POLYIMIDE POLYMER GLASS-FREE CAPILLARY COLUMNS FOR GAS CHROMATOGRAPHY

by Jackie G. Webster

Polymeric polyimide capillary tubing, both uncoated and coated with stationary phases of two polarities, is explored for use as capillary columns for gas chromatography (GC). These glass-free polyimide columns are flexible and their small winding radius may enhance the design of portable GC instruments. Polyimide columns with dimensions of 0.32-mm ID x 3-m L are cleaned, baked out, and coated using the static method. Coating thickness is 0.5 - 1 µm. Separations of volatile organics are investigated isothermally on duplicate sets of polyimide columns by GC with a flame ionization detector, using split injection. The columns are characterized with a sample mass load study, a column reproducibility study, and a van Deemter study. The uncoated polyimide columns are minimally capable of GC separations. The coated polyimide columns successfully separate Grob test mix alkanes, bases, and fatty acid methyl esters, and are comparable to standard fused-silica capillary GC columns.
POLYIMIDE POLYMER GLASS-FREE CAPILLARY COLUMNS

FOR GAS CHROMATOGRAPHY

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# TABLE OF CONTENTS

## CHAPTER 1
INTRODUCTION AND BACKGROUND

| SECTION 1.1: | DEVELOPMENT OF GAS CHROMATOGRAPHY | 2 |
|SECTION 1.2: | THEORETICAL CONCEPTS OF CHROMATOGRAPHY | 7 |
|SECTION 1.3: | CAPILLARY GC COLUMN TECHNOLOGY | 13 |
|SECTION 1.4: | PURPOSE | 18 |
| | REFERENCES | 23 |

## CHAPTER 2
POLYIMIDE POLYMER GLASS-FREE CAPILLARY COLUMNS
FOR GAS CHROMATOGRAPHY

| SECTION 2.1: | INTRODUCTION | 26 |
|SECTION 2.2: | EXPERIMENTAL | 30 |
|SECTION 2.3: | RESULTS AND DISCUSSION | 36 |
|SECTION 2.4: | CONCLUSIONS | 45 |
| | REFERENCES | 78 |
LIST OF TABLES

Table 1.1. Grob Test Mixture Components

Table 2.1. Peak Data for Alkanes Separation on Uncoated Polymeric
Polyimide Capillary Columns

Table 2.2. Peak Data for Aldehyde Elution on Uncoated Polymeric
Polyimide Capillary Columns

Table 2.3. Peak Data for Bases Separation on Uncoated Polymeric
Polyimide Capillary Columns

Table 2.4. Peak Data for Alkanes Separation on 50%-PMS Coated
Polyimide Capillary Columns

Table 2.5. Peak Data for Aldehyde Elution on 50%-PMS Coated
Polyimide Capillary Columns

Table 2.6. Peak Data for Bases Separation on 50%-PMS Coated
Polyimide Capillary Columns

Table 2.7. Peak Data for FAMEs Separation on 50%-PMS Coated
Polyimide Capillary Columns

Table 2.8. Peak Data for Alkanes Separation on 5%-PMS Coated
Polyimide Capillary Columns

Table 2.9. Peak Data for Aldehyde Elution on 5%-PMS Coated
Polyimide Capillary Columns

Table 2.10. Peak Data for Bases Separation on 5%-PMS Coated
Polyimide Capillary Columns

Table 2.11. Peak Data for FAMEs Separation on 5%-PMS Coated
Polyimide Capillary Columns

Table 2.12. Reproducibility Study on 5%-PMS Coated Polyimide Column

Table 2.13. Peak Calculations for van Deemter Study on WCOT
Polyimide Column with 1 µm 5%-PMS
LIST OF FIGURES

Figure 1.1. A Typical van Deemter Curve for a GC Column 20
Figure 1.2. The Structure of PMDA-ODA Polyimide 22
Figure 2.1. Size Comparison of a Polyimide Column and Standard GC Columns 47
Figure 2.2. The Polyimide Column Installed in the GC Oven 47
Figure 2.3. The Column Washer Used to Clean and Coat the Polyimide Columns 48
Figure 2.4. The Vacuum Apparatus Used to Dry the Coated Polyimide Columns 48
Figure 2.5. Initial Bleed Test Results on an Uncoated Polymeric Polyimide Column 49
Figure 2.6. Results of Additional Bleed Tests on an Uncoated Polymeric Polyimide Column 49

