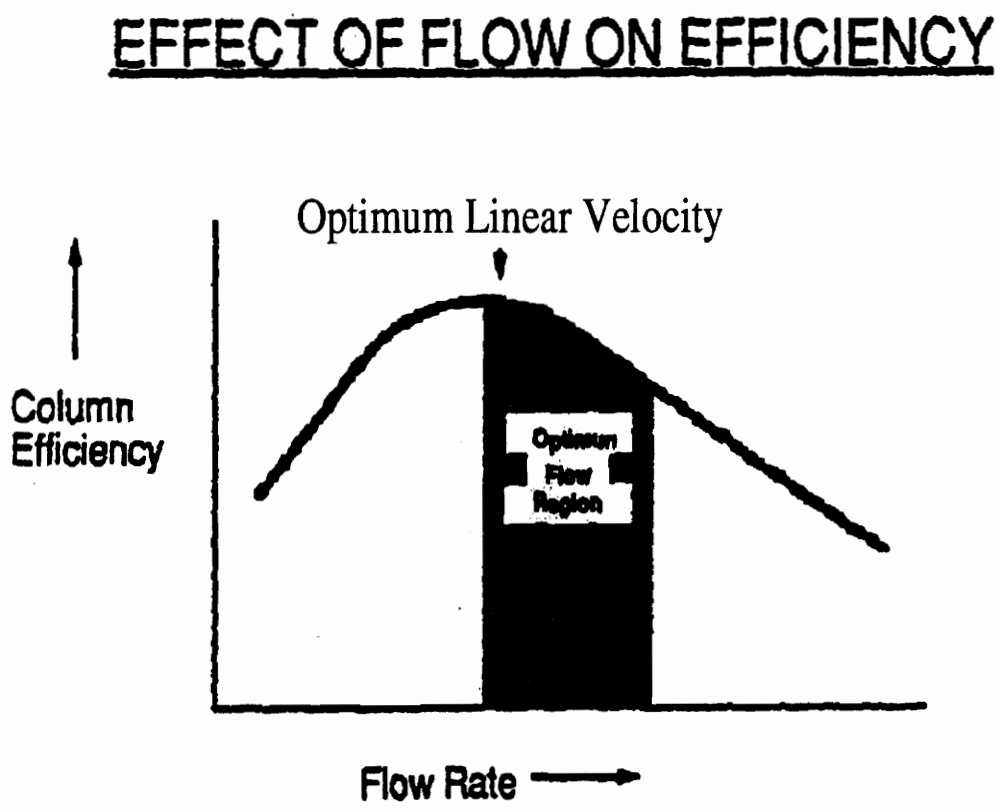

Figure 7: Effect of Flow rate on Column Efficiency (7)

Narrow-bore columns produced greater efficiencies than their wide-bore counterparts. This is due to the fact that mass transfer resistance in the gas phase is reduced. This directly results in a decrease in band broadening. Also, when using narrow-bore columns with thin films the height equivalent to a theoretical plate is roughly equal to the column diameter. Which means that the largest column efficiency is obtained when using a combination of a narrow-bore columns and thin film of stationary

phase. Due to fact that mass transfer in the stationary and mobile phases are minimized.

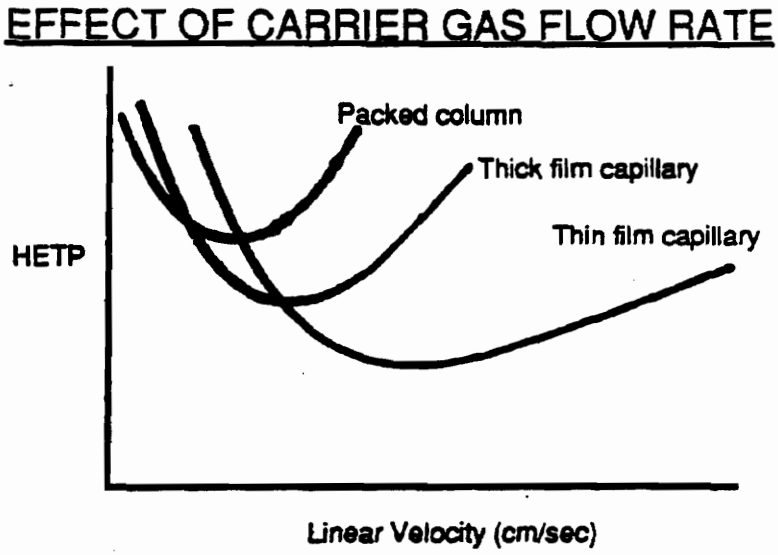

Figure 8: Relationship of Film Thickness to HETP (7)

In the Van Deemter equation, the HETP for a packed column is equal to the sum of the Eddy diffusion, the longitudinal diffusion, and the mass transfer terms:

$$HETP = 2\lambda d_p + \frac{2\gamma D_{gas}}{\mu} + \frac{8k' df^2}{\pi^2(1+k')^2 D_{gas}}\mu \qquad \textbf{eq. 10}$$

Where, H= height equivalent to a theoretical plate

λ =packing constant

d_p= particle diameter

γ= tortuosity factor

D_{gas}= Diffusion Coefficient

μ= linear velocity of the carrier gas

k= capacity factor

df= film thickness

π= constant

Eddy diffusion occurs when there are inconsistencies in the distances of the paths of the mobile phase flows. In packed columns the carrier gas flows through a tortuous channel system and lateral mass transfer can take place by a combination of diffusion and convection; the tortuous flow is responsible for the eddy diffusion coupled with diffusion in the gas phase (10). Band broadening results from the exchange of analyte between flow streams moving at different velocities. This causes band broadening because the vaporized sample molecules take different paths some longer than others. To minimize eddy Diffusion, columns should be packed tightly with particles of equal size with a uniform shape. With particles of uniform size and shape; irregular paths have less tendency to form (11).

When using packed columns the best way to minimize longitudinal diffusion is a fast flow rate and a high molecular weight carrier gas, both will inhibit diffusion in the mobile phase. Longitudinal diffusion increases with time. Using a high carrier gas flow rate will reduce the amount of time the solute spends it the column, thereby, decreasing the B-Term.

The resistance to mass transfer is divided into two parts: the resistance to mass transfer in the mobile phase and the stationary phase. When using packed columns mass transfer in the mobile phase is negligible and mass transfer in the stationary phase is the dominant factor. Mass transfer in the stationary phase is responsible for approximately 90% of the band broadening when using packed columns. This is due to the large stagnant pools of stationary phase. When the stationary phase is not uniformly coated the retention for some of the molecules are significantly larger than for others. This lead to band broadening and decreased column efficiency. Mass transfer in the stationary phase can be minimized when using small pellicular particles coated with a uniform layer of stationary phase.

The height equivalent to a theoretical plate equation (Golay Equation) for open tubular columns is as follows:

$$HETP = \frac{2Dm}{\mu} + \frac{11k^2 + 6k + 1}{24(1+k)^2}\frac{r^2\mu}{Dm} + \frac{2K d_f^2}{3(1+k)^2}\frac{\mu}{Ds} \qquad \textbf{eq. 11}$$

Where, μ= linear velocity
D_m= diffusion coefficient of solute in the mobile phase
D_S= diffusion coefficient of solute in the stationary phase
r= column radius
k= capacity ratio
d_f= film thickness of the stationary phase

The shortest representation of the Van Deemter equation is as follows:

$$A + B/\mu + (C_m + C_S)\mu \qquad \textbf{eq. 12}$$

Where, A= eddy diffusion
B= longitudinal diffusion
C_m= mass transfer in the mobile phase
C_S= mass transfer in the stationary phase
μ= linear velocity

The HETP equation for capillary columns consist of the following terms: longitudinal diffusion, resistance to mass transfer in the mobile phase, and the resistance to mass transfer in the stationary phase. The major difference between the Van Deemter and the Golay equations is the lack of an A term in the Golay equation and the addition of a C_m Term. Open tubular columns are not "packed" with particles; they are empty tubes whose inner surfaces are coated with a smooth and uniform layer of the stationary phase.

