Investigation of Column and Instrumental Parameters for Fast Gas Chromatography Analysis

by

Karen N. Clark-Baker

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Approved:

Harold M. McNair, Chairman

Gary L. Long

Larry Taylor

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Karen Clark-Baker

Dr. Harold McNair, Chairman

Chemistry

(Abstract)

The objective of this study was to determine the capability and applicability of a conventional gas chromatography system for fast chromatography. Many gas chromatographic separations actually require much less time than is actually being spent on the analysis. Capillary columns are known to be very efficient due to the long lengths and thin stationary phase films. However, analysis can be done much faster if shorter column lengths and thinner stationary phases are used because the retention time is a function of the column length and stationary phase film thickness.

This study involves varying a number of column and instrumental parameters in order to determine their effect on the chromatographic analysis time. The parameters which were varied include the column stationary phase film thickness, the column length, the injection volume, the split ratio, the column position, the injector liner and the flow and temperature programming rates. The effect of column length on the average linear gas velocity was also determined by plotting the Golay equation for each. The Golay equation (12) illustrates the effect of the various column parameters on the column efficiency.

The most detrimental effect of decreasing the analysis time is the loss of resolution that may occur. Both shorter lengths and faster than optimum flow rates result in lower resolution. By careful adjustment of some column parameters the loss in resolution can be minimized.

The results of this research show that many gas chromatographic analyses require much less time than is actually spent and that a fast analysis can be achieved with little to no loss in resolution.

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Introduction

Gas chromatography (GC) is a major part of separation science and the principle involved may be defined as the partitioning of a component between two phases, a mobile gas phase and a stationary liquid phase. The principal advantages of GC are that it can be used for complete compositional analysis over a wide range of concentrations with excellent accuracy and reproducible analysis times. The scope of GC separations includes gases, liquids and solids and extends to the separation of complex mixtures, components closely related in chemical and physical structure and mixtures of various different compounds[1]. Since its introduction in 1954 GC has changed dramatically from the early packed columns containing solid support particles coated with a thick stationary phase to the more recent flexible fused silica columns with small internal diameter and very thin films. Instrumental improvements are constantly being made that expand the potential of gas chromatography. One limitation of GC is the relatively long analysis times required for sample separation which limits

the effectiveness of this analytical method. Another limitation is that only volatile compounds can be analyzed.

The first use of chromatography was in 1905 by Ramsey who separated a mixture of gases and vapors[2]. The following year Tswett used a chromatographic column to separate plant pigments. Seeing the colored bands he coined the term "chromatography" which literally means "color writing." In 1941 the concept of partitioning chromatography was enunciated by Martin and Synge who later received a Nobel Prize for their theoretical work. It was not until 1955, however, that the first commercial gas-liquid chromatographic instrument was introduced into the market[3]. Since its introduction there has been an explosion of interest and enthusiasm. It has been estimated that there are approximately 200,000 gas chromatographs currently in use throughout the world[4]. This enthusiasm and interest stems from the versatility of GC. A variety of samples of varying mixtures and concentrations can be separated with GC and the apparatus allows flexibility in terms of injection techniques and detection. The injection techniques include split, splitless, cold-on-column and the detectors, which are chosen to match the analysis sample mixture, include

Flame Ionization (FID), Thermal Conductivity (TCD), Electron Capture (ECD) and Mass Spectroscopy (MS).

The column which is considered the "heart" of the instrument was initially a metal tube packed with small irregularly shaped particles coated with thick layers of stationary phase[1]. These columns were able to handle large sample volumes, however, the analysis times were long and the resolution was poor. In 1957 Dr. M.J.E. Golay proved that open tubular columns coated with a thin, uniform layer of stationary phase could provide better resolution and shorten the analysis times[2]. Today these columns are called capillary columns. They are made of fused-silica with a polyimide coating for added strength. The fused-silica is flexible and has the ability to withstand high temperatures (380°C). Capillary columns are manufactured in a number of internal diameters and a variety of stationary phase film thicknesses. For a long time capillary columns were thought of as long tubes having excellent efficiency. There are cases where due to the complexity of the sample mixture long columns (100 m) are needed. However, there are also a large number of samples where short columns and fast analysis times are possible. This was understood by Desty and Goldup

soon after the introduction of the open-tubular capillary column. Using very short narrow-bore columns, analysis times of seconds were obtained[6]. Guiochon investigated the instrument contributions to the efficiency and analysis times and also obtained separations in seconds. Later Cramers showed the potential of fast GC with the analysis of natural gas, resulting in six peaks in 600 milliseconds[6].

Today, GC has the potential to be a more rapid means of analysis than is currently being practiced. The apparent lack of interest in fast GC is undoubtedly due to the lack of adequate equipment for the routine application of this technique. However, because of progress in instrumentation and column technology reduction of analysis time using commercial equipment is easily obtainable.

Now that fast GC is possible there are two key questions that need to be answered. The first concerns the need for fast chromatography. The best current argument against fast GC is that the sample preparation step is often the more time consuming, thus making the time savings from fast GC negligible. However, this situation can be interpreted differently. If the analysis can be done ten times faster then ten times more sample and

standards can be injected resulting in much better data results. The second question is whether there are any limitations with using fast GC. The largest limitation is that with the conditions used for fast GC peak resolution can be compromised[6].

The objective of this research was to investigate the capability and applicability of a commercial GC for fast chromatography. The resolution and time required for a separation are functions of several interrelated column and instrumental parameters. Column parameters such as the length was evaluated to determine its effect on the analysis time. Instrumental parameters such as the sample inlet, temperature programming rate and detector were evaluated to determine their effect on the analysis time and their contribution to the column efficiency.

Theory

A wealth of information concerning the column and instrument operating conditions can be gained from a simple chromatographic analysis. In fast analyses the primary goal is to reduce the retention time with minimal loss in resolution. A critical step in developing any chromatographic method is determining the resolution required for a separation. Resolution is a measure of the separation of peaks and can be calculated according to Equation 1.

$$R = \frac{2(t_{R_2} - t_{R_1})}{W_{b_2} + W_{b_1}} \quad (1)$$

where

t_R = retention time of components 1 and 2

W_b = peak width at baseline of components 1 and 2

The retention time, t_R, of each component is dependent upon the partitioning of the component between the mobile and stationary phases. The retention

time is the sum of the time spent in the mobile phase, t_o, and the time spent in the stationary phase, t_R'.

$$t_R = t_o + t_R' \quad (2)$$

The t_o term is constant for all components in a mixture and is called the dead time. This can easily be determined from the retention time of a component unretained by the column. The t_R' term is called the adjusted retention time. The relationship between t_R, t_o and t_R' is illustrated in Figure 1.

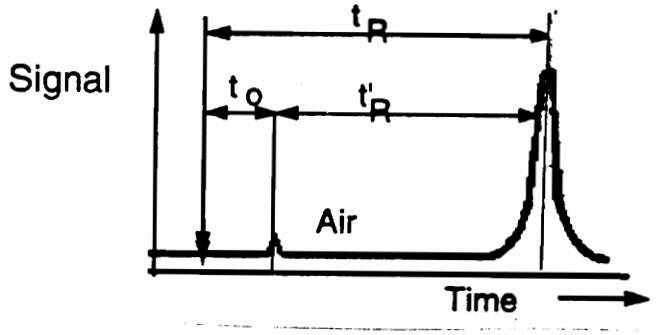

Figure 1: Retention Time. (Reprinted from reference 3.)

The resolution is comprised of three interrelated parameters: capacity, selectivity and efficiency.

$$R = \left(\frac{k}{k+1}\right)\left(\frac{\alpha - 1}{\alpha}\right)\left(\frac{\sqrt{N}}{4}\right) \quad (3)$$

where

k= retention factor

α = separation factor

N = column efficiency factor in terms of the theoretical plate number

The retention factor, k, is a measure of the time spent in the liquid phase.

$$k = \frac{t_R'}{t_o} \quad (4)$$

The ratio of the adjusted retention time to the dead time is a quantitative expression of the distribution of the solute between the two phases. The theory of gas chromatography often visualizes the column as consisting of many small segments where equilibrium between the two phases occurr. In an actual column equilibrium does not occur, however, the partitioning can

be described as a dynamic equilibrium expressed by the partition coefficient, K, according to the following equation[1]:

$$K = \frac{C_s}{C_m} \quad (5)$$

where

C_s = concentration of component in stationary phase

C_m = concentration of component in mobile phase

The partition coefficient is a characteristic of a solute and stationary phase and is constant for a given temperature. The retention factor and partition coefficient are related by the following equation

$$K = k\beta \quad (6)$$

where β = phase ratio. The phase ratio is defined as the volume occupied by the mobile phase relative to that occupied by the stationary phase.

$$\beta = \frac{V_m}{V_s} \quad (7)$$

The relationship between the retention factor and phase ratio is very important. Both are characteristic for a particular column, however, their

product, the partition coefficient is independent of that particular column. Another expression for the phase ratio in capillary columns is Equation 8[7]:

$$\beta = \frac{r_c}{2d_f} \quad (8)$$

where

r_c = column radius

d_f = stationary phase film thickness

For a given solute, the factors affecting the retention factor include the column diameter and stationary phase film thickness from Equation 8, the stationary phase from Equation 7 and the analysis temperature from the partition coefficient.

The separation factor, α, is a measure of the interactions of the solute and the stationary phase. This factor is expressed as the ratio of retention factors between two adjacent peaks.

$$\alpha = \frac{k_2}{k_1} = \frac{K_2}{K_1} \quad (9)$$

The interaction between the solute and stationary phase can include a mixture of nonpolar dispersive and polar interactions. The selectivity

shows how well the two peak maxima are separated. A value greater than 1.1 indicates that separation can be achieved with a reasonable column. Resolution and the separation factor are often confused because they both seem to be a measure of the distance between two adjacent peaks. However, the resolution takes into account the peaks widths. For example, Figure 2 shows two peaks with the same separation factor value, but the resolution is different for the two chromatograms. The resolution for the solid line is R = 1.5 and that for the broken line is R = 4.3[7].

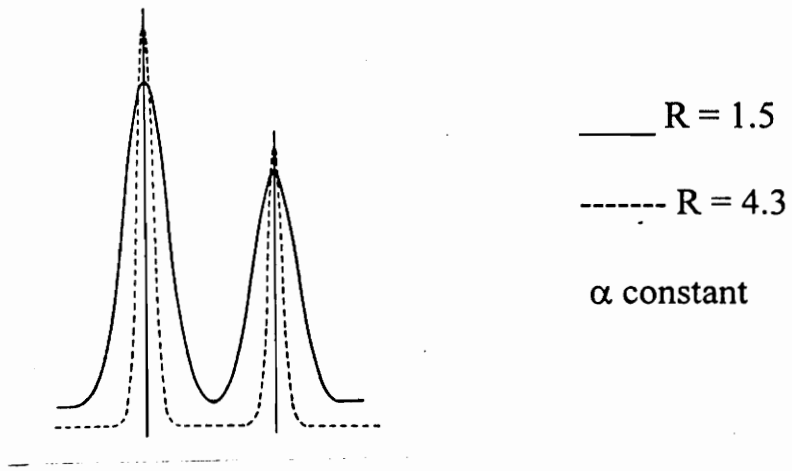

Figure 2: Separation vs. Resolution. (Reprinted from reference 7.)

A resolution value of 1.5 means that there is baseline resolution between the two peaks.

The column efficiency factor is a measure of the "goodness" of the column[1]. There are two methods by which the column efficiency can be expressed. The first is the number of theoretical plates, *N*.

$$N = \left(\frac{t_R}{\sigma}\right)^2 = 16\left(\frac{t_R}{W_b}\right)^2 \quad (10)$$

where

σ = standard deviation of peak maxima

W_b = peak width at base

The idea of using plate numbers for comparison of columns is a carryover from distillation processes where columns were originally composed of plates[3]. The second method by which to express column efficiency is the Height Equivalent to a Theoretical Plate, *H*. This parameter is determined by the following equation:

$$H = \frac{L}{N} \quad (11)$$

where

L = length of column (usually mm)

N = number of theoretical plates

The H is the length of column necessary for one equilibrium to be established between the stationary and mobile phases. For optimum efficiency, H should be minimized, therefore, a large number of theoretical plates would produce a small H value thereby creating a highly efficient column.