Figure 2.7. SEM Scans on Capillary GC Columns 50
Figure 2.8. Overlay of Alkane Separation on Uncoated Polymeric Polyimide Columns 51
Figure 2.9. Overlay of Aldehyde Elution on Uncoated Polymeric Polyimide Columns 53
Figure 2.10. Overlay of Bases Separation on Uncoated Polymeric Polyimide Columns 55
Figure 2.11. Overlay of Alkanes Separation on 50%-PMS Coated Polyimide Columns 57
Figure 2.12. Overlay of Aldehyde Elution on 50%-PMS Coated Polyimide Columns 59
Figure 2.13. Overlay of Bases Separation on 50%-PMS Coated Polyimide Columns 61
Figure 2.14. Overlay of FAMEs Separation on 50%-PMS Coated Polyimide Columns 63
Figure 2.15. Overlay of Alkanes Separation on 5%-PMS Coated Polyimide Columns 65
Figure 2.16. Alkanes Separation on 5%-PMS Coated Fused-Silica Commercial Column 65
Figure 2.17. Aldehyde Elution on 5%-PMS Coated Polyimide Column 67
Figure 2.18. Aldehyde Elution on 5%-PMS Coated Fused-Silica Commercial Column 67
Figure 2.19. Overlay of Bases Separation on 5%-PMS Coated Polyimide Columns 69
Figure 2.20. Bases Separation on 5%-PMS Coated Commercial Fused-Silica Column 69
Figure 2.21. Overlay of FAMEs Separation on 5%-PMS Coated Polyimide Columns 71
Figure 2.22. FAMEs Separation on 5%-PMS Coated Commercial Fused-Silica Column 71
Figure 2.23. FAMEs Separation on Deactivated Fused-Silica Retention Gap and 5%-PMS Coated Polyimide Column 72
Figure 2.24. Sample Mass Load Study 75
Figure 2.25. van Deemter Curve 76
CHAPTER 1
INTRODUCTION AND BACKGROUND
SECTION 1.1: DEVELOPMENT OF GAS CHROMATOGRAPHY

Origins of Gas Chromatography

The genesis of modern gas chromatography (GC) is credited to A.J.P. Martin and R.L.M. Synge who shared the Nobel Prize in Chemistry in 1952 for their invention of partition chromatography techniques for the separation of amino acids. This early chromatography work involved the use of a solid phase such as silica gel tightly packed into a column, and two immiscible liquid phases, initially chloroform and water. Partitioning and separation of the amino acids took place between the solvents as the water (the stationary phase) was held on the silica gel and the chloroform (the mobile phase) moved through the column. An indicator dye was added to the system creating colored bands in the silica gel as the dye reacted with the partitioned amino acids on the basis of their acidity [1].

In his Nobel lecture, Martin mentioned his current research with A.T. James in which they were exploring the use of gas as the mobile phase. Martin envisioned that this gas chromatography technique would partition volatile compounds between a semi-liquid stationary phase coating the packing in a tube and a quickly moving gas phase. Long, narrow tubes of very high separation efficiency would be employed, resulting in the rapid analysis of minute samples.

The development of gas chromatographic instruments and technology was dramatic during the next 40 years. An excellent review of the milestones of this development was published by Bartle and Myers in 2002 [2]. Among these milestones was the development of pneumatic controls which first stabilized column flow rates and pressure and later allowed for computerized control of these parameters. Other key developments were the invention of mass-flow electronic detectors, the development of mass spectrometry for solute detection and identification, and the development of sophisticated computer programs for instrument and method control as well as for data reduction and interpretation.

Initially, all GC separations were performed on columns packed with a solid support material such as silica gel and alumina. The support material was coated with a non-mobile, semi-liquid stationary phase such as glycerol or industrial-grade lubricants. In 1958, Golay presented the theoretical background of an open-tubular, or capillary, column for GC and demonstrated its use [3]. The capillary column Golay described consisted of an outer, or base, material of stainless steel which was coated internally with a stationary phase of dodecyl
phthalate. Its dimensions were 0.25-mm ID x 150-ft L [4]. This basic type of column is in current use today and is referred to as a wall-coated open tubular, or WCOT, column.