The longitudinal diffusion is simply the tendency of the solute band to diffuse perpendicularly away from the concentration center as it moves through the column. The longitudinal diffusion is usually represented by the letter "B". The equation for the longitudinal diffusion is shown below (eq. 11). The longer the sample spends in the column the wider the distribution of the component molecules. The longitudinal diffusion can be minimized by using a fast carrier gas flow rate. This one of the reasons why hydrogen produces better column performance; due to the fact that high flow rates can be obtained with a minimal loss in column efficiency.

$$B = \frac{2D_m}{\mu} \qquad \textbf{eq.13}$$

The diffusion coefficient of the carrier gas is calculated by taking half of the calculated B-term. As previously stated, a carrier gas with a large diffusion coefficient produces higher column efficiency. If there is an increase in temperature the diffusion coefficients increase, also. This due to the fact that the diffusivity of the gas increases with temperature. Conversely, as the molecular weight of the analyte increases the rate of diffusion in the gas phase decreases because it is easier for a smaller molecule to "move through" the gas phase than a larger molecule.

$$D_m = \frac{B\mu}{2} \qquad \textbf{eq. 14}$$

Mass Transfer in the mobile phase is a function of three chromatographic factors; capacity factor, column diameter, and the diffusion coefficient of the carrier gas. The C_m term can be minimized by using narrow-bore columns and by using a carrier gas with a large diffusion coefficient (D_m). Decreasing the column diameter reduces the path of diffusion from the column center to the wall. A carrier gas with a large diffusion coefficient is advantageous because it is easier for the

solute to diffuse to the wall. However, mass transfer in the mobile phase is only important when using thin films and wide diameter columns.

$$C_m = \frac{11k^2 + 6k + 1}{24(1+k)^2} \frac{r^2 \mu}{Dm} \quad \textbf{eq. 15}$$

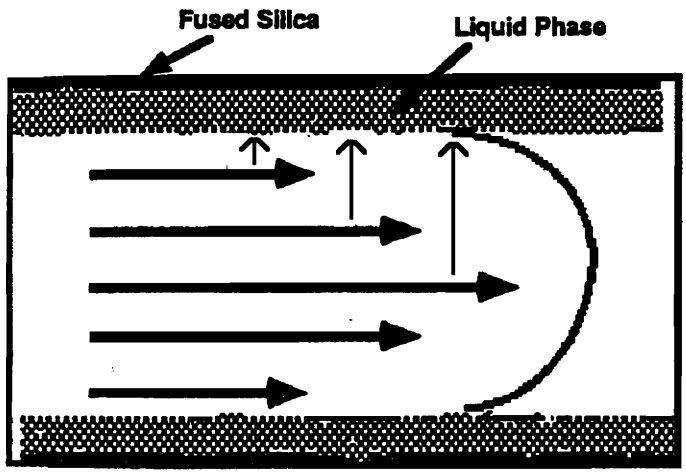

Figure 9: Mass Transfer in the Gas Phase (7)

The C_S term describes the resistance to mass transfer in the stationary phase. Resistance to mass transfer in the stationary phase contains the capacity factor, the film thickness and the diffusion coefficient in the stationary phase. This term is reduced by increasing the rate of diffusion in the stationary phase and by decreasing the film thickness. For thin films (df < 0.4μm) this term is very small.

$$C_s = \frac{2k d_f^2}{3(1+k)^2} \frac{\mu}{Ds} \quad \textbf{eq. 16}$$

The D_S term is a function of temperature and the molecular weight of the analyte. When the temperature is increased the diffusivity of the stationary phase is increased, which results in faster mass transfer of the analyte into and out of the stationary phase. When the molecular weight of the analyte increases, it becomes more difficult for the solute to diffuse

rapidly into the stationary phase. This results in an decrease of D_S which means more band broadening, which is bad!

When the film thickness is reduced, it produces a faster mass transfer in the stationary phase. There are pros and cons in using thin films and thicker films. The characteristics of the sample should determine which type of stationary phase employed. When analyzing extremely volatile compounds thick films produce better resolution. However, when analyzing high boiling compounds it is better to use thin films due to less column bleed at higher temperatures.

The objective of this research is to investigate the effects of carrier gas viscosity on column efficiency. Viscosity is a temperature dependent parameter: when the temperature of a gas is increased, its viscosity is also increased (12). Viscosity is a measure of the resistance of a liquid or gas to flow. The kinetic theory of gases relates the viscosity versus temperature by the following equation:

$$\eta = \frac{a(mkT)^{\frac{1}{2}}}{\pi\sigma^2} \qquad \textbf{eq. 17}$$

where η= Viscosity of the gas at T°K
m= mass of gas molecule
k= Boltzmann Constant
σ= molecular diameter
$\pi\sigma^2$= collision cross-section of rigid spherical molecule
a= constant

According to eq. 17, viscosity is independent of pressure and thus, of the density of the gas. It depends only on the temperature of the gas and its chemical nature. It should also be noted, that when using the same carrier gas a simple method for calculating the viscosity is by relating it an

exponential power "x" of the temperature. The variable x is a constant which differs for each carrier gas.

$$\frac{\eta_i}{\eta_\circ} = \left(\frac{T_i}{T_\circ}\right)^X \qquad \textbf{eq. 18}$$

Equation 17 is just an approximation and therefore it not precise. However, it was found that within a narrow temperature range, it describes fairly accurately the viscosity versus temperature relationship (13).

Understanding viscosity is important in the differences between hydrogen and helium. For example, viscosity is involved in understanding the relationship between the pressure drop of the column and the column flow rate. When the viscosity of the carrier gas is increased by higher temperature the pressure drop along the column increases which results in a slower flow rate for the same pressure. So, in the beginning of the column the flow rate is near the optimum flow rate, however, by the end of the column the flow rate is lowered drastically so that it is out of the optimum range of the Van Deemter plot. This ultimately leads to a decrease in column efficiency. The benefit of using hydrogen is that the increase in the viscosity with an increase in temperature is smaller than with helium or nitrogen. This results in hydrogen faster flow rates for hydrogen near the end of the column. The pressure drop across the column is related to the viscosity by the equation:

$$\Delta p = \frac{8L\eta\mu}{r_c^2} \qquad \textbf{eq. 19}$$

Where Δp= pressure drop
L= column length
η= viscosity
r_c= radius of the column
μ= linear velocity of the carrier gas

The Stokes-Einstein equation relates diffusivity to temperature, viscosity and to the size of the molecule:

$$D = \frac{RT}{6\pi r\eta N} \qquad \textbf{eq. 20}$$

Where R= gas constant
T= temperature (kelvin)
N= Avogadro's number
r= radius of the solute molecule
η= viscosity in Poise (g/cm*sec)
π= 3.14

For a given analyte, all constants can be consolidated into one: C.

$$D = C \times \frac{T}{\eta} \qquad \textbf{eq. 21}$$

It is important to know whether diffusivity will increase or decrease with temperature. To investigate this, the relationship between viscosity and temperature is necessary. With this relationship, the following can be proven:

$$\frac{\eta_i}{\eta_\circ} = \left(\frac{T_i}{T_\circ}\right)^X$$

$$\eta_i = \frac{T_i^X}{T_\circ^X} \times \eta_\circ$$

$$\eta_i = E \times T_i^X$$

$$D = C \times \frac{T}{E \times T_i^X}$$

$$D = \frac{T^1}{T^X}$$

$$D = A \times T^{1-X}$$

$$X < 1$$

The viscosity is only a function of temperature. Substituting this relationship in equation 19 yields the relationship of viscosity with temperature. The exponent (x) in the viscosity relationship is smaller than 1 for all carrier gases. This means that diffusivity will always increase with increasing temperature which ultimately results in faster mass transfer in the mobile phase. During the course of this research it was realized that the diffusivity increases more with temperature than viscosity. Hydrogen consistently demonstrates higher rates of diffusion in the gas phase at higher temperatures due to its lower viscosity and higher diffusivity.

Experimental

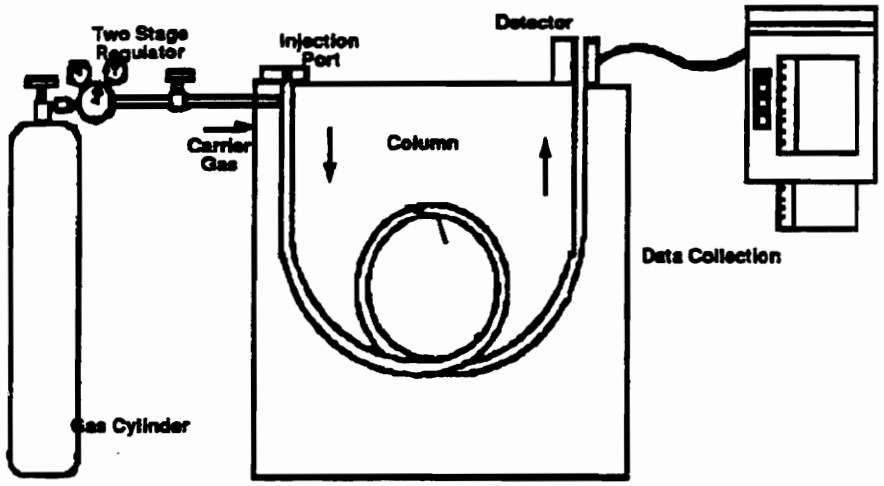

Figure 10: Schematic instrumentation of a Gas Chromatograph (7)

The instrumentation used in this research consisted of a Hewlett Packard model 5890 series II Gas Chromatograph with a Flame Ionization Detector. The gas chromatograph was coupled with a Hewlett Packard model 7673 autosampler. The flame ionization detector was supported by a Packard Instruments Zero Air Generator and a Packard Instruments model 9400 Hydrogen Generator. The hydrogen generator also provided the hydrogen which was used as the carrier gas in this research. The source of helium was 99.999% pure, GC grade helium.

The columns used were of HP-5 (5% Phenyl and 95% Methyl Polysiloxane) with an internal diameter of 0.2 millimeters and a length of 12 meters. The objective of this research required that mass transfer in the mobile phase be calculated when using both a thin film and a thick film. The chosen film thickness were 0.20μm and 0.50μm, respectively. However, other column characteristics changed as little as possible.