The Golay equation for capillary columns relates H to the three principal contributing factors in band broadening.

$$H = \frac{B}{\mu} + C_m\mu + C_s\mu \quad (12)$$

The first term is the molecular diffusion term, B.

$$B = 2D_g \quad (13)$$

where

D_g = diffusion coefficient of solute in gas phase

This coefficient can be found by dividing the B term from the golay equation by two. The effect of molecular diffusion is broadening

of the analyte peak in the gas phase as the solute passes through the column. To reduce the *B* term a large average linear gas velocity is necessary. This reduces the time for diffusion.

The second term is the mass transfer in the mobile phase, C_m.

$$C_m = \frac{r^2\left(1+6k+11k^2\right)}{24D_g\left(1+k\right)^2} \quad (14)$$

This term relates the retention factor, *k,* and the column radius, *r*, to band broadening. Because the column radius is squared it has a large effect on the column efficiency when thin films are used (small C_s).

The last term is the mass transfer in the stationary phase, C_s.

$$C_s = \frac{2kd_f{}^2\mu}{3(1+k)^2 D_l} \quad (15)$$

where

d_f = stationary phase film thickness

D_l = diffusion coefficient of the component in the stationary phase

This term relates the retention factor, the diffusion coefficient in the liquid phase and the stationary phase film thickness to band broadening. The

stationary phase film thickness is a squared term so it plays a large role in the column efficiency. By using columns with thin films the effect of the C_s term on band broadening is decreased.

In summary, the factors affecting the column efficiency include the column internal diameter, the column length, the stationary phase film thickness, the linear gas velocity and both D_g and D_l.

The rate of band broadening, H, is often graphed versus the average linear gas velocity. The average linear gas velocity can be calculated from Equation 16.

$$\mu = \frac{L}{t_0} \quad (16)$$

The plot of H verses μ is called a Golay plot for open tubular columns and can be described as an asymmetric hyperbole. There are two important characteristics in the Golay plot. The first is the point of minimum H. This point corresponds to the optimum average linear gas velocity for maximum efficiency.

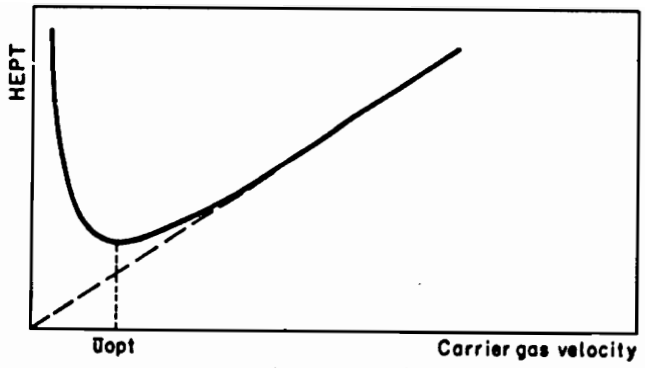

Figure 3: Golay plot for open tubular columns. (Reprinted from reference 2.)

The second important characteristic in the Golay plot is how the plot behaves after the minimum. At velocities greater than the maximum the mass transfer terms, C_m and C_s, dominate. Ideally a small slope would be advantageous so that an increase in the average linear gas velocity would produce a minimal change in the column efficiency.

The choice of carrier gas can best be expressed by examining the following Golay plot.

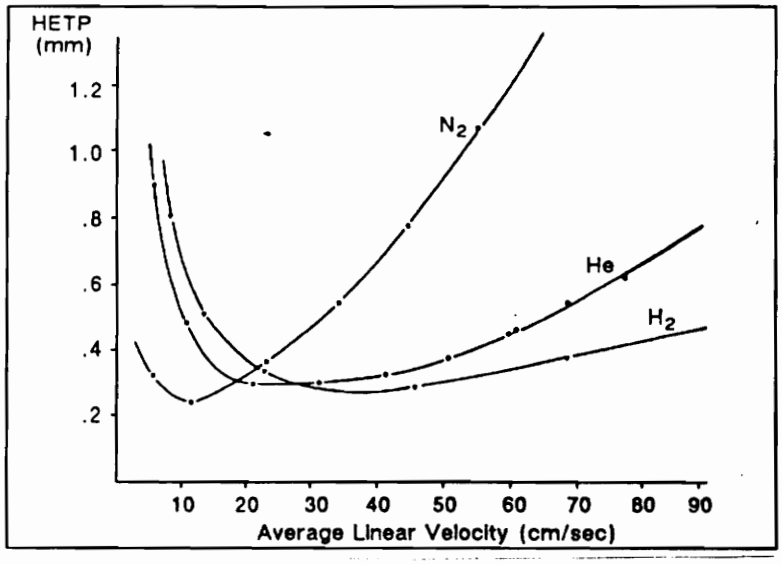

Figure 4: Carrier gas efficiency curves. (Reprinted from reference 1.)

The carrier gas with the smallest diffusion coefficient produces the highest column efficiency. In this case the carrier gas with the lowest diffusion coefficient is nitrogen. However, the optimum average linear gas velocity is in a very narrow region. The efficiency decreases sharply on either side of the optimum velocity. Also notice that this optimum occurs at a lower velocity than helium and hydrogen so speed is sacrificed when using nitrogen. The carrier gas with the highest diffusivity is hydrogen. With hydrogen the optimum velocity occurs at faster flow rates and the slope after the minimum is relatively flat. Therefore, as the velocity is increase above the optimum the efficiency is not affected significantly. Helium has a

diffusivity coefficient between that of nitrogen and hydrogen. The curve minimum occurs over a relatively wide range of velocity values and therefore with increasing velocity the column efficiency is not affected too drastically. Both He and H_2 are useful for fast analyses. With increasing temperature the diffusion coefficients also increase[10]. When doing a temperature programmed analysis the differences between the hydrogen and helium are reduced. Helium is also much safer and therefore was used in this research.

The parameters evaluated in this research include some in both the column and the instrumentation. As shown previously the principle column variables are the column length, the column internal diameter and the stationary phase film thickness.

The column length is important in that it is directly proportional to the number of theoretical plates, *N*, and therefore the column efficiency. Very long columns produce superior efficiency and this is often needed when analyzing a complex mixture (over 40 peaks). However, shorter columns can be used when great efficiency in not needed.

The column internal diameter affects the column efficiency as seen from the C_m term in the Golay equation (12). Increasing the internal diameter also increases the amount of stationary phase. Larger columns can, therefore, accept greater sample amounts than smaller columns.

The stationary phase film thickness as just mentioned affects the sample capacity and the column efficiency as seen from the C_s term in the Golay equation (12).

Equally important as the column parameters are the instrumental parameters. The instrumental variables include the sample inlet, the allowable temperature programming rate and the detector time constant.

The sample inlet provides an interface through which the sample enters the column. This must contribute minimally to the analyte band width in order to maximize column efficiency. When doing a fast analysis it is important that the sample remains in the injector only a small amount of time and because small columns are used that the amount of sample that enters the column is also small. We need small volumes injected rapidly with no peak tailing. For these reasons split injection was the injection choice for this research. Split injection was the first sample introduction

method developed for capillary gas chromatography. In split injection the hot injector immediately vaporizes the sample[8]. The carrier gas enters the injector through the total flow controller and is divided into two streams. One stream purges the septum at a rate of 3 mL/min to eliminate tailing that might be caused by diffusion of the sample. The second stream enters the vaporization chamber and mixes with the sample. This flow is split at the column inlet and only a fraction of the sample enters the column.

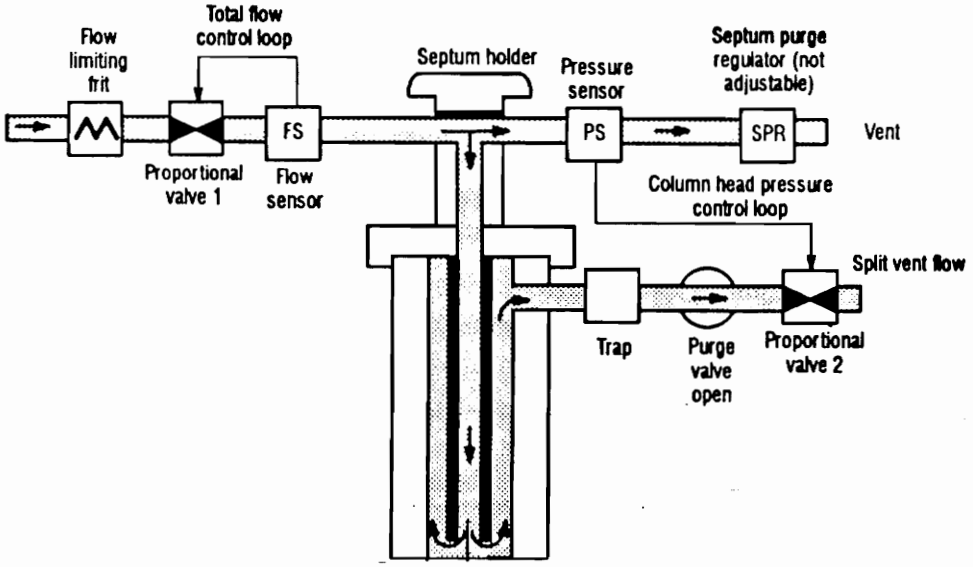

Figure 5: Split Injector. (Reprinted from reference 9.)

The vaporization chamber is a straight liner 2 mm in diameter with glass wool positioned approximately one-third of the way down the tube. In the

vaporizing chamber a problem exists in trying to rapidly evaporate the sample. This problem is based upon the Leidenfrost phenomenon[10]. According to the Leidenfrost phenomenon liquids are not able to touch surfaces heated above their boiling points. This occurs because the initial contact of the liquid with the hot surface causes evaporation that forms a cushion of vapors between the surface and the remaining liquid. An example is the phenomenon of water droplets dancing on hot stoves. Increasing the temperature of the surface will decrease the evaporation time, but will also produce more vapors that will push the remaining liquid further from the surface. This phenomenon produces two effects in GC. The first is that the repelled liquid glides past the hot injection liner surface and into the column without being evaporated. The second effect is that discrimination between analytes of different boiling points occur. There are three methods by which this phenomenon can be decreased or eliminated. The first method is to use a hot syringe needle. Put the empty syringe needle inside the injector for several seconds before injecting the sample. The hot needle produces partial evaporation inside the needle. When injected rapidly nebulization occurs and produces fine droplets that

evaporate without contacting the surface. In fast GC very fast injection is needed so an autosampler is necessary making the hot syringe needle method impossible.

The second method is to stop the sample by adding packing material. An evaporating liquid cools the source of heat. If the cooling is enough to reduce the surface temperature to the boiling point of the liquid then the liquid can contact the surface. This process occurs when using packing materials (like glass wool) that have a low thermal mass. Initial contact by the liquid cools the fibers and allows the sample to collect in the packing material and evaporate.

The third method is to use liners with solid obstacles. The obstacles hinder the liquid from falling through the column and enhance the mixing of the sample with the carrier gas[10].

Pressure can be a very useful parameter in an analysis[11]. Until recently all capillary GC instruments only offered a constant pressure mode of operation. In this mode the pressure remains the same throughout the analysis. When temperature programming in the constant pressure mode the viscosity of the carrier gas increases causing the flow to decrease, thereby

losing efficiency. Instruments are now offered that can maintain constant flow by increasing the pressure throughout the analysis. This is called Electronic Pressure Control (EPC). Flow/pressure programming allows the user to vary the flow or pressure at any time throughout the experiment and control the rate of change.