Among the many materials studied in the ensuing years as the base material for capillary columns, glass was preferred due to its relative inertness, smoothness, and low cost. Desty is credited with the design of a laboratory device for drawing and coiling glass capillary tubing, which made the production of these columns possible in research labs around the world [5]. In 1979, the use of fused-silica columns, adopted from the fiber optic industry, was pioneered by Dandeneau and Zerenner [6]. Among the advantages of the fused-silica column base material when compared to glass was improved flexibility, strength, and chemical inertness. This column technology remains the most commonly used in modern laboratories and will be discussed in detail later in this chapter.

Overview of the GC Instrument

Modern GC instruments are designed to offer multiple analytical approaches to sample introduction, sample separation, analyte detection, and data collection. While it is not in the scope of this research thesis to discuss these many options, a brief description of the typical GC instrument configuration is appropriate [7-9].

Sample introduction is performed by using a micro-syringe to inject a small aliquot of sample (typically 1 µL) through a polymeric septum into the injection port of the instrument. The injection port is lined with a tube-shaped deactivated glass liner and is heated to a temperature which will quickly vaporize the injected sample. The modern GC will employ an autosampler injection system to minimize fluctuations in sample injection technique.

When using capillary GC columns, sample overloading of the column is of great concern. To control the actual mass loading of sample on the column, the GC is commonly operated in the split mode. Immediately following injection, a majority of the vaporized sample is split off and swept out of the injection port by the carrier gas and is vented from the instrument. The sample split ratio is adjusted by the analyst according to the detection levels required for the analysis. The small portion of the sample which remains in the injection port is swept onto the analytical column as quickly as possible by the carrier gas to prevent analyte discrimination. Analyte discrimination occurs when the lightest, most volatile analytes are volatilized and swept onto the analytical column in concentrations disproportional to their actual concentrations in the sample.
Once the sample leaves the injection port and begins to move through the GC column, analytes begin to partition themselves between the stationary phase coating the column and the mobile phase, the carrier gas. Over time, differences in the distribution constants of the analytes between the stationary and mobile phases, as affected by the system temperature and the flow rate of the mobile phase, result in the separation of the analytes into discrete bands. Temperature control is a critical factor, particularly when quantitative analyses are being performed and reproducibility of results is imperative. To this end, attention to the design of the GC oven is important, and it is typically a large physical part of a lab-based instrument.

Electronic pressure control (EPC) is also critical for reproducibility in GC analysis as it maintains a stable pressure between the injector and the column and maintains a stable gas flow rate during analysis. Many modern GC instruments are equipped with both temperature and pressure programming capability. Changing the temperature and/or the mobile phase pressure of the GC column as separation proceeds allows the more heavily-retained analytes to be separated in a shorter time when compared to an isothermal, or single-temperature, analysis.

There is a wide variety of electronic detectors for GC instruments. One of the most commonly used is the flame ionization detector (FID). The FID is a robust, stable detector whose advantages include being highly sensitive to nearly all organic compounds. Fluctuation in the presence of gas impurities or with changes in temperature, carrier gas flow-rate, and pressure is minor. The FID demonstrates good linearity over about seven orders of magnitude.

Inside the FID, a small hydrogen-air flame burns at the tip of a jet. The analytical column end is inserted into the FID and carrier gas sweeps the analytes eluting from the column into the flame. Organic compounds in the flame are degraded into single-carbon species which then mix with oxygen in the flame according to the following equation:

$$CH^* + O^* \rightarrow CHO^+ + e^-$$ (1.1)

The ion current is measured between two electrodes, typically the burner tip and a collector electrode. The FID response is proportional to the number of carbon atoms present, and, therefore, shows linear response to varying concentrations of analytes based on the number of carbons that they introduce into the flame. The FID signal is electronically processed by an integrator and produces a chromatogram based on signal and time, typically in pA and minutes, respectively.
Computerized control of the GC instrument allows the analyst to program the many analytical parameters in order to achieve the best results for the separation at hand. Once developed, computerized methods can be saved and reused on subsequent samples, thereby assuring that analytical results are comparable from run to run. Standardization, quality control, and analytical data can be stored and retrieved as needed.