Table 1: Column Characteristics

Specifications	HP-5	HP-5
Length	12 meters	12 meters
film thickness	0.50μm	0.20μ
Stationary Phase	cross-linked	cross-lined

Homologous series of alkanes were used as samples: hexadecane, octadecane, eicosane, docosane, tetracosane, hexacosane, octacosane and triacontane. The alkanes were ordered from Aldrich Chemical Company (Milwaukee,Wisconsin). Hexane was used as the solvent consistently throughout all the analysis. The hexane was ordered from Fisher Scientific (Pittsburgh, Philadelphia). The concentrations were approximately 175 ppm for each sample component.

The split injection technique was used in this research. The split ratio was maintained at 50:1 for all injections. This split ratio was used in order to minimize the effects of discrimination among the analytes and to produce the maximum reproducibility. A autosampler was employed in this research to provide precision in the volumes of the solute injected. The Van Deemter plots were constructed by taking the average of the HETP value and the standard deviation of these data points were used to calculate the error bars.

$$\bar{X} = \frac{N_1 + N_2 + N_3 + N_4}{4} \qquad \textbf{eq. 22}$$

$$sd = \sqrt{\frac{\left(\left|\bar{X} - X\right|\right)^2}{n-1}} \qquad \textbf{eq. 23}$$

The Van Deemter/Golay plots were constructed using Kaleidagraph software. The data points were fitted with the Golay equation for capillary columns (eq. 11) and the longitudinal diffusion term and the mass transfer terms were extracted.

$$HETP = \frac{2B}{X} + C * X$$

Where B= Longitudinal Diffusion

C= Combined Mass Transfer

x= Linear Velocity

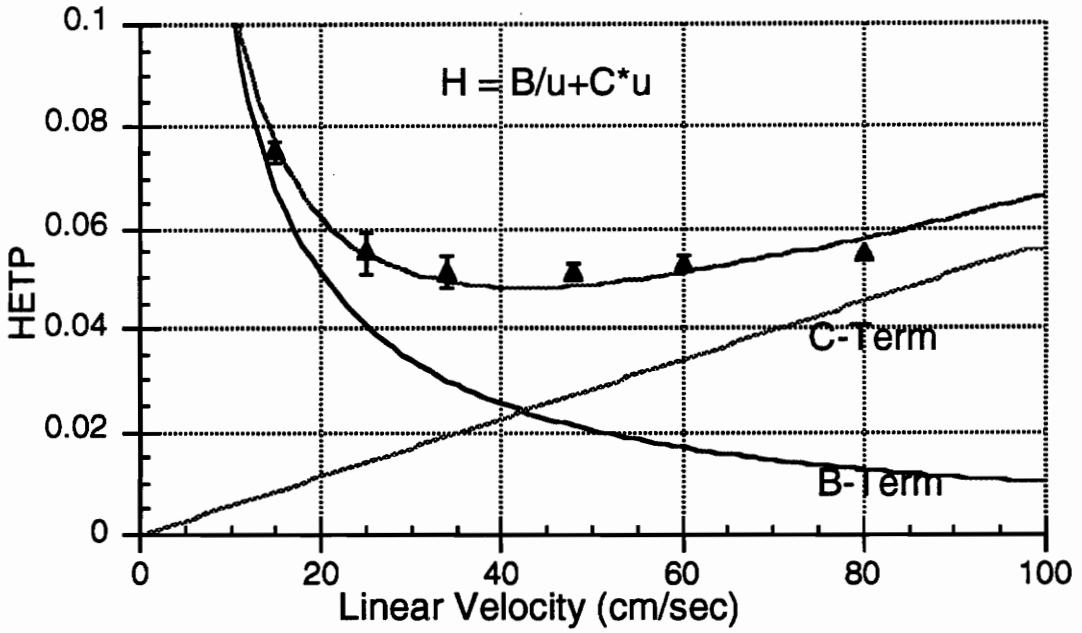

Figure 11: Golay Plot which illustrates the Longitudinal Diffusion (B-Term) and Mass Transfer (C-Term) for C_{26} at 250°C.

The legend includes the error associated with each term. The diffusion coefficients are calculated by taking half of the B-Term, so, the error associated with the diffusion coefficients are also roughly equal to half the calculated value (14). Mass transfer in the mobile phase can be calculated by substituting the unknown diffusion coefficient into equation 13. Now the mass transfer in the stationary phase can be calculated by subtracting the mass transfer in the mobile phase from the total C-Term.

Mass transfer in the mobile phase was calculated for the six replicate injections. The variance was calculated using equation 23.

. **Table 2:** GC Operating Conditions

Oven Temperatures	200 °C, 250 °C, and 275 °C
Injector Temperature	275 °C
Detector Temperature (**FID**)	300 °C
Volume Injected	1 µl
Sample Concentrations	175 ppm
Split Ratio	50:1

In order to calculate diffusion coefficients, isothermal analysis must be performed to eliminate pressure drops and changes in viscosity of the carrier gas. Operating temperatures were chosen based upon the changes that occurred in the gases viscosity . According to **figure 1,** at the chosen temperature range there is a dramatic increase in the viscosity of the carrier gas. Also, the analysis time played an important role in choosing the temperature range. We needed to elute as many components as possible within a fairly short analysis time.

The Van Deemter plots were constructed by maintaining constant chromatographic conditions, such as, injection volume, split ratio, and the column type while changing the linear velocity of the carrier gas. The basic theory behind the Van Deemter/Golay Plots are that the efficiency changes at different linear velocities. And a Golay curve is constructed in order to determine precisely what flow rate produces the best column efficiency. The minimum resolution acceptable for this research was baseline resolution of 1.5.

Results and Conclusions

Part 1: Diffusion Coefficients

The first task in completion of the research objectives was to calculate the diffusion coefficients for the analytes in our solutions. The diffusion coefficients for hydrogen at 200°C, 250°C, and 275°C will be discussed followed by helium. The diffusion coefficients in the mobile phase are equal to half of the longitudinal diffusion value. The diffusion coefficients are affected by the molecular weight of the analyte, the type of carrier gas, and the temperature.

As the molecular weight of the analyte increases the diffusion in the gas phase decreases. It is simply easier for smaller molecules to diffuse through the mobile phase, therefore, their rate of diffusion is faster. The larger the molecule the more resistance to mass transfer the molecule experiences; so the rate of diffusion is slow.

Characteristics of the carrier gas, such as, the molecular weight and the viscosity affect the diffusion coefficients. Therefore, the diffusion coefficients are greatest when using hydrogen, followed by helium, and then nitrogen.

The diffusion coefficients increase with increasing temperature due to an increase in the diffusivity of the carrier gas. All diffusion coefficients are in units of cm^2/sec.

Table 3: Diffusion Coefficients and Standard Errors for Alkanes Hydrogen at 200°C

carbon number	B-Term (cm^2/sec)	Error	D_m (cm^2/sec)	Error
18	.860	.042	.43	.021
20	.678	.018	.34	.009
22	.618	.012	.31	.006
24	.599	.030	.30	.015

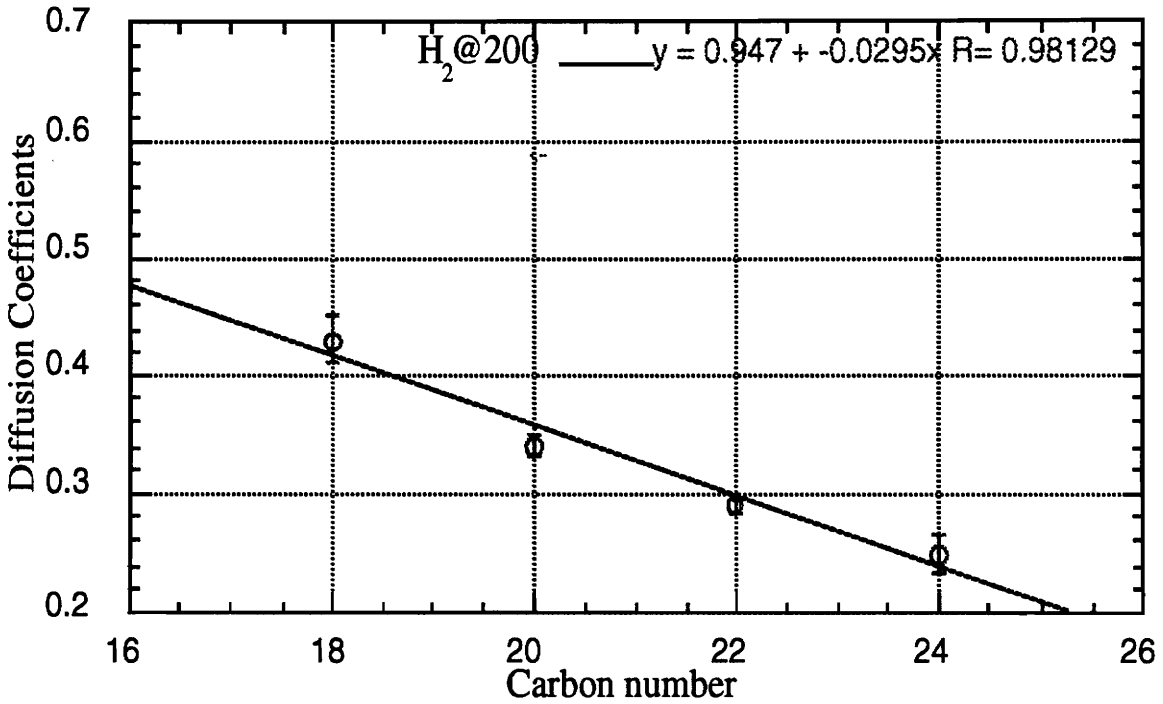

Figure 12: Shows linear relationship between the Diffusion Coefficients and Carbon Number for Hydrogen at 200°C