When a gas is heated it becomes more viscous and harder to push through the column. Equation 17 illustrates the effect the temperature has on the viscosity.

$$\eta \propto \frac{T^{3/2}}{\left(T + 1.47T_b\right)} \quad (17)$$

where

η = viscosity

T = temperature, °K

T_b = boiling point of gas, °K

The flow of the carrier gas through the column can be described by Equation 18.

$$F = \left[\frac{60\pi r^4}{16\eta L}\right]\left[\frac{\left(p_i^2 - p_o^2\right)}{p_o}\right]\left[\frac{p_o}{p_{ref}}\right]\left[\frac{T_{ref}}{T}\right] \quad (18)$$

where

F = outlet flow in mL/min

r = column radius

η = viscosity of gas at column temperature

L = column length

p_i = inlet pressure

p_o = outlet pressure

p_{ref} = 1 atm

T_{ref} = 25°C

T = column temperature

The flow under constant pressure conditions can be determined by Equation 18. However, the inlet pressure under constant flow conditions can also be determined. When doing temperature programming in the constant flow mode the following equation is used by the EPC system.

$$p_{i2} = \left[\left(\frac{T_2}{T_1} \right)^{1.7} \left({p_i}^2 - {p_o}^2 \right)_1 + {p_o}^2 \right]^{1/2} \qquad (19)$$

The equation determines the inlet pressure necessary to maintain a constant flow as the temperature is increased[12].

The column temperature is a second important instrumental parameter. Programming the temperature adjusts the retention times of the analyte peaks. In a fast analysis a fast rate of temperature programming is necessary to quickly elute the peaks. The temperature programming rates possible for the instrument used are dependent upon the temperature range. The rates for our HP model 6890 (240 V) are as follows:

Temperature Range(°C)	Rate (°C/min)
50 - 75	120
75 - 115	95
115 - 175	65
175 -	45

The detector is the third important instrumental parameter. The ideal detector should be able to rapidly detect a chromatographic peak. The flame ionization detector (FID) was used in this research. The FID was introduced in 1959 by McWilliam and Dewar in Australia and Harley et al. in South Africa[2]. The FID is the most commonly used detector because it responds with high sensitivity to nearly all organics; it does not respond to inorganics and its response does not fluctuate with small changes in flow, pressure or temperature. The FID has a low minimum detectable quantity ($\approx 10^{-11}$g), a wide linearity range ($\approx 10^{6}$) and it also has excellent stability[13]. The mechanism of detection is as follows.

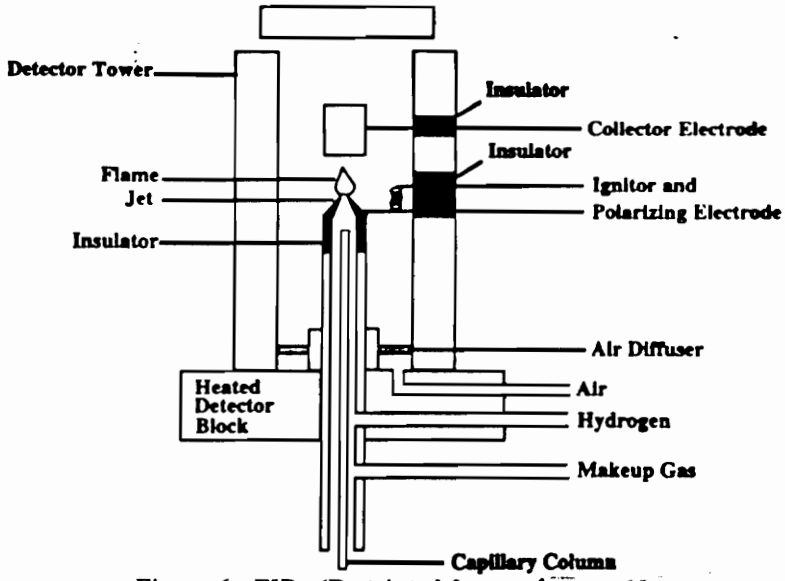

Figure 6: FID. (Reprinted from reference 13.)

Two gases, hydrogen and helium, flow through the jet and expand outward. The air flows around the jet in a laminar flow. As the sample moves through the jet it enters the hydrogen rich reaction zone and undergoes degradation and forms a group of single carbon species. Upon interaction with oxygen the following chem-ionization reaction occurs.

$$CH + O \rightarrow CHO^{+} + e$$

$$CHO^{+} + H_2O \rightarrow H_3O^{+} + CO$$

The unstable CHO^{+} ions react rapidly with the H_2O produced in the flame to generate a hydroxonium ion which is the primary positive charge carrier. The positively charged ions are collected at the electrode and produce an increase in the current. The hydroxonium ion production occurs once for every 100,000 carbons. Therefore, the response of the FID is proportional to the number of carbon atoms[(2)].

Experimental

The instrumentation in this research consisted of a Hewlett Packard model 6890 Gas Chromatograph with a flame ionization detector. A Hewlett Packard model 7673 autosampler and Hewlett Packard Chemstation software were also used. The flame ionization detector was supported by a Packard Instruments model 9400 hydrogen generator, GC grade air and GC grade nitrogen. The helium and hydrogen carrier gases were also GC grade. All experiments were performed using helium as carrier gas except Part 1, Carrier Gas Flow Optimization.

The objective of this research was to determine the dependence of the column and instrument parameters upon the analysis time and resolution. Each of the following experiments were designed so that only one column or instrumental parameter was changed at any given time. The column and conditions will be specified for each. A mixture of nine hydrocarbons was used as a test sample: nonane, decane, undecane, dodecane, tridecane, tetradecane, pentadecane, hexadecane and heptadecane. The alkanes were purchased from Aldrich Chemical Company (Milwaukee, Wisconsin).

Hexane, ordered from Fischer Chemical Company (Fair Lawn, New Jersey), was used as solvent. The concentrations of each hydrocarbon was approximately 200 ppm. The injector and detector temperatures remained constant at 250°C and 300°C respectively. A 2 mm straight liner with glass wool and a constant flow was used in all experiments unless stated otherwise. All other conditions will be specified.

Part 1: Column Parameters

A. Carrier Gas Flow Optimization

The column used was a HP-5, 100 μm I.D., 0.17 μm d_f. The lengths studied were 10, 5 and 1 m. The optimization was performed for an impurity in hexane. The operating conditions were as follows:

Table 1: Operating Conditions - Flow Optimization

Conditions	10, 5, 1 m
Oven Temperature	50°C
Injector Volume	0.1 μL
Split Ratio	100:1

The optimum flow was determined by varying the average linear velocity. The Height Equivalent to a Theoretical Plate (H) was calculated from Equation (11). H was plotted vs. the average linear gas velocity(μ). The plot, called a Golay Plot, was constructed using Excel software. Each point represents the average of three replicate injections.

B. Column Length

The column used was a HP-5, 100 μm I.D., 0.17 μm d_f. The lengths studied were 10, 5 and 1 m. The mixture of nine hydrocarbons was used as analysis sample. The operating conditions were as follows:

Table 2: Operating Conditions - Column Length Study

Conditions	10 m	5 m	1 m
Oven Temperature	Initial:150°C for 1 min Ramp 1:45°C/min	Initial:115°C for 0.1 min Ramp1:65°C/min to 175°C Ramp 2:45°C/min to 200°C	Initial:85°C for 0.1 min Ramp 1:95°C/min to 115°C Ramp 2:65°C/min to 150°C
Injector Volume	0.5 μL	0.5 μL	0.5 μL
Split Ratio	100:1	100:1	100:1

Part 2: Instrumental Parameters

A. Inlet

1. Injection Volume

The column used was a HP-5, 1 m, 100 μm I.D., 0.17 μm d_f. The injection volumes were 0.2 μL and 0.1 μL. All other conditions were as in Table 3. Only the solvent was used as analysis sample.

Table 3: Operating Conditions - Injection Volume

Conditions	0.2 μL	0.1 μL
Oven Temperature	90° C	90°C
Split Ratio	400:1	400:1
Average Linear Gas Velocity	155 cm/sec	155 cm/sec

The injection volume was varied in order to observe the effect that the injection volume has on the solvent profile. A replicate of five injections was made. A fast rate of transfer from the inlet to the column is necessary to minimize the solvent peak broadening.

2. Split Ratio

The column used was a HP-5, 1 m, 100 μm I.D., 0.17 μm d_f. The split ratio was varied from 100:1 to 400:1. All other conditions are listed in Table 4. Only the solvent hexane was studied.

Table 4: Operating Conditions - Split Ratio Study

Split Ratios	**100:1, 200:1, 300:1, 400:1**
Oven Temperature	90°C
Injector Volume	0.2 μL
Average Linear Gas Velocity	245 cm/sec

The split ratio was varied from 100:1 to 400:1 in order to observe the effect that the split ratio has on the solvent profile. A replicate of five injections was made. Here also a fast rate of transfer of the sample from the inlet to the column is necessary. If this does not occur the inlet may be overloaded, resulting in poor peak shapes and unresolved peaks.

3. Flow Programming

The column used was a HP-5, 1 m, 100 μm I.D., 0.17 μm d_f. Both constant flow and programmed flow were studied. The sample used was a mixture of sixteen polycyclic aromatic hydrocarbons (PAH): naphthalene, acenaphthylene, acenaphthalene, fluorene, phenanthrene, anthracene, fluoranthrene, pyrene, benzo(a)flouranthrene, chrysene, benzo(b)flouranthrene, benzo(k)flouranthrene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)pyrene and indeno(1,2,3-ed)pyrene. The PAH mixture was ordered from Supelco (Bellefonte, PA). Chloroform, ordered from EM Science (Gibbstown, NJ), was used as solvent. The concentrations of each PAH in the analysis sample was approximately 200 ppm. The operating conditions are listed in Table 5.

Table 5: Operating Conditions - Flow Programming

Conditions	1 mL/min Constant	2 mL/min Constant	1 mL/min for 0.1 min, then increase 50 mL/min^2 to 2 mL/min	2 mL/min for 0.1 min, then decrease 50 mL/min^2 to 1 mL/min
Oven Temperature	Initial:90°C for 0.1 min Ramp 1:65°C/min to 175°C Ramp 2:45°C/min to 275°C	Initial:90°C for 0.1 min Ramp 1:65°C/min to 175°C Ramp 2:45°C/min to 275°C	Initial:90°C for 0.1 min Ramp 1:65°C/min to 175°C Ramp 2:45°C/min to 275°C	Initial:90°C for 0.1 min Ramp 1:65°C/min to 175°C Ramp 2:45°C/min to 275°C
Injector Volume	0.2 µL	0.2 µL	0.2 µL	0.2 µL
Split Ratio	400:1	400:1	400:1	400:1
Average Linear Gas Velocity	155 cm/sec	155 cm/sec	155 cm/sec	155 cm/sec

The flow was varied in order to determine its effect on the solvent profile.

A replicate of four injections of each flow was made.

4. Inlet Liner

In an effort to eliminate or reduce the broad solvent peak shape two different liners were studied. The column used was a HP-5, 1 m, 100 μm I.D., 0.17 μm d_f. The liners used were: (1) a laminar cup splitter and (2) a 2 mm straight liner with glass wool. Only the solvent hexane was used as test probe and a replicate of five injections was made. All other conditions are listed in Table 6.

Table 6: Operating Conditions - Inlet liner Study

Conditions	Laminar Cup Splitter 2 mm Straight with Glass Wool
Oven Temperature	90°C
Injector Volume	0.2 μL
Average Linear Gas Velocity	155 cm/sec

5. Column Position

In another attempt to eliminate or reduce the broad solvent peak the distance the column was inserted into the inlet was studied. The

manufacturer recommended a column distance inside the inlet of 4 - 6 mm. The column position was varied from 5 mm to 10 mm in order to determine whether the solvent peak shape was dependent upon the column position. Only the solvent hexane was used and a replicate of five injections was made. All other conditions are listed in Table 7.

Table 7: Operating Conditions - Column Insertion Distance

Conditions	5 mm, 10 mm
Oven Temperature	90°C
Injector Volume	0.2 μL
Average Linear Gas Velocity	155 cm/sec

B. Temperature Programming Rate

In order to visualize the effect the temperature programming rate has on the analysis time and resolution two rates were studied. The column used was a HP-5, 1 m, 100 μm I.D., 0.17 μm d_f. The operating conditions as well as the temperature programming rates used are listed in Table 8. The analysis sample used was the mxture of nine hydrocarbons.