Trends in Portable GCs

Gas chromatographs designed for field portability have been marketed by large and small manufacturers with a wide array of approaches taken to reduce the size, weight, and complexity of lab-based instruments. Generally, these instruments are designed for field sampling of hydrocarbon components for the petroleum and chemical industry.

The footprint for one of these instruments, the 3000 Micro GC sold by Agilent Technologies, is 15 x 37 x 41 cm. This instrument is designed to contain multiple analytical modules, each consisting of an injector, column, flow control valving, and a thermal conductivity detector. Complex samples may be analyzed by utilizing multiple analytical modules with serial injections. This portable GC is designed with micro-electromechanical system (MEMS) devices for sample injection, with volumes ranging from 1 – 10 µL. Samples must be gaseous at operating temperature and pressure. The detectors are also MEMS in design. Detection levels are in the <10 – 20 ppm range. Carrier gas is contained in a rechargeable on-board gas cylinder, compatible with helium, hydrogen, and other gases. Separations are conducted isothermally with temperature ranges from 15 – 180 ºC. Fused-silica columns are available for the portable GC with lengths ranging from 4 – 10 m. Column IDs offered are 0.15 or 0.32 mm, with film thicknesses of 1 – 2 µm in a range of polarities. Columns may be wall coated open tubular (WCOT) or porous layer open tubular (PLOT). The columns are wound in factory-sealed modules in a coil with a diameter of approximately 8 cm [10].

Seacoast Science, Inc. has recently introduced a portable mini-GC which utilizes their patented polymers (e.g., fluoroalcohol polycarbosilanes and polysiloxanes) for both separation and detection of organic vapors. The dimensions of the mini-GC are approximately 23 x 28 x 13 cm. Utilizing MEMS technology, the instrument uses air as a carrier gas, electronic heating of a proprietary column, and detection by an array of chemi-capacitative sensor arrays. These sensors are micro-machined on silicon wafers, fitted with MEMS electrodes, and coated with polymers which selectively absorb target analytes. The interaction between the target analyte and the
polymers changes the dielectric properties of the polymers and results in a change in capacitance. The capacitance measurements are made by a readout chip and a microcontroller on a circuit board. The circuit board can be connected to a computer for data capture and system control. The literature claims a dynamic range of 0.1 – 500 ppm with a fixed volume injection capacity of 0.5 – 20 μL [11].

The Seacoast Science sensing technology is being incorporated into a mini-GC designed for academic lab classroom use by Vernier Software and Technology. This instrument was announced in June, 2009, and will be available for delivery in September, 2009. The mini-GC measures approximately 11 x 13 x 19 cm. It will utilize an 11-m stainless steel column lined with fused silica and coated with a non-polar stationary phase. This mini-GC will use ambient air as the carrier gas, and it is capable of temperature programming up to 120 °C and pressure regulation up to 20 kPa above ambient. Injection is by syringe, ranging from 0.01 – 0.50 μL. The literature claims separation capability for nine groups of organic compounds, ranging from C₁ – C₁₂, with boiling points below 175 °C [12].

Although not commercially available, the fabrication, assembly, and testing of a “lab on a chip” gas chromatograph, has been described by Lu, et al, at the University of Michigan [13]. The MEMS device components of this micro-GC included a calibration-vapor source, a sample preconcentrator/focuser, an analytical column, and a chemiresistor array detector. The column was etched into 3-cm² square-spiral on a silicon chip and then coated with a polydimethylsiloxane stationary phase. The authors demonstrated the ability of the micro-GC to separate and quantify an 11-vapor mixture in air at ppm concentrations in <1 minute.
SECTION 1.2: THEORETICAL CONCEPTS OF CHROMATOGRAPHY

Extraction Theory

Liquid-liquid extraction is based on a system’s ability to distribute a solute between two immiscible liquid phases. A discussion of liquid-liquid extraction theory is a basis for understanding the theory of gas-liquid chromatography theory [8].