Table 4: Diffusion Coefficients for Hydrogen at 250°C

Carbon Number	B-Term	Error	Diffusion Coefficients	Error
20	1.22	.088	.61	.044
22	1.28	.140	.64	.070
24	.94	.082	.47	.041
26	.90	.072	.45	.038

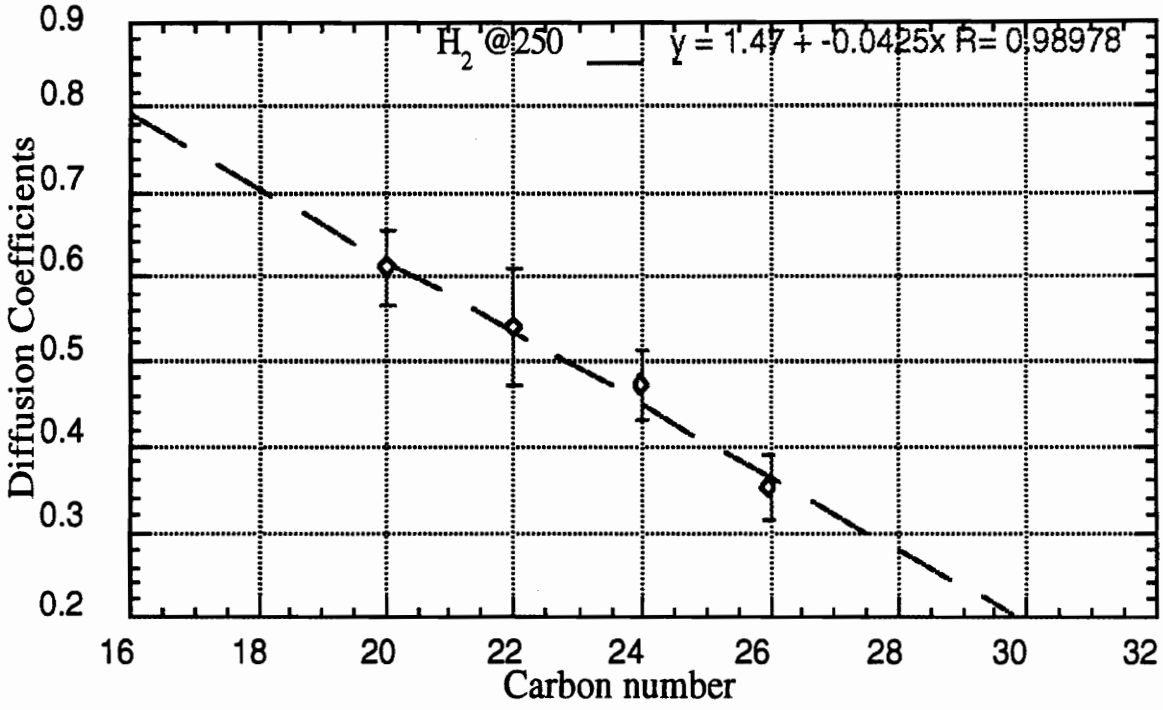

Figure 13: Relationship between the Diffusion Coefficients and Carbon Number of Hydrogen at 250°C

Table 5: Diffusion Coefficients and the Errors for Hydrogen at 275°C

Carbon Number	B-Term	Error	D_m cm^2/sec	Error
24	1.88	.078	.94	.039
26	1.76	.045	.88	.023
28	1.26	.040	.63	.020
30	1.18	.067	.59	.033

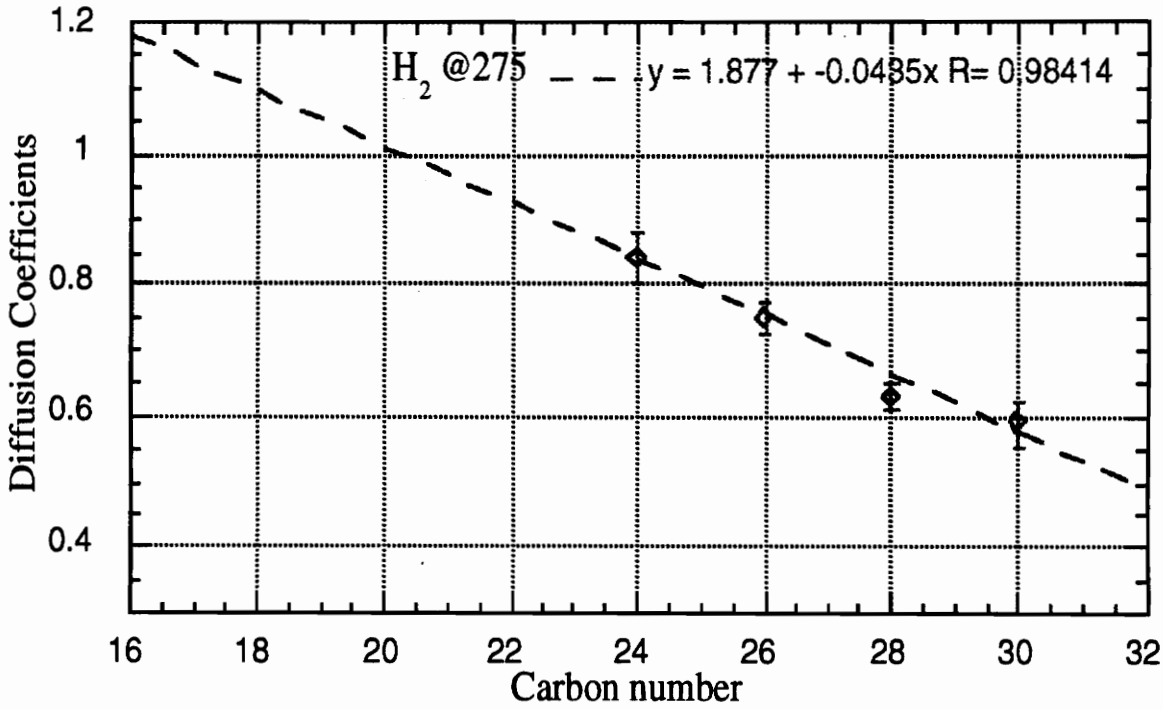

Figure 14: Diffusion Coefficients for Hydrogen at 275°C

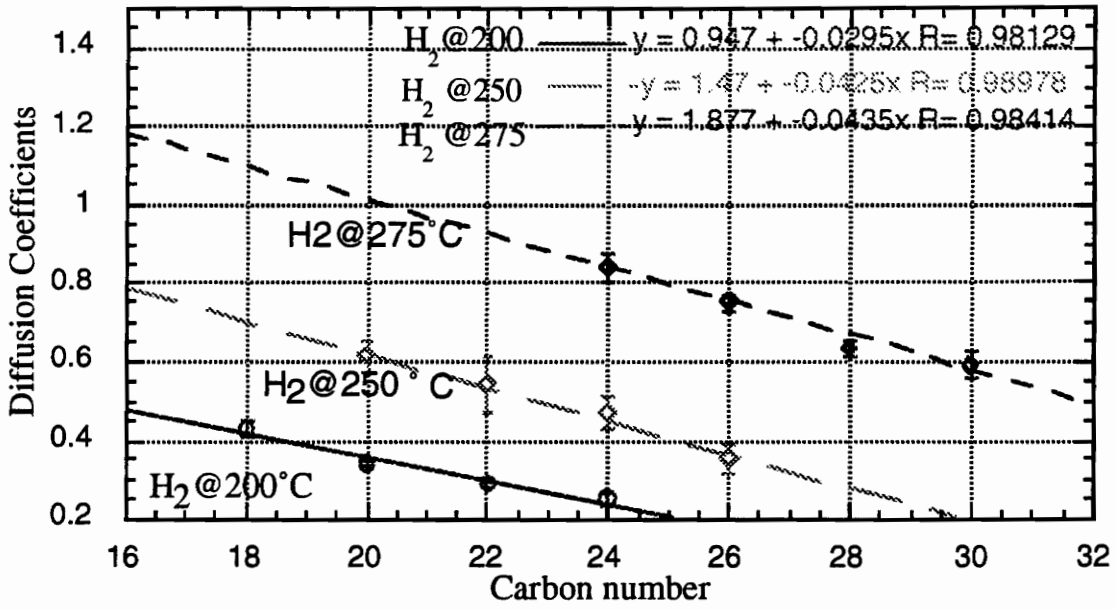

Figure 15: Diffusion Coefficients of Hydrogen at 200°C, 250°C, and 275°C

The graphs of the diffusion coefficients versus carbon number clearly follow the already established trend where the diffusion coefficients decrease with increasing molecular weight and increase with temperature. The correlation coefficient of this data is r= 0.98, so, a good linear fit was obtained for the three curves. In comparing the diffusion coefficients, it was expected that the slopes of the regression equations for hydrogen at 200°C. 250°C, and 275°C would be the same.