Table 8: Operating Conditions - Temperature Programming

Conditions	Rate 1	Rate 2
Initial Temperature	85°C for 0.1 min	85°C for 0.1 min
Ramp 1	85°C/min to 115°C	95°C/min to 115°C
Ramp 2	55°C/min to 150°C	65°C/min to 150°C
Injection Volume	0.5 µL	0.5 µl
Split Ratio	400:1	400:1
Average Linear Gas Velocity	155 cm/sec	155 cm/sec

The maximum temperature programming rate was used in order to determine whether this was a limiting factor in using a conventional GC for fast analysis.

C. Detector Sampling Rate

As noted in the experimental section the detector used was a flame ionization detector. The detector must be able to accurately respond to rapidly changing signals. In order to determine the effect of the detectors time constants, 50, 100 and 200 Hz were studied. The hydrocarbon mixture

was used as the sample analysis. The peaks from each were overlaid to compare the areas and widths of each peak for each time constant. The conditions used are listed Table 9. A replicate of five injections was made for each time constant.

Table 9: Operating Conditions - Detector

Conditions	50, 100, and 200 Hz
Injection Volume	0.5 µL
Split Ratio	100:1
Average Linear Gas Velocity	155 cm/sec

Results

Part 1: Column Parameters

A. Carrier Gas Flow Optimization

A range of average linear gas velocities for each column length was plotted against H using Excel. The analysis sample was a hexane impurity, the temperature used was 50°C, and the carrier gas was hydrogen.

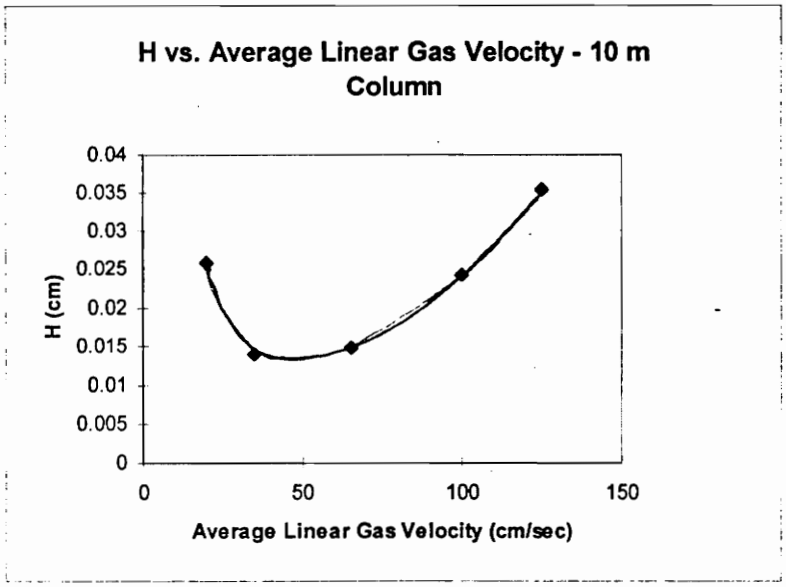

Figure 7: Golay Plot - 10 m Column

Figure 7 was plotted using the 10 m column. The average linear gas velocity ranged from 20 - 125 cm/sec. Instrumental hydrogen safety

shutdowns due to large flows prevented any further increases using the 10 m column.

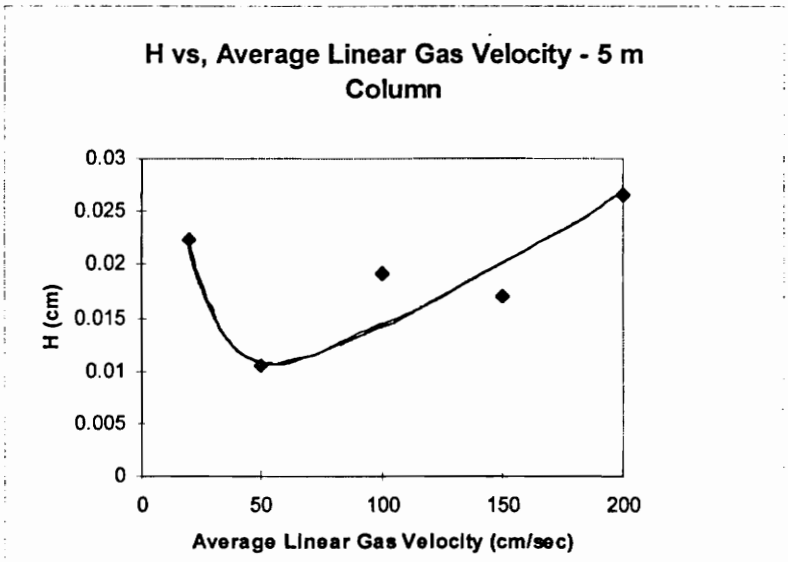

Figure 8: Golay Plot - 5 m column

Figure 8 was plotted using the 5 m column. The average linear gas velocity ranged from 20 - 350 cm/sec. Hydrogen safety shutdowns again prevented any further increases.

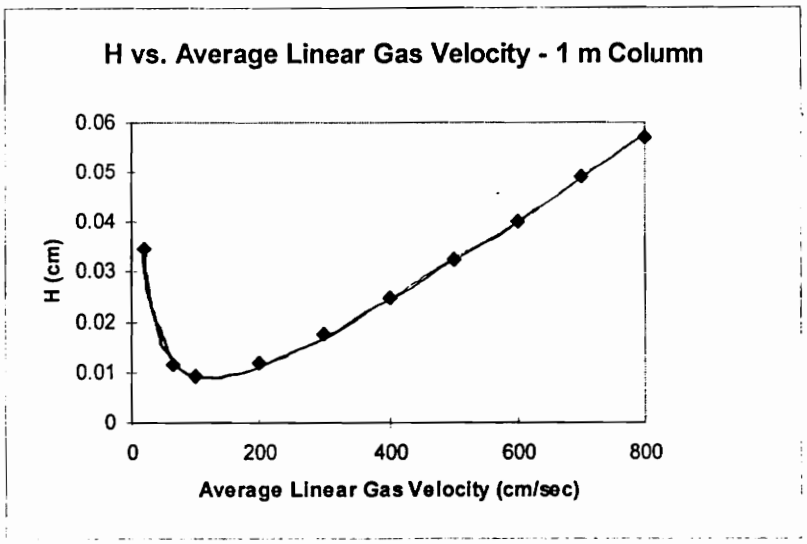

Figure 9: Golay Plot - 1 m Column

Figure 9 was plotted using the 1 m column. The average linear gas velocity for this column ranged from 20 - 800 cm/sec.

Hydrogen and helium carrier gases were also compared using the 1 m column. All other conditions were the same. The differences in efficiency can be seen from Figure 10. The squares represent the helium and the circles represent the hydrogen. The hydrogen can reach higher linear velocities and does not decrease in efficiency as rapidly as does helium. The slope of the hydrogen curve is 4.96×10^{-5} and the slope of the helium curve is 1.20×10^{-5}.

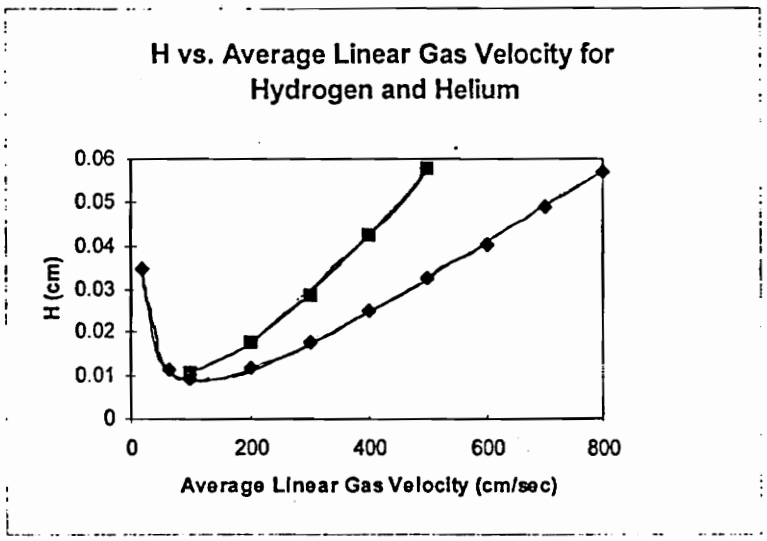

Figure 10: Golay Plot for Hydrogen and Helium

B. Column Length

Figure 11 shows the effect of column length on analysis time and resolution. The analysis time of the hydrocarbon mixture for the 10 m column was 2 minutes and 45 seconds, for the 5 m column 2 minutes and 10 seconds and for the 1 m column the analysis time was 38 seconds. The resolution for the lengths decreased with diminishing column lengths; however, there was still baseline resolution for all peaks. This shows, therefore, that the analysis time can be decreased with shorter columns and that the resolution is not compromised.

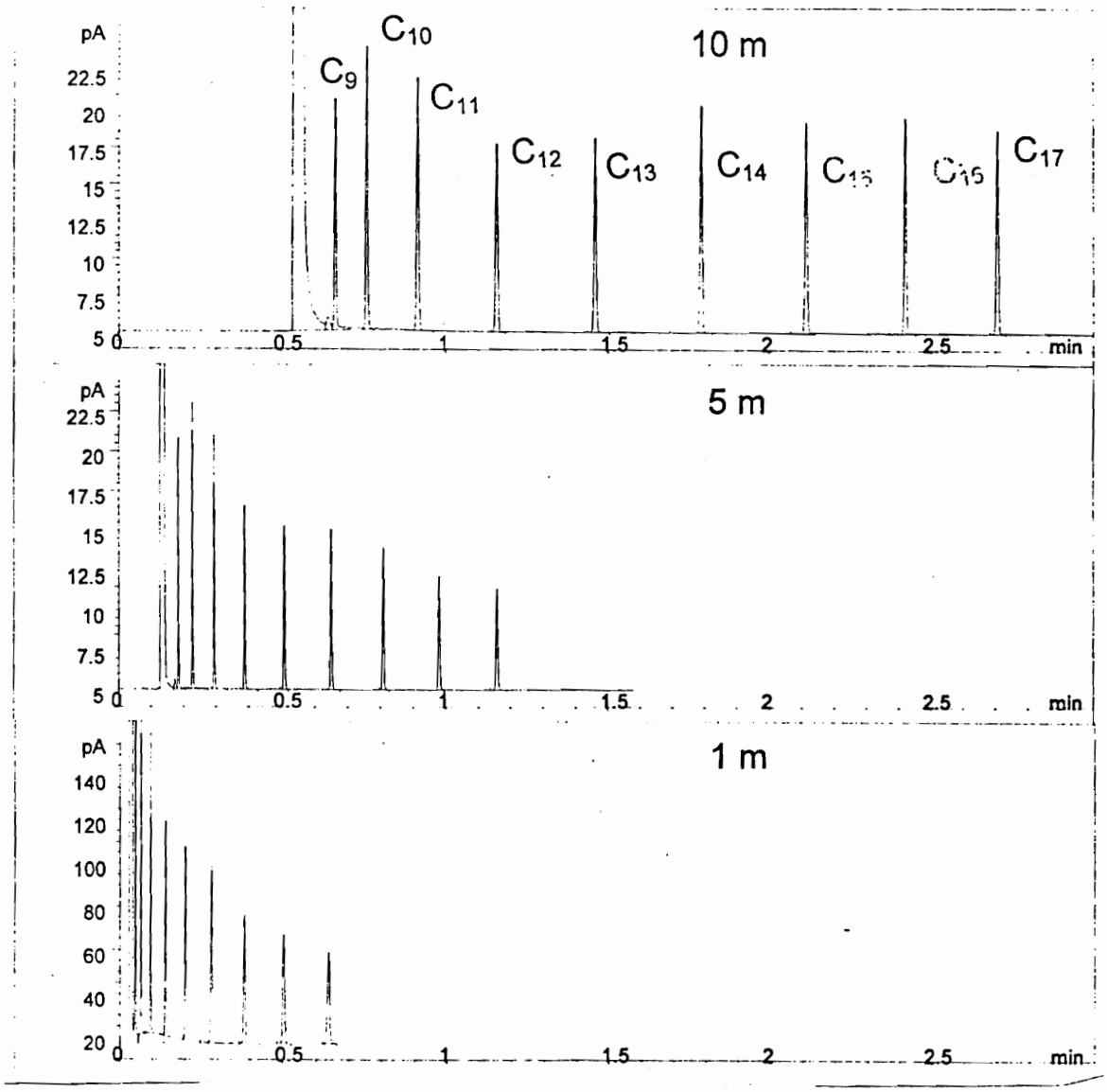

Figure 11: Effect of Varying Column Length. Analytes were a mix of nine hydrocarbons, C_9-C_{17}. Temperature conditions were as follows: 10 m - Initial 150°C for 1 min, increase 45°C/min; 5 m - Initial 115°C for 0.1 min, increase 65°C/min to 175°C, increase 45°C/min to 200°C; 1 m - Initial 85°C for 0.1 min, increase 95°C/min to 115°C, increase 65°C/min to 150°C.