When a liquid-liquid extraction comes to equilibrium, the equilibrium or distribution constant, $K_C$, is the ratio of the concentration of the solute in each of the liquid phases, $A_1$ and $A_2$:

$$K_c = \frac{[A_2]}{[A_1]} \quad (1.2)$$

The chemical equilibrium constant, $K_C$, can be expressed in terms of the mass of the solute in each phase and the relative volumes of each phase:

$$K_c = \frac{(W_A)_2/MW_A}{V_2} \div \frac{(W_A)_1/MW_A}{V_1} = \frac{(W_A)_2}{(W_A)_1} \cdot \frac{V_1}{V_2} \quad (1.3)$$

where $W_A$ is the mass in grams of the analyte, $MW_A$ is the molar mass of the analyte in grams/mole, and $V_1$ and $V_2$ are the volumes of the liquid phases. In liquid-liquid chromatography, the retention factor, $k$, is defined in terms of the ratio of moles of the analyte, $n$, in liquid phase 2 to liquid phase 1:

$$k = \frac{(n_A)_2}{(n_A)_1} = \frac{[A_2]V_2}{[A_1]V_1} \quad (1.4)$$

The phase ratio, $\beta$, in liquid-liquid chromatography is expressed as:

$$\beta = \frac{V_1}{V_2} \quad (1.5)$$

Combining equations 1.4 and 1.5 defines the equilibrium constant, $K_C$, as the product of the retention factor, $k$, and the phase ratio, $\beta$:

$$K_C = k\beta \quad (1.6)$$

This equation can also be applied to the theory of retention in gas chromatography, and is the connection between the theoretical aspects of the two systems. $K_C$ is constant at a given temperature for any solute - stationary-phase pair in gas chromatography, regardless of column dimensions. The phase ratio, $\beta$, can be expressed in terms of the relative volumes ($\pi r^2 L$) of the mobile phase and the stationary phase in a capillary GC column:

$$\beta = \frac{(r_c - d_f)^2 \pi L}{[r_c^2 - (r_c - d_f)^2] \pi L} \quad (1.7)$$
where \( r_c \) is the radius of the column, \( d_f \) is the thickness of the stationary phase, and \( L \) is the length of the column. Using the assumption that \( 2d_f r_c \ll r_c^2 \) in the numerator and that the \( d_f^2 \) term is negligible, this equation can be simplified to:

\[
\beta = \frac{r_c}{2d_f}
\]  

(1.8)

Two columns of different lengths but having the same stationary phase will behave similarly at a given temperature if the phase ratios of those columns are approximately equal. The phase ratio, \( \beta \), will decrease as film thickness, \( d_f \), increases or as the diameter of the column decreases, with a corresponding increase in retention factor \( k \).

Capillary GC Column Performance

After injection, the volatile components of a sample will move through the GC column swept forward by the carrier gas and retarded by the chemical and physical interactions the component molecules have with the stationary phase. The sum of these interactions determine the time at which the sample component will work its way through the column and appear at the detector. These interactions are directly affected by: the column geometry (radius, length), the stationary phase physical characteristics (thickness, wettability on the column), the stationary phase chemical characteristics (polarity, acid/base properties, orientation of functional groups on the surface), the temperature of injection and separation, the pressure and flow rate of the carrier gas, and the density and diffusion characteristics of the carrier gas. These factors need to be balanced by the analyst to obtain the optimal separation of the compounds of interest.

Assuming that in GC the separation is a series of Gaussian peaks, important descriptors of the chromatogram can be calculated. These metrics have been accepted and used by chromatographers for many years. A few key expressions are included here for reference.

Equation 1.6 shows the relationship between the distribution coefficient, \( K_C \), and the retention factor, \( k \). The retention factor, \( k \), can be derived as:

\[
k = \frac{t_R - t_M}{t_M} = \frac{t'_R}{t_M}
\]  

(1.9)

where \( t_R \) is the retention time of the component, \( t_M \) is the retention time of an unretained component on the column and \( t'_R \) is the difference between the retention times. Differences in the physical characteristics of any two columns can affect \( t_R \) values significantly. It is more
appropriate to use the ratio \( k \), which corrects the \( t_R \) value from the starting point of the unretained compound and compensates for the differences in flow rate and column dimensions.