Diffusion Coefficients for Helium at 200°C, 250°C, and 275°C

The diffusion coefficients for helium were calculated in the same manner as for hydrogen. The same trends are expected. The diffusion coefficients should decrease with molecular weight and increase with temperature. However, we expect the diffusion coefficients of helium to be lower than the diffusion coefficients calculated for hydrogen due to heliums higher viscosity.

Table 6: Diffusion Coefficients for Helium at 200°C

Carbon number	B-Term	Error	Diffusion Coefficients	Error
18	.492	.034	.246	.017
20	.382	.032	.191	.016
22	.282	.034	.141	.017
24	.204	.028	.102	.014

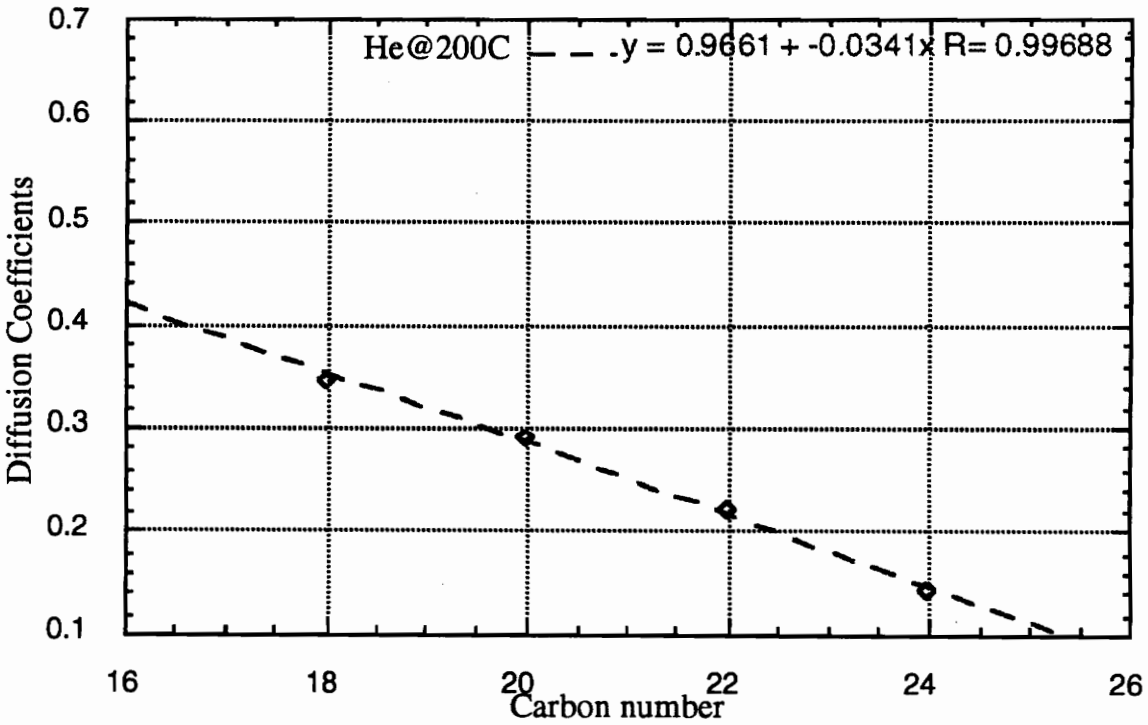

Figure 16: Diffusion Coefficients for Helium at 200°C

Table 7: Diffusion Coefficients for Helium at 250°C

Carbon Number	B-Term	Error	Diffusion Coefficient	Error
22	.794	.0306	.397	.0153
24	.690	.0438	.345	.0219
26	.564	.098	.282	.049
28	.526	.0432	.263	.0216

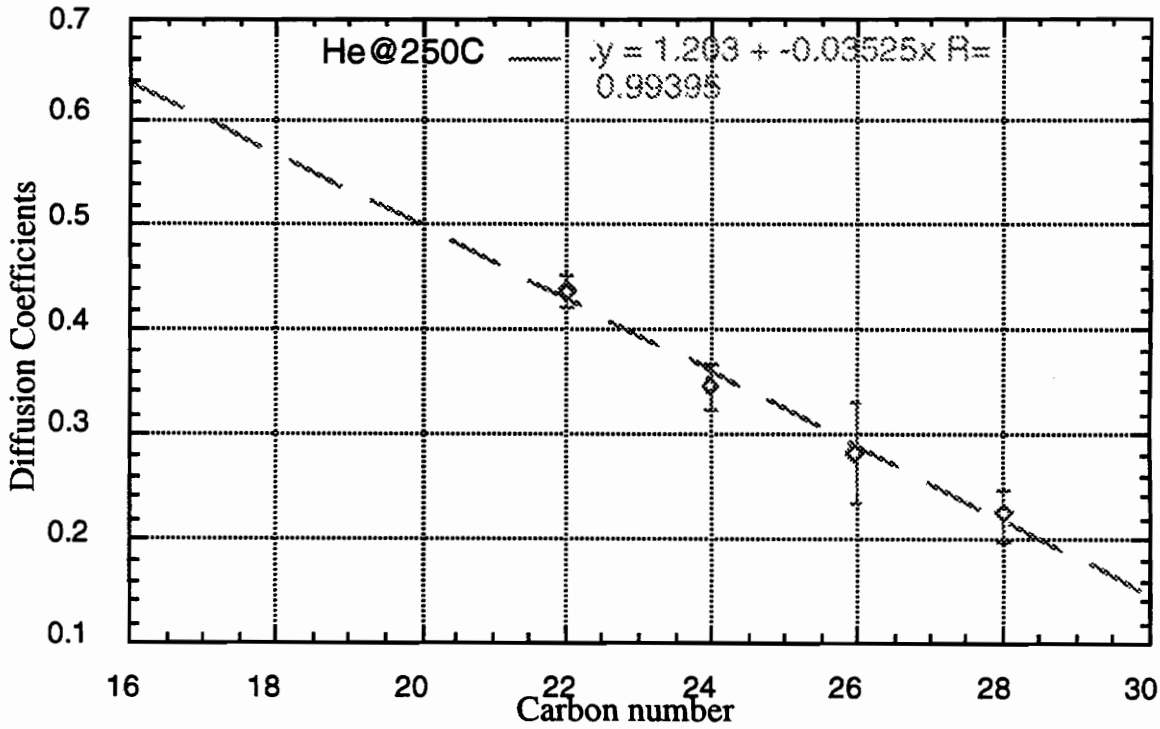

Figure 17: Diffusion Coefficients for Helium at 250°C

Table 8: Diffusion Coefficients for Helium at 275°C

Carbon Number	B-Term	Error	Diffusion Coefficients	Error
24	1.50	.066	.75	.033
26	1.39	.028	.699	.014
28	1.08	.044	.541	.022
30	0.99	.049	.495	.025