Part 2: Instrumental Parameters

A. Inlet

1. Injection Volume

Figure 12 shows the effect of injection volume on the solvent peak shape. A fast rate of transfer from the inlet to the column is important. Using the 0.2 μL injection volume all of the sample is not transferred to the column at the same time, suggesting sample inlet problems. This is a problem because the remainder of the sample left in the inlet will come onto the column later. The overloading does not appear to be column overload because it is only the solvent that produces the extra peak. The analyte peaks do not see this effect.

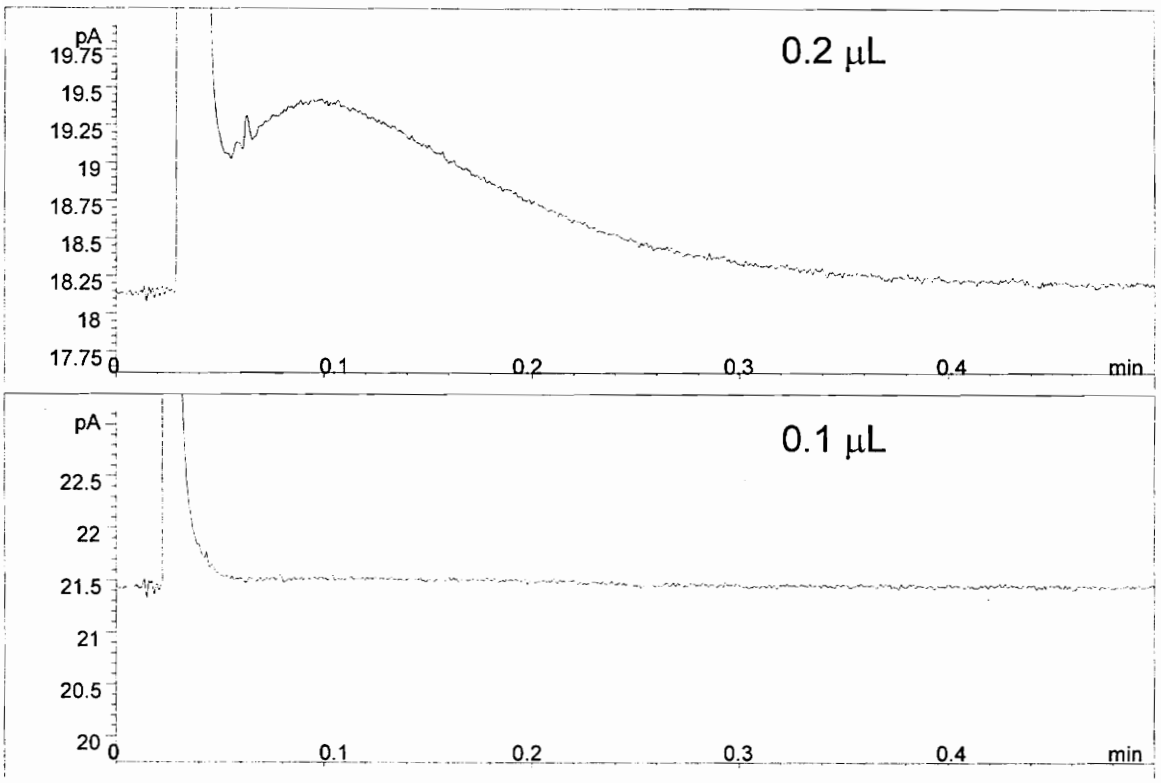

Figure 12: Effect of Injection Volume on Solvent Peak. Analyte was hexane and conditions 90°C, 1 mL/min and 400:1 split ratio were used.

2. Split Ratio

Here also a fast rate of transfer from the inlet to the column is important. Figure 13 shows the effect that the split ratio has on the solvent profile.

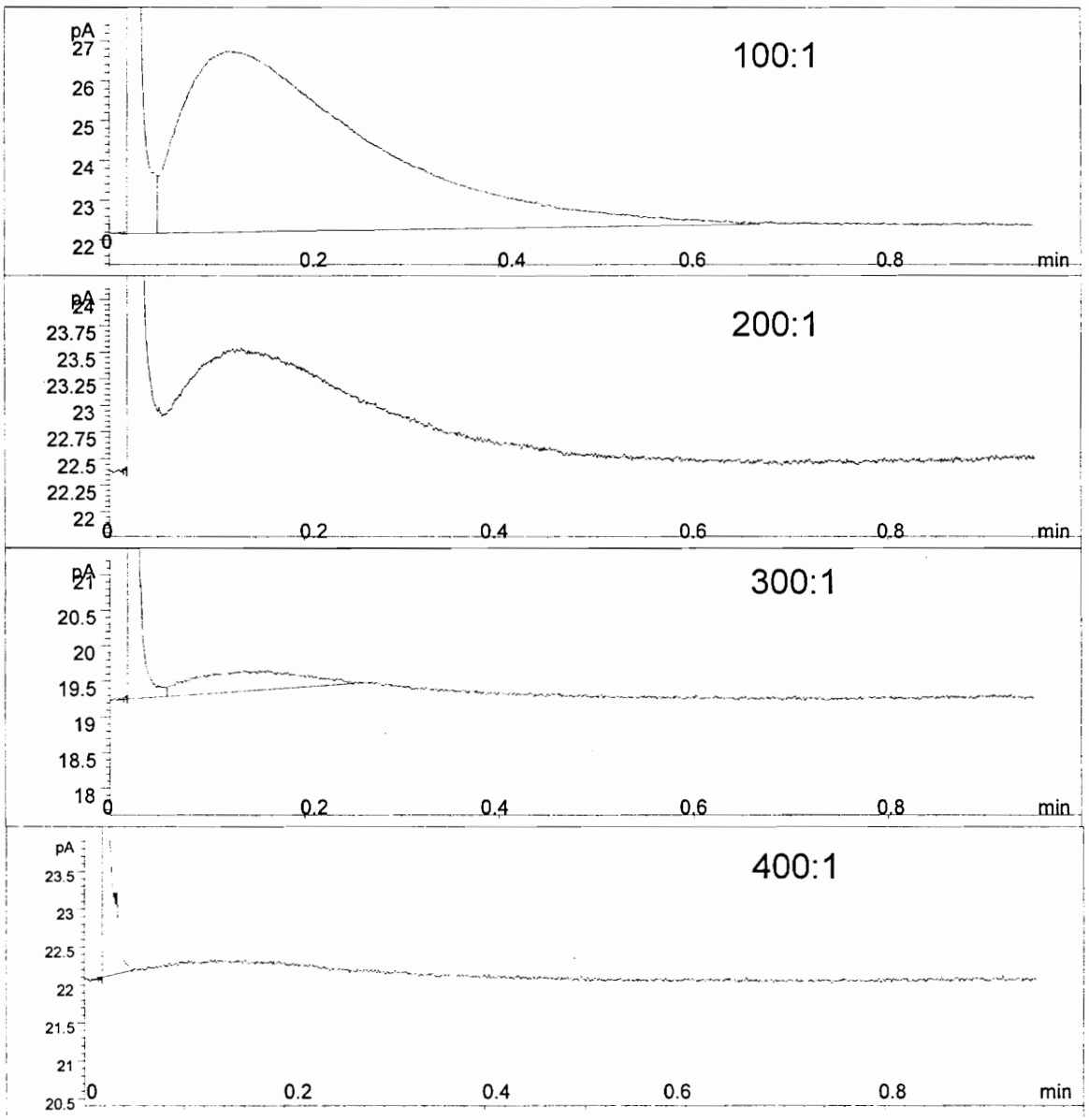

Figure 13: Effect of Varying Split Ratio. Analyte was hexane and conditions were 0.2 µL injection volume, 90°C and 2 mL/min.

Using a split ratio of 100:1, for example, 100 parts of the sample exits through the purge vent and only 1 part enters onto the column. As the split

ratio is increased the amount of sample lost increases and therefore the amount of sample that enters onto the column decreases. The bimodel solvent peak decreases with increasing split ratio suggesting that a high split ratio is necessary for a fast transfer.

3. Flow Programming

Figure 14 shows the affect the rate of flow has on the solvent peak. In (a) the flow is held constant at 1 mL/min and the bimodel solvent peak is present. In (b) the flow is held constant at 2 mL/min. Although the bimodel solvent peak has decreased in relation to (a), it is still present. In (c) the flow was initially held constant at 1 mL/min for 0.01 min. It was then increased at a rate of 50 mL/min^2 to 2 mL/min. The flow changes very rapidly here, in less than 2 seconds, to 2 mL/min where it remains constant. The solvent peak does not elute until 2 seconds and the bimodel solvent peak is not present. In (d) the flow was initially held constant at 2 mL/min for 0.01 min. It was then decreased at a rate of 50 mL/min^2 to 1 mL/min. The flow changes very rapidly here, again in less than two seconds to 1 mL/min where it remains constant. The solvent peak does not elute until after two seconds and the bimodel solvent peak is not present. Although

there is no explanation for this at this time, there seems to be a benefit to programming the flow at the injection.