Peak separation can be expressed as the relative retention of two consecutive peaks on a chromatogram, \( \alpha \):

\[
\alpha = \frac{K_2}{K_1} = \frac{k_2}{k_1} = \frac{t'_{R2}}{t'_{R1}}
\]  

(1.10)

where \( t'_{R2} > t'_{R1} \). [14]

By convention, the width of the base of a chromatographic peak, \( w_b \), is equal to \( 4\sigma \), where \( \sigma \) is the standard deviation of a chromatographic peak and can be expressed as:

\[
\sigma = \frac{t_R}{\sqrt{N}}
\]  

(1.11)

where \( N \) is the column efficiency, and can be derived as:

\[
N = \frac{t_R^2}{\sigma^2} = \frac{t_R^2}{\left(\frac{w_b}{4}\right)^2} = 16\left(\frac{t_R}{w_b}\right)^2
\]  

(1.12)

Using the peak width measurement at \( \frac{1}{2} \) peak height, \( w_h \), helps to reduce errors caused by baseline drift and peak asymmetry. \( N \) can then be expressed as:

\[
N = 5.54\left(\frac{t_R}{w_h}\right)^2
\]  

(1.13)

The resolution of peaks on a GC column is defined as \( R_S \):

\[
R_S = \frac{2\Delta t}{w_{b1} + w_{b2}}
\]  

(1.14)

where \( w_{b1} \) and \( w_{b2} \) are the width of the resolved peaks in seconds. Where two peaks overlap, this equation can be modified to utilize the peak \( w_h \) values of the peaks:

\[
R_S = \frac{1.18\Delta t}{w_{h1} + w_{h2}}
\]  

(1.15)

Relating these column properties together in one equation can be done, provided that the value of \( N \) is similar for both peaks and that the average of the two peak widths is equal to the peak width of the second peak:

\[
R_S = \frac{1}{4}\sqrt{N}\left[(\alpha - 1)/\alpha\right][k_2/(1 + k_2)]
\]  

(1.16)

or

\[
N = 16R_S^2 \left[\alpha/(\alpha - 1)\right]^2 \left[(1 + k_2)/k_2\right]^2
\]  

(1.17)
The value of the separation factor, $\alpha$, must be greater than 1 for resolution to occur. Increasing the value of $\alpha$ incrementally has an immediate positive effect on resolution which levels off about $\alpha \approx 2$. For values of $k > 0$, resolution increases markedly until $k \approx 5$. It is most beneficial to improve the separation factor of a system so that resolution can be achieved with the smallest possible value of $N$ and the shortest separation times [9].

**Band Broadening in GC Separations**

As the sample components move from the injection port through the capillary column and out to the detector, the discrete bands representing each separated component will be subject to broadening due to physical and chemical interactions in the column. A commonly used value, HETP or $H$, the height equivalent of a theoretical plate, is a metric for determining the efficiency of discrete separations in a GC column:

$$H = \frac{L}{N}$$

where $L$ is the column length in mm. The inverse relationship to $N$ means that an efficient column will have a small $H$ value, indicating that band broadening is minimized.

A more thorough kinetic approach to determining the causes and results of band broadening was published by J.J. van Deemter in 1956 [15]. A simplified van Deemter equation for band broadening in a packed GC column is:

$$H = A + \frac{B}{u} + C_S u$$

where $u$ is the linear velocity of the mobile phase in cm/sec, $A$ is the term for eddy diffusion through the solid support in the packed column, $B$ is the term for longitudinal diffusion of the mobile phase through the column, and $C_S$ is the term for resistance to mass transfer of the solute in the stationary phase. Figure 1.1 shows a typical van Deemter curve and the contribution of each term.

For capillary GC columns, the $A$ term is dropped since there is no packing in the column. There are two $C$ terms with the additional term being for resistance to mass transfer of the solute in the mobile phase, $C_M$:

$$H = \frac{B}{u} + C_S u + C_M u$$
The value of $H$ needs to be minimized in order to obtain the narrowest chromatography peaks. As $u$ increases, the effect of longitudinal diffusion, the $B$ term, is reduced, but the mass transfer effect, the $C$ terms, is increased [7].

**Optimizing Capillary GC Column Performance**

The analyst must determine the optimal linear velocity of the mobile phase in order to minimize the $B$ and $C$ terms, and by so doing, minimize $H$. A study is performed where determinations of a standard are made over a range of linear velocities, $u$, and the value of $H$ is calculated for each analysis. The values of $H$ are graphed against the values of $u$ to yield a van Deemter plot.

In theory, the point at which the graph shows a minimum for $H$ is considered to be the optimum value for $u$, or the $u_{opt}$ for the column, as shown in Figure 1.1. If analyses are performed at this linear velocity, or close to it, the band broadening due to the kinetic effects ($B$ and $C$ terms) will be minimized, $H$ will be minimized, and column efficiency, $N$, will be maximized.