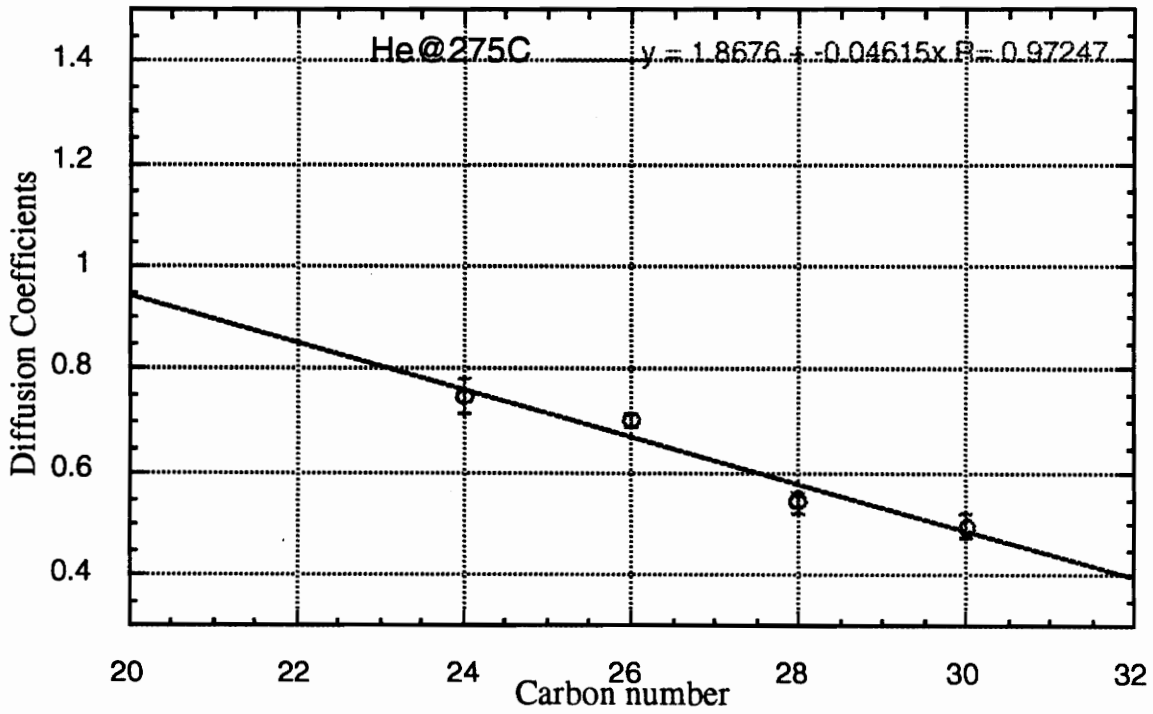

Figure 18: Diffusion Coefficients for Helium at 275°C

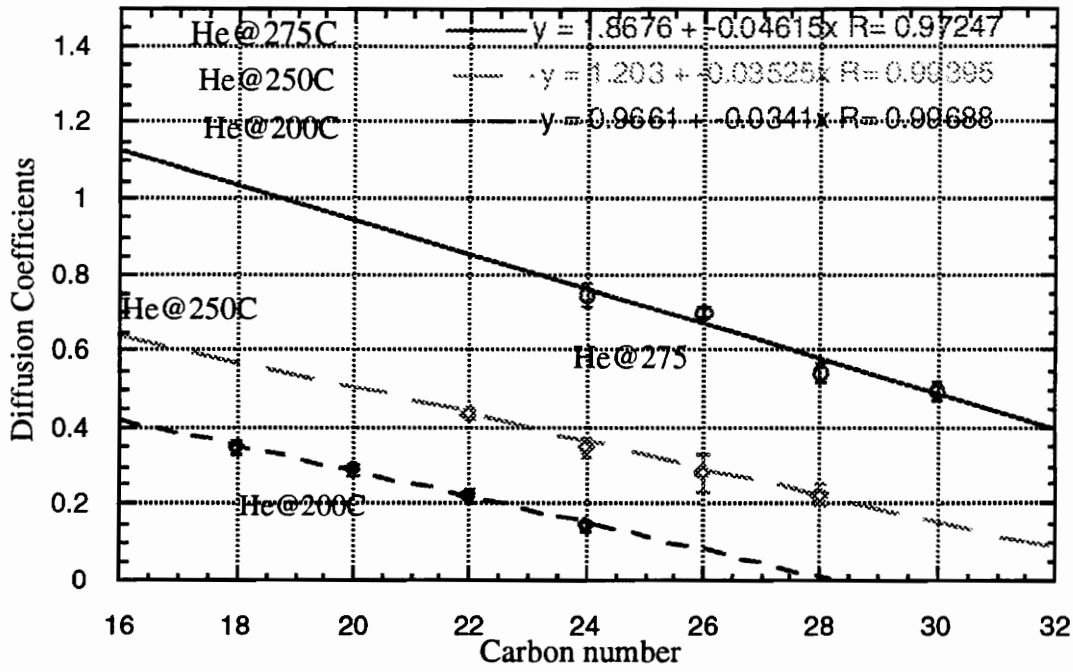

Figure 19: Diffusion Coefficients for Helium at 200°C, 250°C, and 275°C

The data for helium exhibits a good linear fit. The correlation coefficients for the curve fits are r=.98. However, there is some variation in the slopes of the curves.

Comparison of Diffusion Coefficients

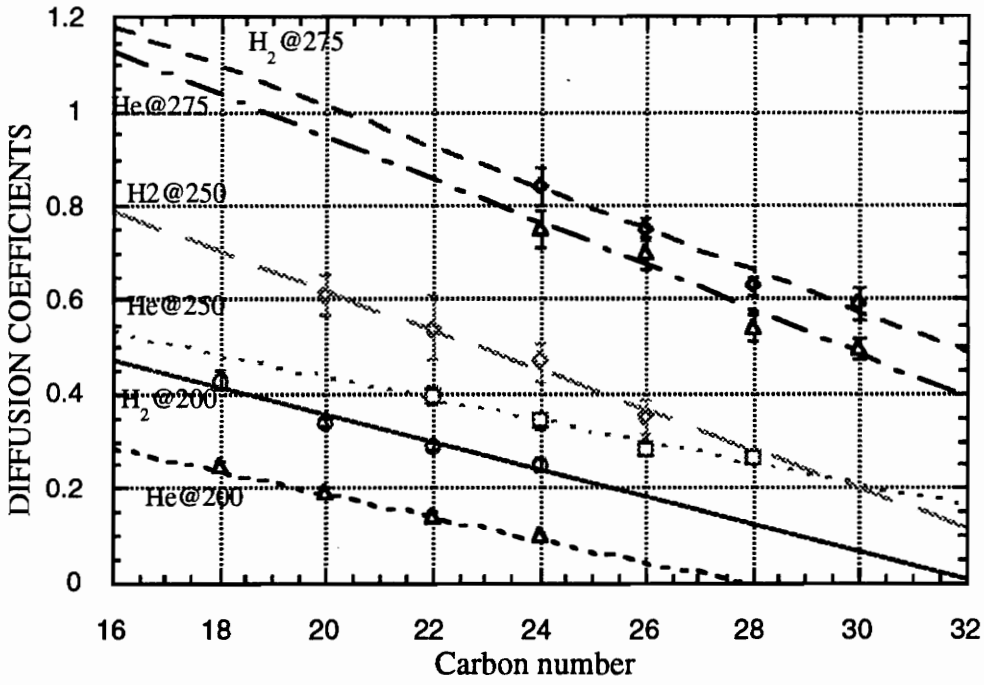

Figure 20: Diffusion Coefficients for Hydrogen and Helium at 200°C, 250°C, and 275°C for Alkanes

The data for hydrogen and helium follow the previously established trends where the diffusion coefficients increase with temperature and decrease as the molecular weight increases. However, hydrogen consistently produced larger diffusion coefficients. This higher rate of diffusion will reduce the amount of time required for the solute to diffuse from the center of the column to the surface of the stationary phase which results in increased column efficiency.

Unexpectedly, the curves for helium at 250°C and hydrogen at 250°C intersect. This is probably due to experimental error because the line intersects outside of the experimental range. A problem is the lack of literature available concerning the experimental values of the diffusion

coefficients, particularly, for higher molecular weight compounds. So, it is not possible to calculate the % error on these data points.

A two factor ANOVA was performed to determine whether the precision of the slopes of our lines were statistically different with varying temperature and whether the precision of the slopes are statistically different with respect to hydrogen and helium.

H_o: The precision of the slopes are not statistically different at varying temperatures

H_1: The precision of the slopes are statistically different

F_{cal}= .01
F_{crit}= 3.325

Since, Fcal is lower than Fcrit the null hypothesis was retained. There is not a significant difference in the precision of the slopes.

H_0: There is no significant difference between the precision of the slopes of hydrogen and helium

H_1: There is a significant difference between the precision of the slopes of hydrogen and helium

F_{cal}= .125
F_{crit}=4.102

Fcal is less than Fcrit, so, the null hypothesis is retained there is not a significant difference between the precision of the slopes of hydrogen and helium.

The slopes of hydrogen and helium should be different because helium increases in viscosity more with temperature. A t-test at the 95% confidence level was performed in order to compare the slopes of the regression curves. The error on the regression curves was calculated using Statview software. The formula for comparing two means is as follows:

$$S_p = \sqrt{\frac{n_1 - 1(Sb1)^2 + n_2 - 1(Sb2)^2}{n_1 + n_2 - 2}} \qquad \textbf{eq. } 25$$

Where, S_p= pooled standard deviation
n_1= data set for the first regression line
S_{b1}= Standard deviation of the slope of the first regression line
n_2= data set for the second regression line
S_{b2}= Standard deviation of the slope of the second regression line

Once the pooled standard deviation is calculated it can be substituted into the following equation determine T_{cal}:

$$T_{cal,\frac{\alpha}{2},\gamma} = \frac{b_1 - b_2}{S_p} \qquad \textbf{eq. } 26$$

Where, T_{cal}: calculated t-value
b_1: slope of the first regression line
b_2: slope of the second regression line
S_p: pooled standard deviation
$\frac{\alpha}{2}$: .05 (95% Confidence Interval)
γ= Degrees freedom of the data set

If the calculated t-value is less than the t-crit then the null hypothesis is accepted.

H_o: The slopes of Hydrogen and Helium are the same
H_i: The slopes of Hydrogen and Helium are significantly different

Table 9: T-Test at 95% Confidence Level of the slopes of Hydrogen and Helium at 200°C, 250°C, and 275°C

slope	$b_1(h)$	n_1	S_{b1}	b_2	n_2	S_{b2}	T_{cal}	T_{crit}
H_2/He at 200°C	.021	4	.006	.024	4	.001	.604	2.45
H_2/He at 250°C	.033	4	.013	.023	4	.003	.918	2.45
H_2/He at 275°	.065	4	.014	.046	4	.003	1.63	2.45

The T_{cal} for the slopes are all less than T_{crit}, so, the null hypothesis is retained is there in no difference in the slopes of hydrogen and helium at the different temperatures. It was predicted that the slopes would be different. Perhaps if there were more data, the test would be more powerful and a difference would be observed.