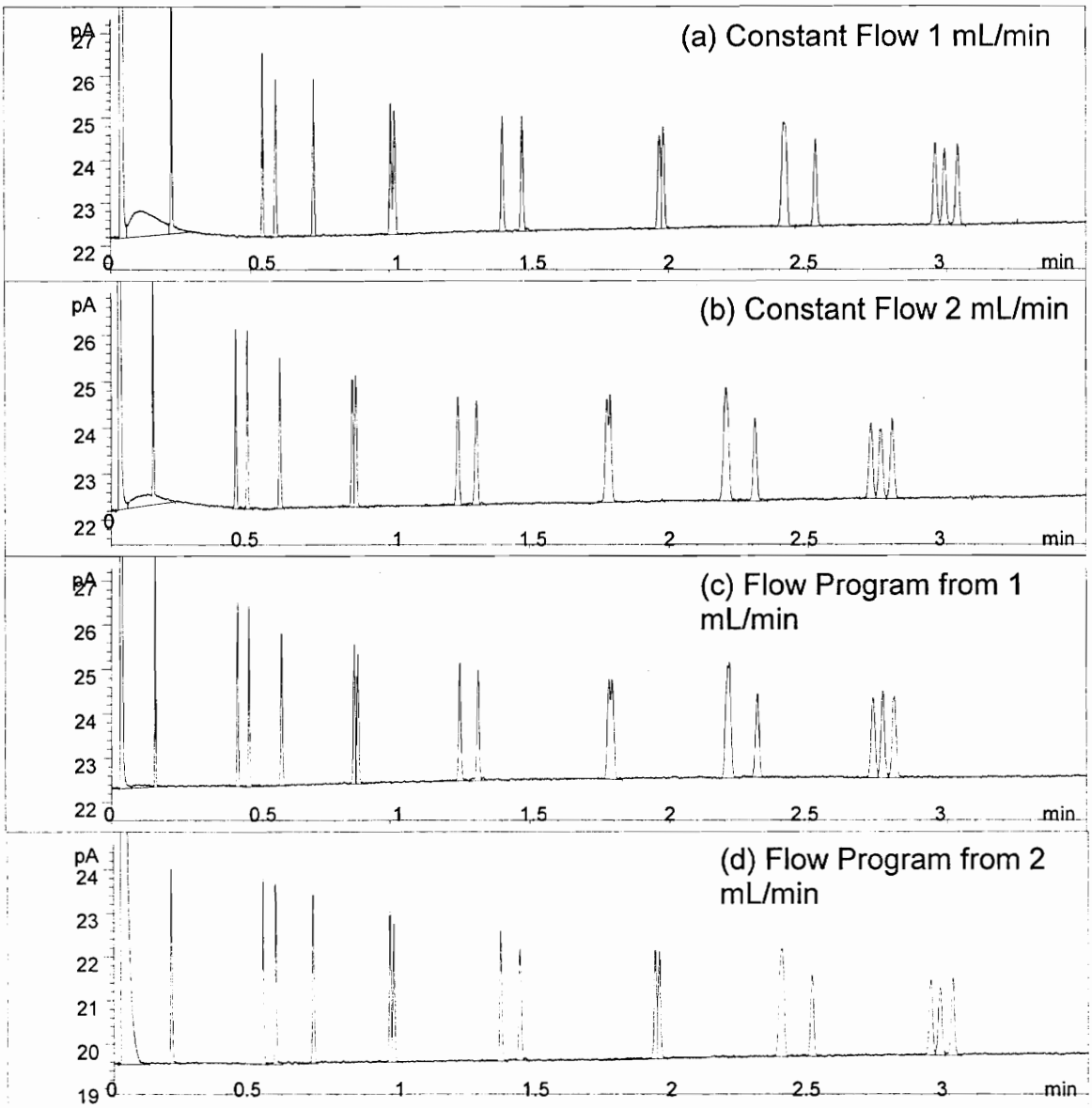

Figure 14: Effect of Flow Programming. Analytes were sixteen polycyclic aromatic hydrocarbons in chloroform and conditions were 1 mL/min, 0.2 μL injection volume and 400:1 split ratio

4. Inlet Liner

Solvent evaporation is influenced by the amount of time the sample remains inside the injector and the Leidenfrost phenomenon. In order to induce nebulization before reaching the column two different liners were used. The first, (a) the laminar cup splitter, uses obstacles inside the liner to enhance mixing and the second, (b) the straight liner, uses glass wool packing material. Figure 15 shows that neither liner is completely effective at transfering all the sample to the column at the same time.

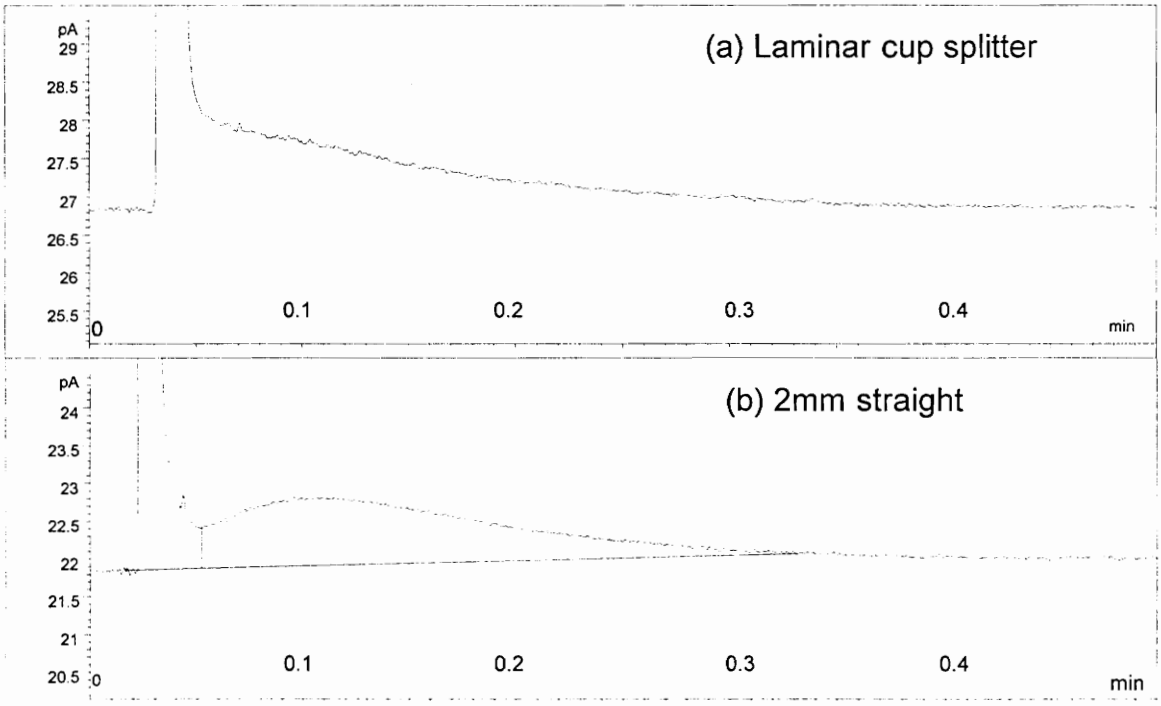

Figure 15: Effect of Varying Liner. Analyte was hexane and conditions were 90°C, 1 mL/min and 0.2 µL injection volume.

5. Column Position

The manufacturer recommended column position is 4 - 6 mm inside the injector. In Figure 16 the column position was varied from 5 mm to 10 mm inside the injector in hopes of reducing or eliminating the broad solvent peak.

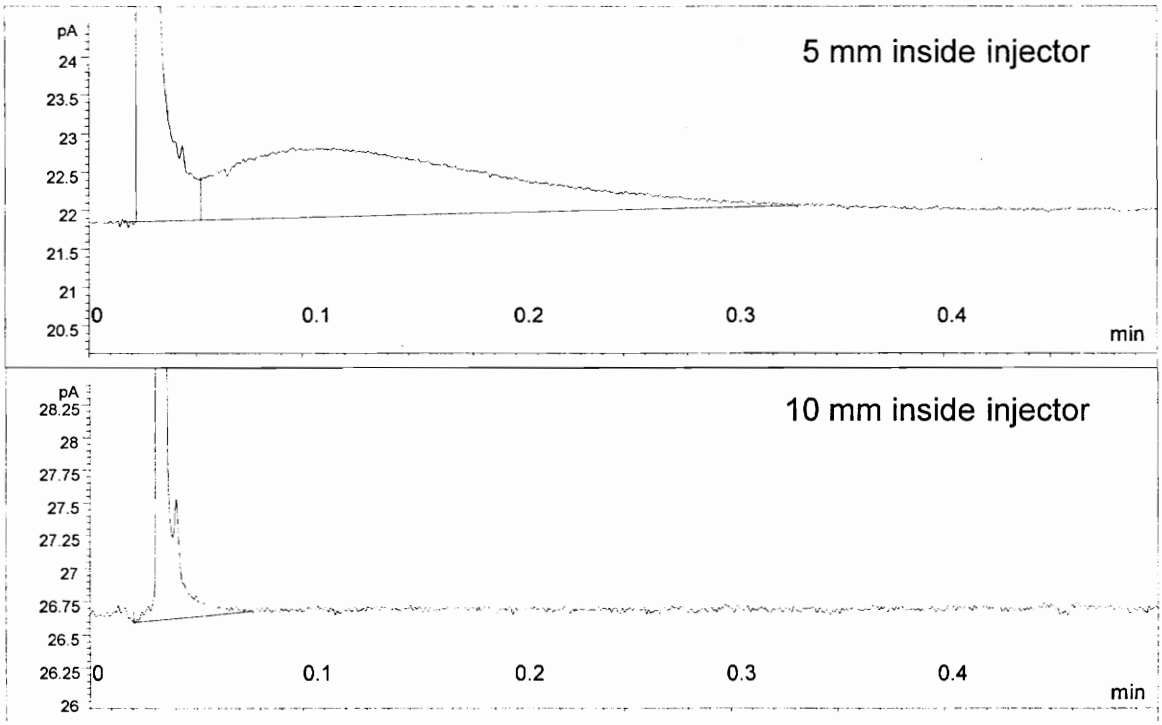

Figure 16: Effect of Varying Column Position. Analyte was hexane and conditions were 90°C, 1 mL/min and 0.2 µL injection volume.

The figure shows that the column position has a dramatic effect on the solvent peak shape. With the column positioned 10 mm inside the injector there seems to be a faster transfer of all the sample to the column at one

time. This suggests that when using the column positioned 5 mm inside the injector only part of the sample enters the column and another part possibly moves past the column entrance, hits the bottom of the inlet and returns up to the colulmn entrance where it enters the column at a later time. Positioning the column twice as far into the inlet can prevent this from occuring.

B. Temperature Programming Rate

The retention time is proportional to the rate of temperature programming. Figure 17 shows the analysis of the same mixture using two different temperature programming rates.

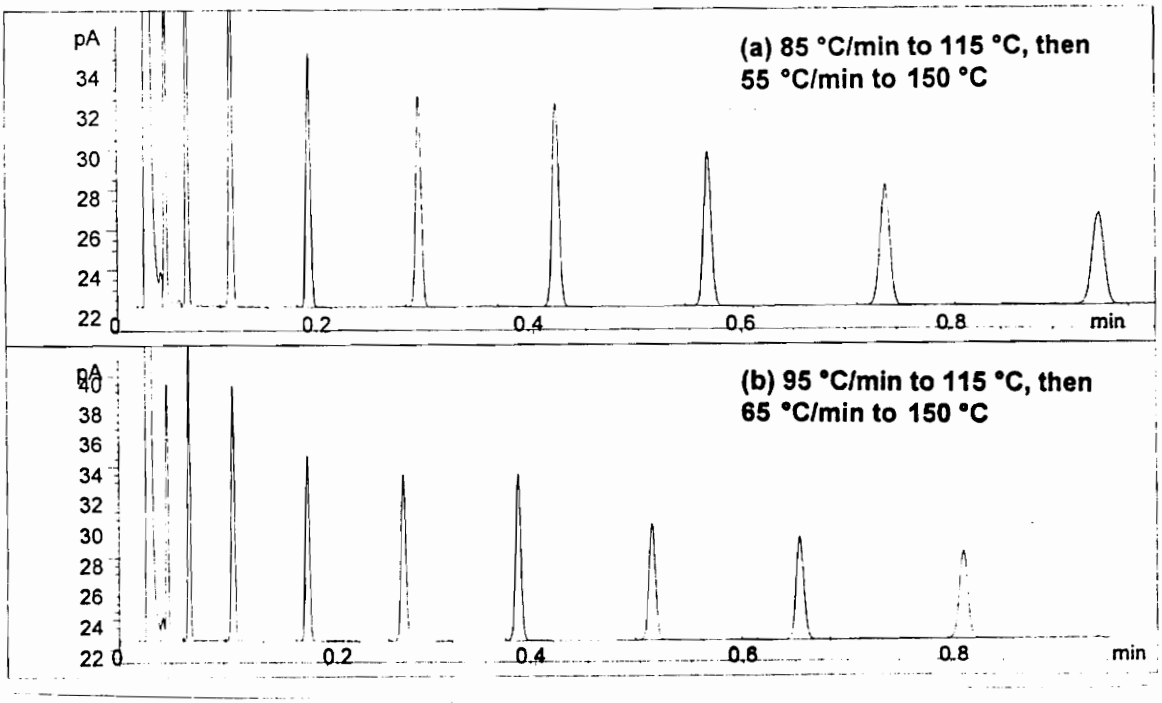

Figure 17: Effect of Temperature Programming Rate. Analyte was the nine hydrocarbon mix and conditions were 1 mL/min, 400:1 split ratio and 0.5 μL injection volume.