For short capillary columns, the slope of the right-hand side of the van Deemter curve has been observed to be flatter than that of longer columns. A broader range for $H_{min}$ and $u_{opt}$ has also been observed for shorter columns. This is caused by reduced gas compression effects compared to that seen with the higher inlet pressures required for a longer column.

To calculate a value for $u_{opt}$, Equation 1.20 is differentiated with respect to $u$ neglecting the $C_Su$ term, and set to equal zero. Then, $u_{opt} = \sqrt{B/C_M}$. The resulting equation contains a term, $j$, from the $C$ term, which is a gas compressibility correction factor [8]. The term $j$ is directly proportional to $u_{opt}$, but inversely proportional to the ratio, $P$, of the inlet and outlet pressures of the column, $P_i/P_o$. For longer columns, the value of $P$ increases at higher mobile phase velocities since more pressure is required at the inlet. The value of $j$ then decreases, so the value of $u_{opt}$ becomes smaller and the slope of the curve to the right of $u_{opt}$ is steeper. In short columns, $u$ can be increased near the optimum without a significant increase in $P$, so the value of $u_{opt}$ stays unchanged over a relatively broad portion of the van Deemter curve and the slope of the curve to the right of $u_{opt}$ is flatter.

Another analytical protocol which must be optimized by the analyst is the mass loading of the sample on the analytical column. This is especially important when employing a very narrow or short capillary column. If the column is overloaded with sample, separation of analytes
may not occur due to broadening of peaks and baseline drift. Column overloading can also result in fronted or tailing peaks which can affect sample quantitation. A sample mass load or column overload study is performed by running a series of standards of increasing mass load in isothermal conditions. The values of \( N \) are calculated and are graphed against sample mass load. As sample mass load increases, the efficiency of the column, \( N \), will decrease. Analyses should be performed at a mass loading which optimizes column efficiency.

In 1978, K. Grob Jr., et al, published the results of their work to develop a standardized mixture of components to be utilized by analysts to monitor the performance of their fused-silica GC columns, both when the columns were new and as they aged with use over time [16]. The Grob test mixture has become a standard for assessing the performance of the GC column and the entire chromatographic system.

The Grob test mix was developed and optimized for fused-silica GC columns of low polarity, medium film thickness range (0.08 – 0.4 \( \mu \)m), and column IDs of 0.25 – 0.35 mm, with a minimum length of 10 m [9]. The test separation should be run at optimum flow conditions, with a temperature ramp from 40 °C to 190 °C, at a rate of 6 °C/min, with the last retention time at about 25 min [17]. As listed in Table 1.1, each component serves as a measure of critical aspects of a good column, including percent recovery, peak shape, separation efficiency, adsorption due to surface activity of the column, and acid/base character of the column [8,17].
SECTION 1.3: CAPILLARY GC COLUMN TECHNOLOGY

The Manufacturing of GC Capillary Columns

Column technology for GC is considered to be mature and well-developed. According to the 2003 Gas Chromatography User Study conducted by LCGC North America, 91% of respondents used fused silica capillary columns in their GC instruments and they used them for the majority of their analyses. About 41% of respondents indicated that they still used packed GC columns occasionally, but these columns represent less than 20% of the commercial column market [18].

The typical capillary GC column consists of an open tube of fused silica coated on the outside with a polyimide polymer protective coating and coated on the inside with a liquid stationary phase. This configuration is referred to as a wall-coated open tubular (WCOT) column. Other types of open tubular columns include the support-coated open tubular (SCOT) column and the porous-layer open tubular (PLOT) column. The SCOT column has the inner wall of the capillary lined with a thin layer of a support material which has the stationary phase adsorbed onto its surface. The PLOT column has only a thin layer of adsorbent material coated on the inner wall of the capillary.

A brief description of the WCOT column manufacturing process is instructive when considering the benefits of an alternative column design. The fused silica for all columns produced today comes from a small group of manufacturers whose main business is the optical fiber industry. The first step in column manufacturing is to melt the open-tubular fused silica at a precise temperature in an inert atmosphere and draw it down to the required outer diameter, OD, which controls the inner diameter, ID. Residual glass stresses from the drawing process and ovality, or out-of-round condition, are two major quality issues resulting from this process.