Part 2: Mass Transfer in Mobile Phase

Mass transfer in the gas phase was calculated in order to determine the effects of viscosity on column efficiency. It was expected that mass transfer in the mobile phase would be slower at higher temperatures due to the viscosity of the mobile phase and that C_m (sec) would be significantly faster when using hydrogen as the carrier gas. Our results were surprising.

Table 10: Mass Transfer Data for Hydrogen at 200°C, 250°C, and 275°C

Carbon Number	C_m 200(sec)	error	Carbon Number	C_m 250°C	error	Carbon Number	C_m 275°C	error
18	7.63e-05	3.21e-07	20	3.16e-05	2.43e-07	24	3.45e-05	1.14e-06
20	9.21e-05	1.98e-06	22	4.13e-05	8.98e-07	26	4.21e-05	6.91e-07
22	1.95e-04	4.4e-07	24	6.18e-05	5.23e-07	28	5.82e-05	2.82e-07
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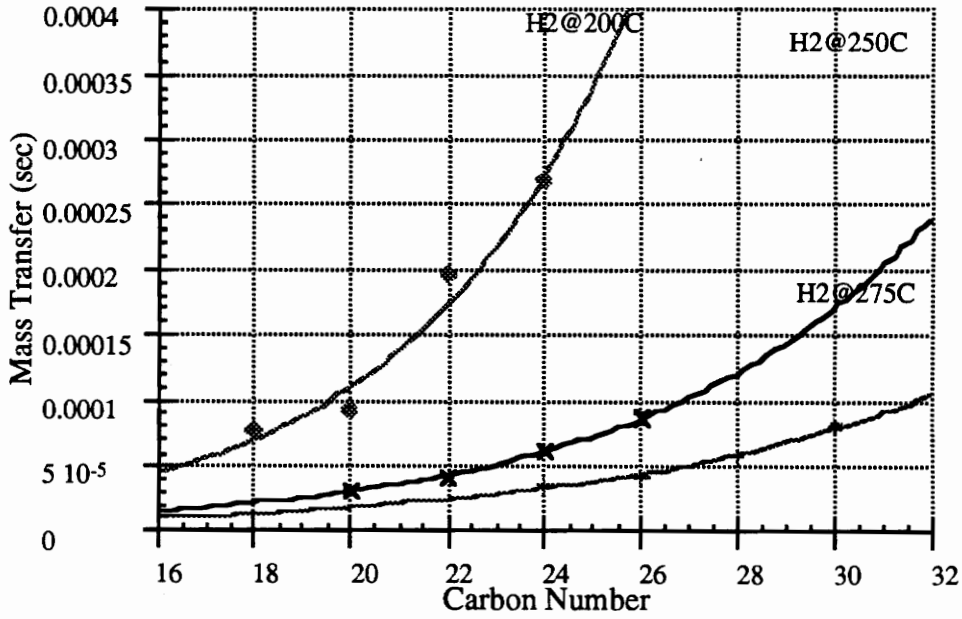

Figure 21: Mass Transfer Data for Hydrogen at 200°C, 250°C, and 275°C

Table 11: Mass Transfer Data for Helium at 200°C, 250°C, and 275°C

Carbon Number	C_m 200(sec)	error	Carbon Number	C_m 250°C	error	Carbon Number	C_m 275°C	error
18	1.3e-04	4.5e-06	24	9.9e-04	6.3e-06	24	4.36e-04	3.1e-06
20	2.0e-04	5.6e-06	26	1.4e-04	1.2e-06	26	6.89e-05	2.5e-06
22	3.0e-04	8.9e-06	28	2.0e-04	4.1e-06	28	9.82e-05	5.2e-06
24	4.3e-04	3.2e-06				30	1.2e-04	1.3e-06

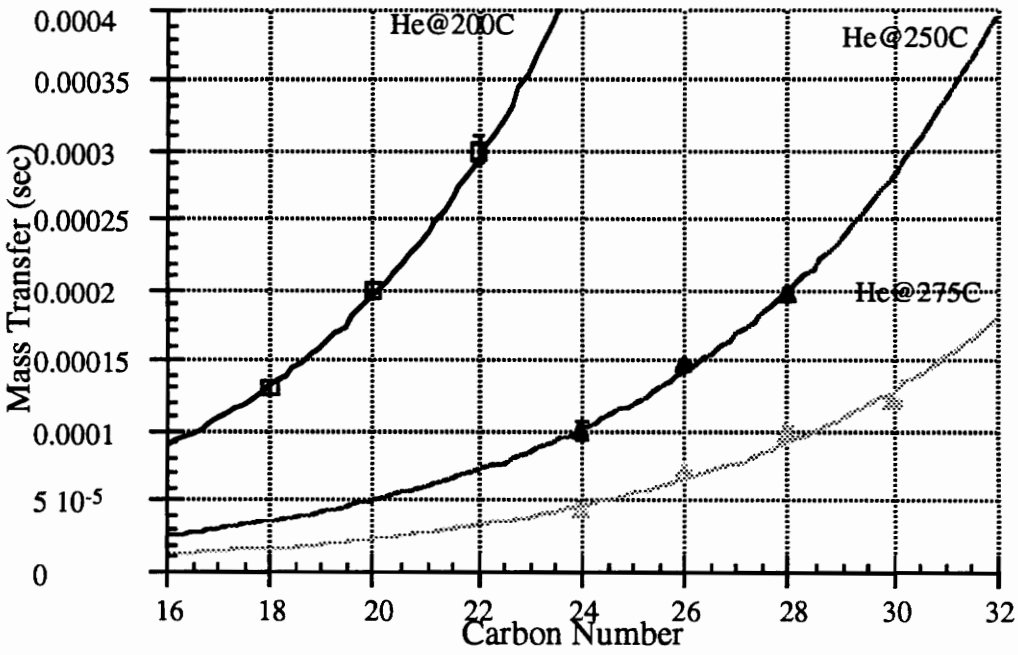

Figure 22: Mass Transfer Data for Helium at 200°C, 250°C, and 275°C

Discussion of Mass Transfer Data

The rate of mass transfer in the gas phase was calculated by substituting the diffusion coefficient for each solute into eq. 15.

$$C_m = \frac{11k^2 + 6k + 1}{24(1+k)^2} \frac{r^2 \mu}{Dm}$$

Mass transfer in the mobile phase is a function of capacity factor, column radius, and the diffusion coefficient of the solute in the mobile phase. The mass transfer data illustrates that when using hydrogen as a carrier gas the rate of mass transfer is consistently faster than that of helium. Due to the larger molecular diameter of helium it is more difficult for the solute molecules to penetrate the gas layer, therefore, the rate of diffusion is slower than hydrogen.

The C_m was calculated using Microsoft Excel 6.0 where all the raw chromatographic data was organized. The mass transfer data is expressed in units of time (second).

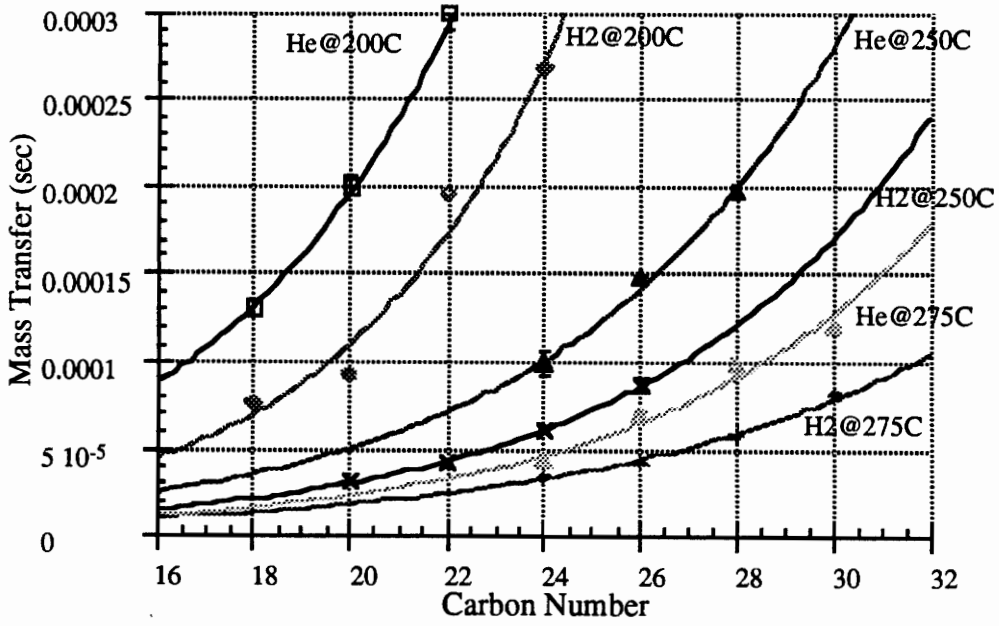

Figure 23: Mass Transfer Data for Hydrogen and Helium at 200°C, 250°C, and 275°C

The data clearly shows the rate of mass transfer in the gas phase increases with temperature and decreases with molecular weight. One would expect the rate of mass transfer to decrease with increasing temperature due to the increased viscosity of the carrier gas. It was envisioned that the more viscous the mobile phase the slower the rate of mass transfer in the gas phase. However, when the temperature increases the diffusivity of the carrier gas increases more than the viscosity which results in 54% faster rate of mass transfer in the mobile phase for eicosane in hydrogen at 200°C. So, the diffusivity of the carrier gas plays a more important role than viscosity on column efficiency.