In both chromatograms the initial temperature is 85°C for 0.1 min. In (a) the rate of program is 85°C/min to 115°C and then 55°C/min to 150°C. In (b) the rate of program is 95°C/min to 115°C and then 65°C/min to 150°C. This demonstrates that as the rate of program increases the analysis time decreases. In (b) there is still a large amount of empty baseline so this rate of temperature program is not the optimum rate. However, for the instrument used this represents the maximum heating rate for these heating zones. This is, therefore, a limitation of this instrument.

C. Detector Sampling Rate

Figure 18 shows the peak shape of the same compound with changing time constant. The peak widths show no change, but the peak areas appear to increase with increasing time constant suggesting better monitoring of the peaks. However, there is no significant difference in area between the 100 Hz (3.81 pA•sec) and 200 Hz (3.82 pA•sec).

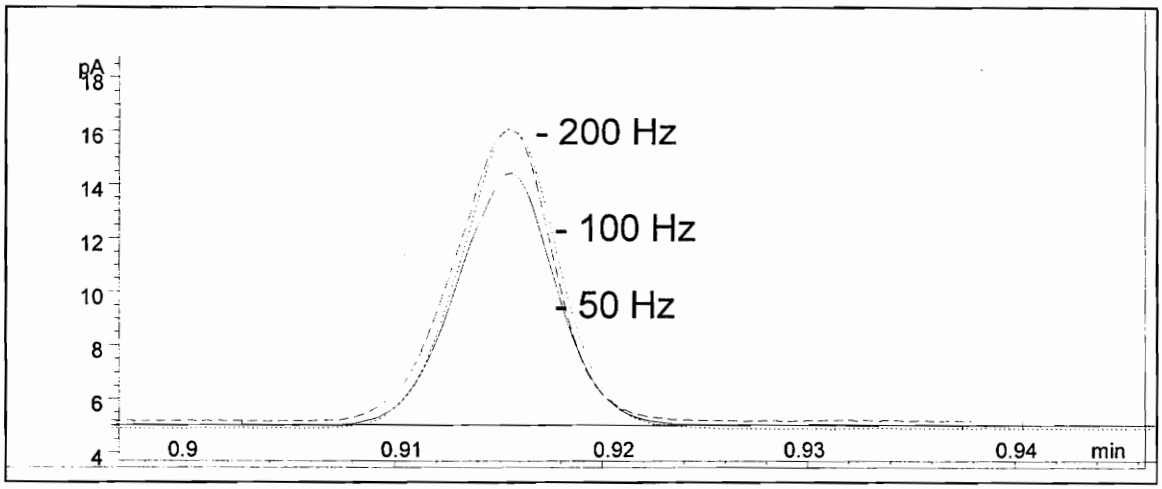

Figure 18: Detector Sampling Rate. Analyte was tetradecane and conditions were 0.5 μL injection volume, 1 mL/min and 100:1 split ratio.

Part 3: Examples

Real samples were prepared and a fast analysis was compared against a typical analysis to show the change in analysis time.

A. The first example is the test mixture of nine hydrocarbons. Figure 19 shows the difference in analysis time for a fast and typical analysis. The top chromatogram (a) was provided by Dr. Marisa Bonilla who produced this chromatogram while working on another research project. The column used was a DB-5, 15 m, 250 μm, 0.25 μm d_f. The analysis took approximately ten minutes. The bottom chromatogram is an example of a fast analysis. The column used was a HP-5, 1 m, 100 μm, 0.17 μm d_f and the analysis time was approximately 48 seconds, approximately 12 times faster than the normal analysis.

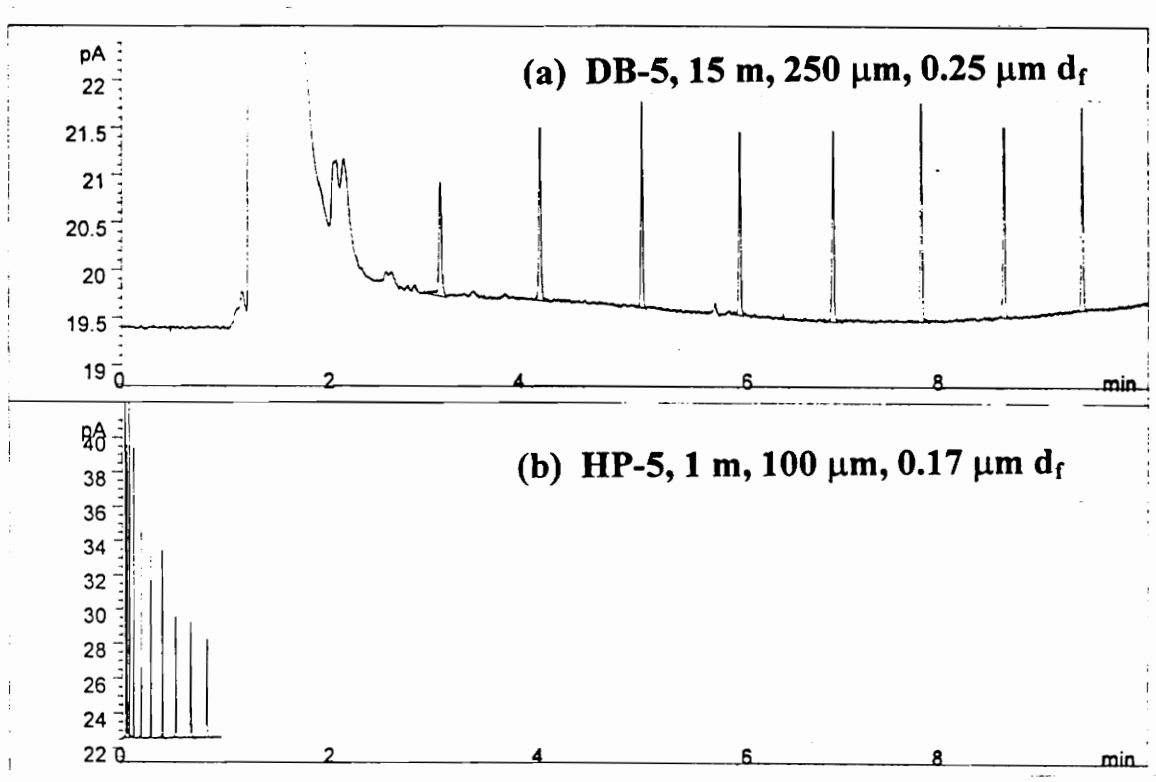

Figure 19: Hydrocarbon mixture

This chromatogram has been expanded in figure 20.

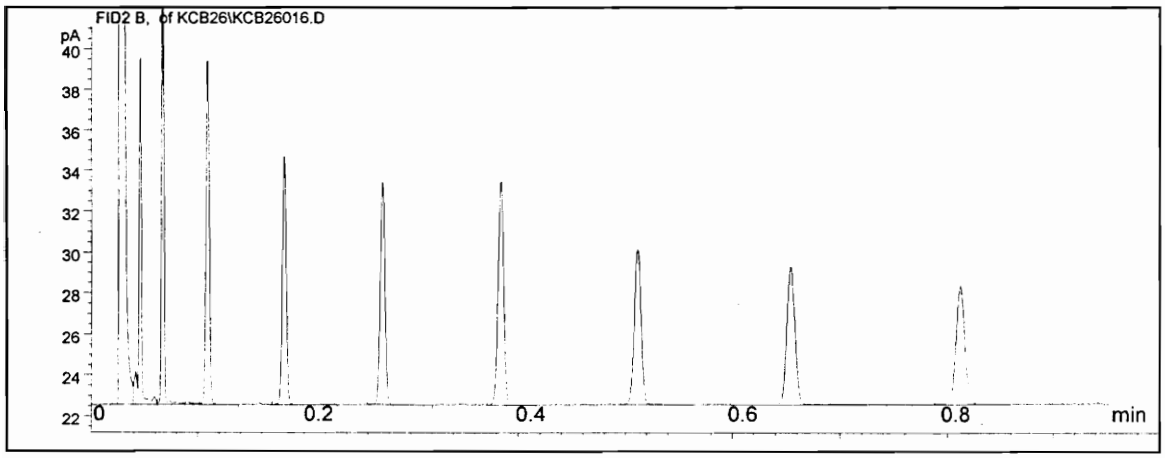

Figure 20: Hydrocarbon mixture - Fast analysis

Table 10 shows that although the resolution values have decreased they are well above the value needed for baseline resolution (1.5) and therefore the resolution is excellent.

Table 10: Hydrocarbon mixture

COMPOUND		RETENTION (min)		RESOLUTION (R)		REPRODUCIBILITY OF R (%RSD)	
		1 m	15 m	1 m	15m	1m	
C9		0.046	3.102	4.87	8.4	0.7512	
C10		0.067	4.073	5.08	23.82	1.4486	
C11		0.109	5.063	8.38	27.81	1.9339	
C12		0.181	6.018	11.4	28.08	1.0335	
C13		0.274	6.924	12.37	26.97	1.6454	
C14		0.384	7.78	12.67	26.55	1.6417	
C15		0.512	8.59	12.39	24.74	1.4044	
C16		0.654	9.358	11.31	23.87	2.4732	
C17		0.812	10.086	11.02	22.17	4.1187	

B. The second example is a mixture of sixteen polycyclic aromatic hydrocarbons (PAH). Figure 21 compares the analysis times for a fast and typical analysis. The top chromatogram and the resolution values used in the statistical analysis (a) was provided by Mr. Yuwen Wang who produced this chromatogram while working on another research project. The column used in his research was a PE-1, 30 m, 250 μm, 0.25 μm d_f. The analysis took approximately 37 minutes. The bottom chromatogram is an example of a fast analysis. The column used was a HP-5, 1 m, 100 μm, 0.17 μm d_f and the analysis time was approximately 2 minutes and 48 seconds, approximately 12 times faster than the normal analysis.

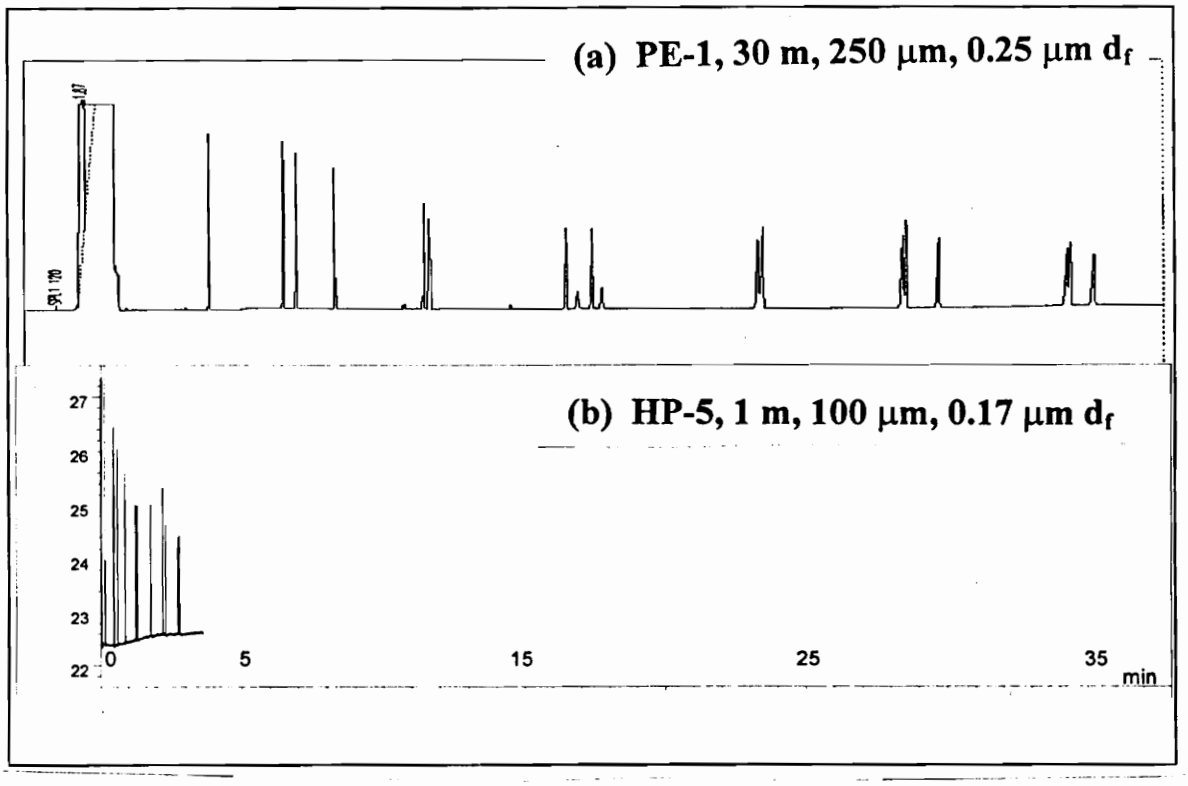

Figure 21: PAH mixture

This chromatogram has been expanded in Figure 22.