As illustrated by figure 23, mass transfer exhibits an exponential relationship with molecular weight. In order to confirm, the log of the mass transfer was plotted versus carbon number. The data shows a linear relationship which confirms that a exponential relationship exist between mass transfer and molecular weight.

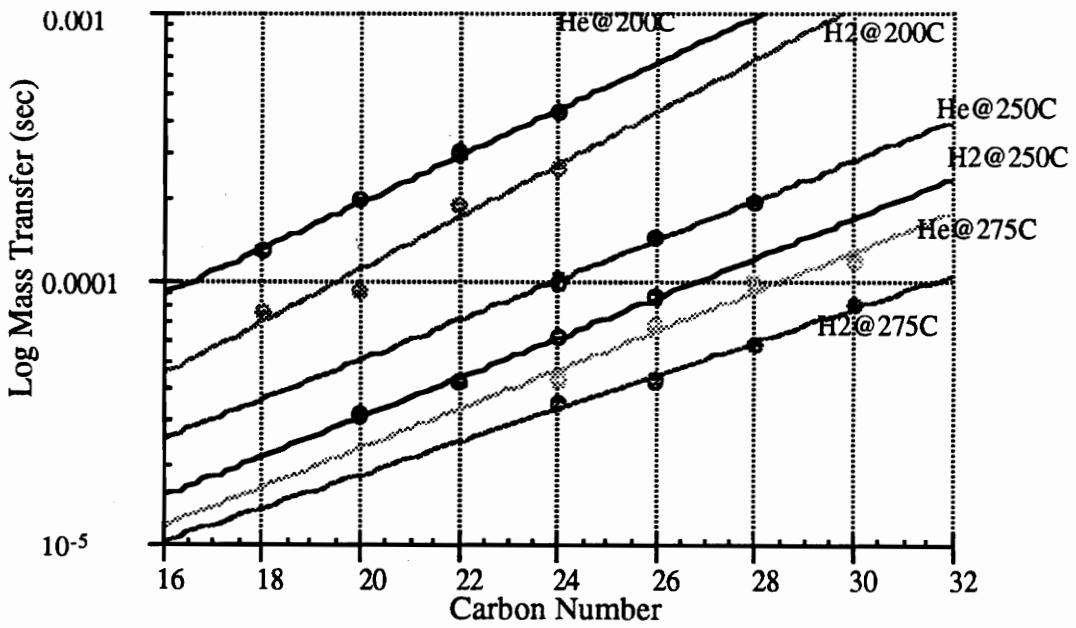

Figure 24: Log of Mass Transfer Data for Hydrogen and Helium at 200°C, 250°C, and 275°C

Conclusions

Throughout this report Van Deemter plots were used as a means to measure column efficiency. Which allow us to calculate both diffusion coefficients and resistance to mass transfer in the mobile phase.

Definitely, when using thin films, mass transfer in the stationary phase becomes negligible and mass transfer in the mobile phase dominates. The primary goal in capillary gas chromatography is to produce as many theoretical plates as possible. Thus minimizing HETP which is desirable. This report proves that, when using thin films, hydrogen is the carrier gas of choice due to the faster diffusion in the gas phase and its lower viscosity. Initially, it was felt that there was a need to study the effects of carrier gas viscosity when employing a thick-film column. However, when using a thick film stationary phase mass transfer in the gas phase only represents <5% of the total C-term (15). Because resistance to mass transfer in the stationary phase is great the influence of the carrier gas is negligible. Which means it is not beneficial to use hydrogen when employing a thick film.

There is a 41% faster rate of mass transfer when using hydrogen rather helium as the carrier gas for eicosane at 250°C. Originally it was believed that hydrogen was a better carrier gas due to its lower viscosity. However, this research illustrates that the diffusivity increases more with temperature than the viscosity. Which results in faster mass transfer. This research shows that the diffusivity of n-alkanes in hydrogen is consistently greater than helium at a range of temperatures which explains why hydrogen is the better carrier gas.

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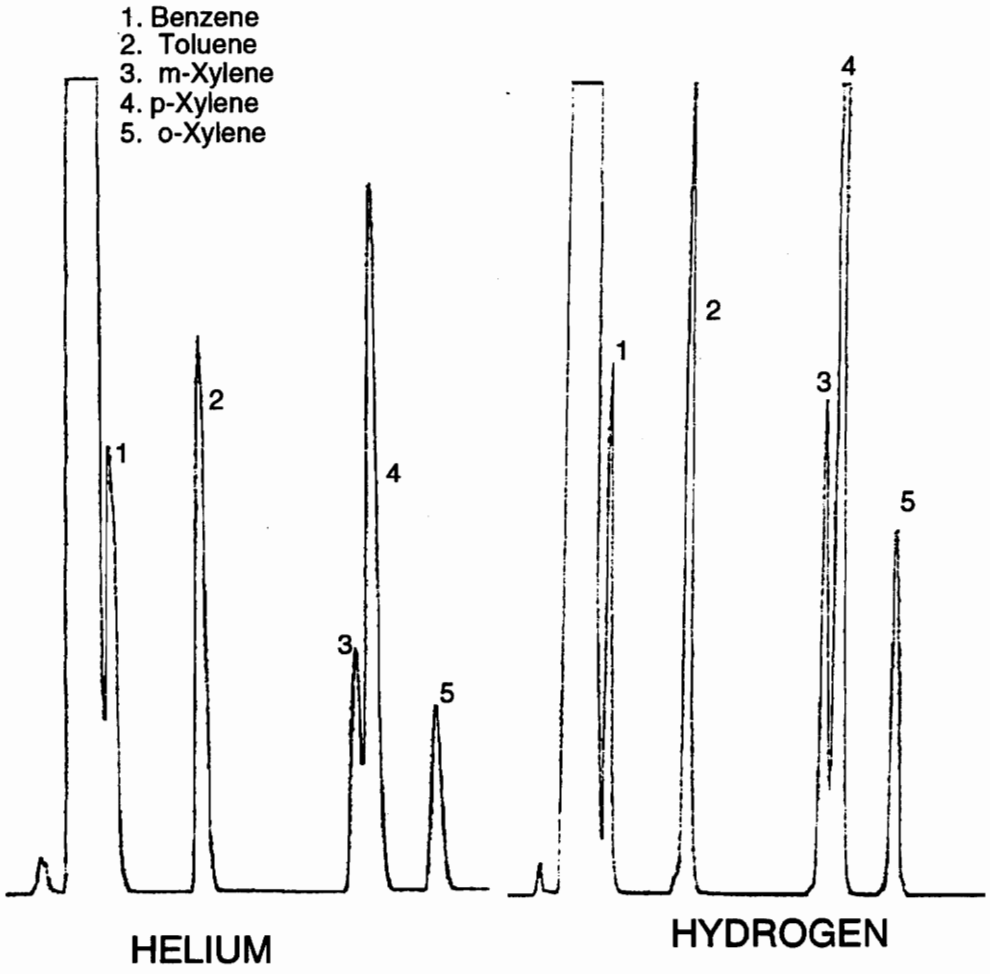
Appendix A - Chromatograms of the performance of Hydrogen and Helium



Appendix B - Efficiency Values for Hydrogen and Helium

Efficiency Comparison between Hydrogen and Helium

Temp.	Hydrogen (40cm/sec) N(plate num)	Helium (35 cm/sec) N(plate num)	% Improvement
40 °C	4.48 E4	4.47 E4	0.18%
60 °C	4.13 E4	4.08 E4	1.00%
80 °C	3.87 E4	3.70 E4	4.00%
100 °C	3.51 E4	2.04 E4	41.0%

* Efficiency values for Ortho-Xylene

Appendix C - Resolution values for Hydrogen and Helium

Resolution Comparison of Hydrogen and Helium

Temp.	H_2 (40 cm/sec) R	He (35cm/sec) R	% Improvement using hydrogen
40 °C	3.46	3.37	2.60%
60 °C	2.71	2.66	1.80%
80 °C	1.62	1.54	5.20%
100 °C	1.08	0.88	19.0%

*Resolution between m-xylene and p-xylene

Appendix D - Retention Times for Hydrogen and Helium

Comparison of Analysis Time between H_2 and He

Temp	H_2 (40cm/sec) Tr (min)	He (35 cm/sec) Tr (min)	% Faster analysis using Hydrogen
40 °C	6.48	9.17	42.0%
60 °C	2.98	4.18	40.0%
80 °C	1.66	2.35	41.0%
100 °C	1.14	1.58	38.0%

* Retention Time for Ortho-Xylene

Vita

Stephanye Dawn Armstrong was born May 19, 1971 in Winston-Salem, North Carolina. She graduated from Winston-Salem State University on May 8, 1993 with a Bachelor of Science in Chemistry. While there she became a proud and active member of The Alpha Kappa Alpha Sorority, Inc. In September 1993, she came to Virginia Polytechnic Institute and State University to pursue graduate study.