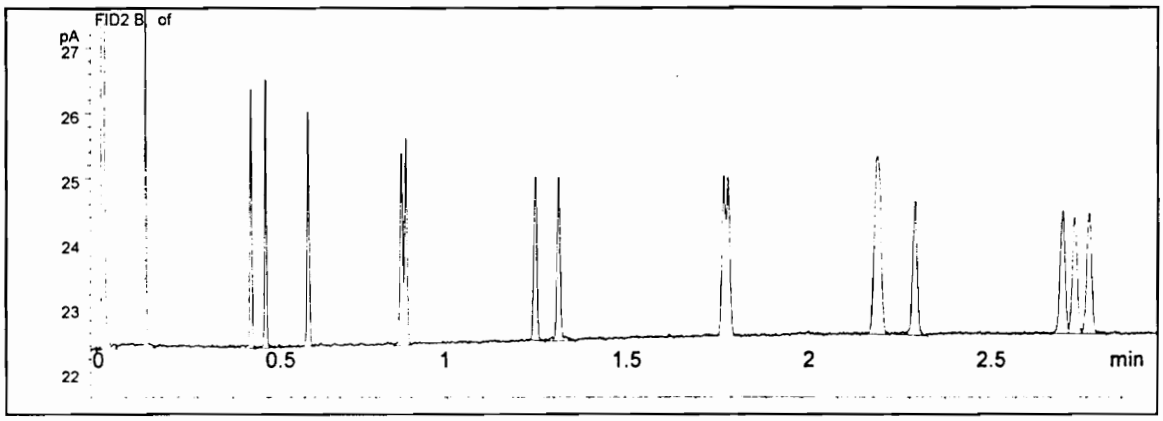

Figure 22: PAH mixture - Fast analysis

Table 11 shows the resolution values for each. For the peaks not separated by the fast analysis the typical analysis does not have baseline resolution either so the resolution lose is minimal for the fast analysis.

Table 11: PAH mixture

COMPOUND		RETENTION (min)		RESOLUTION (R)		REPRODUCIBILITY OF R (%RSD)	
		1 m	15 M	1 m	15m	1m	
1		0.155	6.149			6.762	
2		0.45	8.663	39.95	52.93	2.542	
3		0.491	9.905	4.45	7.99	0.844	
4		0.609	10.412	11.55	22.9	3.093	
5		0.871	13.431	21.62	43.5	1.542	
6		0.884	13.631	0.95	2.37	1.573	
7		1.25	18.266	26.47	54.81	2.875	
8		1.3158	19.14	4.33	9.25	0.815	
9		1.784	24.79	16.2	48.29	0.669	
10			24.961		1.26		
11		2.215	29.668	10.75	35.4	0.763	
12			29.791		1.02		
13		2.318	30.887	3.33	9.45	0.846	
14		2.732	35.25	16.21	30.32	1.274	
15		2.767	35.37	1.39	0.85	1.501	
16		2.808	36.175	1.65	5.71	0.768	

C. The third example is a mixture of eleven phenols: phenol, 2-chlorophenol, 2-nitrophenol, 2,4-dimethylphenol, 2,4-dichlorophenol, 4-chloro-3-methylphenol, 2,4,6-trichlorophenol, 2,4-dinitrophenol, 4-

nitrophenol, 2-methyl-4,6-dinitrophenol and pentachlorophenol. The Phenol mixture was from Supelco (Bellefonte, PA); Methylene chloride, from Fischer Scientific (Fair Lawn, NJ), was used as solvent. Figure 23 shows that a typical analysis of eleven phenols can take twenty-two minutes (chromatogram from Supelco). Figure 24 shows a fast separation of the eleven phenols in only 54 seconds, approximately 16 times faster than the normal analysis. Table 12 shows the resolution values for each peak.

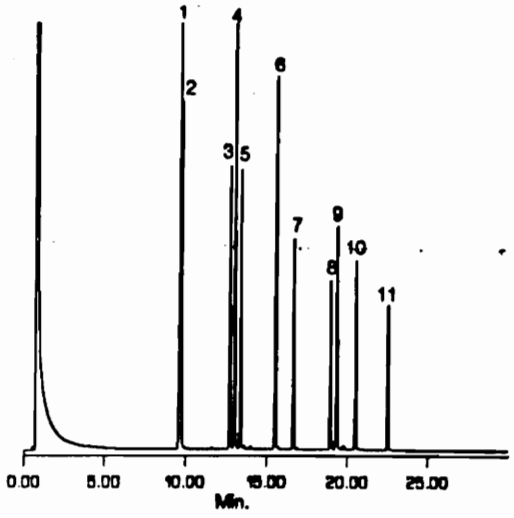

Figure 23: Phenol mixture in methylene chloride. Chromatogram provided by Supelco.

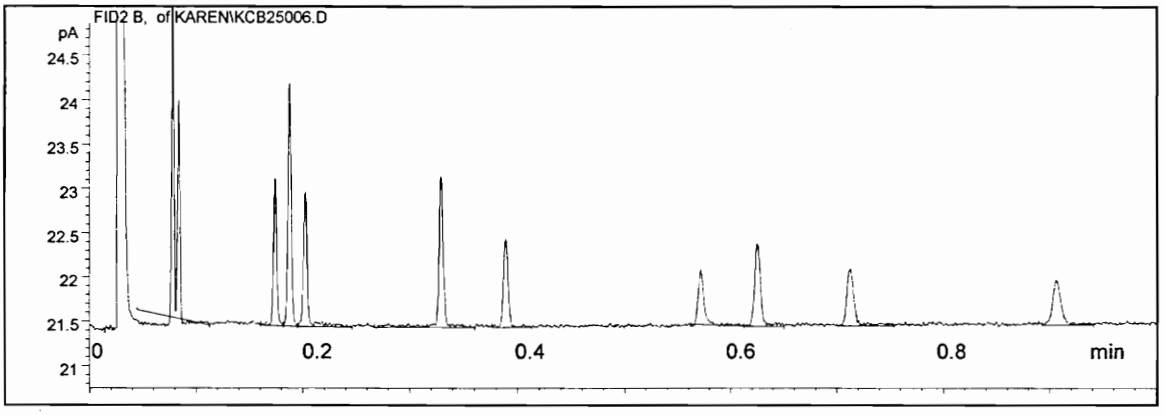

Figure 24: Phenol mixture in methylene chloride - Fast analysis

Table 12: Phenol mixture

COMPOUND	RETENTION (MIN)	RESOLUTION
1	0.78	
2	0.84	1.6
3	0.174	18.51
4	0.188	2.33
5	0.202	2.41
6	0.329	20.17
7	0.389	8.51
8	0.572	21.96
9	0.625	5.6
10	0.713	8.18
11	0.906	15.61

Part 4: Statistical Analysis

In order to statistically show how the resolution values of each peak in the fast analysis compare to those of a typical analysis a differential statistical analysis analysis was performed on the PAH analysis using the resolution values obtained for both the 1 and 30 m columns.

H_o: The resolution values are not statistically different for the two different analysis.

H_1: The resolution values are statistically different.

F_{cal}: 3.98

F_{crit}: 2.14

The f_{cal} is calculated from Table 13. Since the F_{cal} is greater than F_{crit} the resolution values for the two different analysis are statistically different. However, when compared to a resolution value of 1.5, that needed for baseline resolution, it is apparent that the fast analysis has achieved this in 11 out of 15 cases.

To visually compare the resolution values for both the fast analysis and a typical analysis with a baseline resolution value of 1.5 the Log Resolution for each was plotted in Figure 25.

Table 13: Statistical Analysis of polycyclic aromatic hydrocarbons

Compound	Resolution		Log Resolution	
	1 m	30 m *	1 m	30 m
1	39.95	52.93	1.601	1.723
2	4.45	7.99	0.648	0.902
3	11.55	22.9	1.062	1.359
4	21.62	43.5	1.3346	1.638
5	0.95	2.37	-0.022	0.374
6	26.47	54.81	1.422	1.738
7	4.33	9.25	0.636	0.966
8	16.2	48.29	1.209	1.683
9		1.26		0.100
10	10.75	35.4	1.031	1.549
11		1.02		0.008
12	3.33	9.45	0.522	0.975
13	16.21	30.32	1.209	1.481
14	1.39	0.85	0.143	-0.070
15	1.65	5.71	0.217	0.756
Baseline resolution	1.5		0.176	

* 30 m resolution values obtained from Mr. Wang.

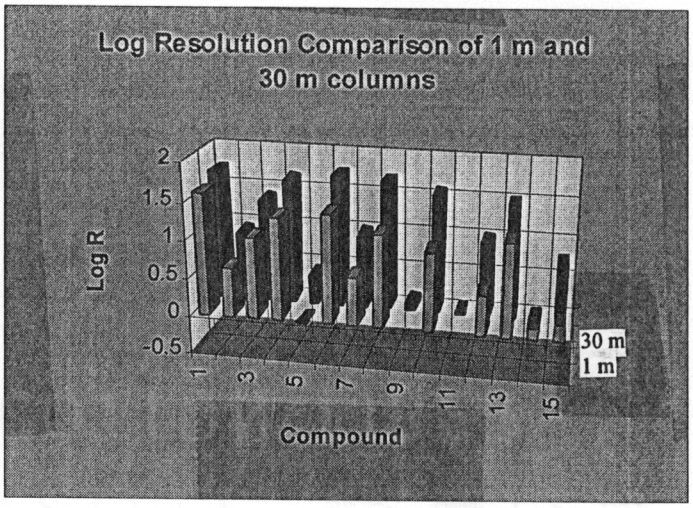

Figure 25: Log Resolution comparison of 1m and 30 m columns for PAH.

The dark bars represent the 30 m column and the light bars represent the 1 m column. This analysis shows that the resolution is indeed compromised in a fast analysis compared to a typical analysis. However, the resolution is not compromised when compared to a baseline resolution value.

Conclusion

Many routine GC analyses require less time than is actually being spent. By examing the Golay plot in Figure 10 it is evident that carrier gas velocities for helium and hydrogen can be increased without a great loss in efficiency to provide a faster analysis. The retention time and resolution as seen from the results section are dependent upon the column length, the stationary phase film thickness and the temperature programming rate. However, the overall chromatographic performance is also dependent upon the instrument.

The objective of this research was to show the applicability and capability of a commercial GC (HP model 6890) for fast chromatography. Sample introduction produced the most problems. Using smaller injection volumes, high split ratios and changing the column position inside the injector all improved chromatographic results. Other features such as flow/pressure programming can also be helpful. The FID was capable of responding accurately to fast GC analyses. The only area in the conventional GC that produced a limitation was the oven temperature

programming rates. Even using 220V, the temperature programming rate was not sufficient although it was acceptable. Overall, the Hewlett Packard model 6890 is very capable of performing fast chromatography.

In an industrial environment a quick analysis is often necessary. By using a conventional GC and adjusting the column and instrumental parameters faster analyses can be performed easily in an industrial environment in order to produce quicker results.

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Vita

Karen Nicole Clark-Baker was born April 28, 1972 in Abingdon, Virginia. She graduated from Emory & Henry College in May 1994 with a Bachelor of Science in Chemistry. On July 10, 1994 she was married to Robert Scott Baker and in August 1994 she came to Virginia Polytechnic Institute and State University to begin graduate studies.