As the tubing is being drawn, it passes through an open-cup applicator where polyamic acid liquids are applied to the outside of the column. The column is then pulled through a curing oven where the polyamic acid is dehydrated to form a polyimide protective coating. This coating and curing process continues in series for an average of six coatings. The polyimide protects the fused silica from moisture and abrasive damage which can result in column failure. Quality control problems which occur in this stage of manufacture include uneven coating thickness and/or cure rate which can lead to blistering of the polyimide coating [19].
The finished WCOT columns are essentially straight due to their fused-silica core. The columns are immediately wound onto wire cages designed to hold them securely in three dimensions in the GC oven. These columns are susceptible to winding stress on the fused silica core which can lead to column breaks and failure. Because of this limitation, most GC columns are wound on hangers with approximately 20-cm diameters. The size of the column hangers requires a relatively large oven design for lab-based GC instruments.

**Surface Treatment and Coating of Fused-Silica Capillary Columns**

The surface of the fused silica will typically be made up of silanol groups (–SiOH), with some trace metal contamination and absorbed water. The surface of the fused silica must be chemically prepared prior to coating with the stationary phase for two reasons. First, the untreated silanol groups will behave as active sites on the column which can react with sample components through the thin layer of stationary phase, affecting their chromatography in a non-reproducible fashion. Secondly, the surface of the fused silica must be chemically uniform to maximize the wettability of that surface with the stationary phase to ensure complete coating.

The first step in surface preparation is to acid wash the fused-silica surface to remove trace metals. Typically, the fused-silica is then treated to rehydroxylate the surface so that it is uniformly covered with silanol groups. When a nonpolar fused-silica surface is required, the surface is silanized by treatment with chlorosilanes or disilazanes which leave the surface covered uniformly with methyl silica groups such as –O-SiO(CH$_3$)$_2$ or –O-Si(CH$_3$)$_3$. This surface is uniform, hydrophobic, and nonpolar, which makes it suitable for coating with nonpolar to moderately polar stationary phases [8].

Highly polar stationary phases such as polyethylene glycol can be applied to the rehydroxylated fused-silica surface in a manner that deactivates the surface during the coating process. Other processes, such as deactivation through vapor deposition, can be used to prepare the silica surface for stationary phases with other polarities and separation characteristics.

The stationary phases in use on modern GC capillary columns range from nonpolar to highly polar, with many specialty phases developed for specific analyte separation. The GC user survey cited previously showed that three of the top four stationary phases in use by respondents were based on methyl silicone: 100% methyl silicone (nonpolar); 5%-phenyl methyl silicone, or 5%-PMS, (nonpolar); and 50%-PMS, (moderately polar). The other popular stationary phase is polyethylene glycol, or PEG (polar).
The methyl-silicone-based stationary phases are particularly suited to GC because they exhibit high viscosity over a wide temperature range (up to 350 °C). They have a low glass transition temperature, so they remain liquid at low operating temperatures. The Si-O bonds make the phases flexible and provide good diffusivity. These phases can be cross-linked and bonded to the fused silica layer to make them more chemically stable and less apt to bleed off of the column at high operating temperatures. Since they are available in varying polarities, they can be used to perform a wide range of separations.

The coating of capillary GC columns can be performed by the dynamic or the static method. The dynamic method involves filling the column with a solution of the stationary phase in a suitable solvent and then forcing the solution out of the column with a slow stream of dry, inert gas. This leaves a thin film of the stationary phase on the column wall, which is then dried by continued flushing with the carrier gas. This is a faster method than the static method, but it is difficult to determine the precise coating thickness on the capillary wall. The drying process may also push more of the stationary phase to the end of the column, resulting in uneven coating thickness.

The static method of column coating involves preparing the solution of the stationary phase in a percentage designed to coat the wall of the capillary with a precise thickness. The thickness of the stationary phase can be calculated, in µm, from:

\[
d_f = \frac{r}{2\beta} = \frac{dc}{400}
\]

where \(r\) is the radius of the capillary, \(\beta\) is the phase ratio, \(d\) is the capillary diameter (in µm) and \(c\) is the concentration of the stationary phase in volume percent. To make the stationary phase solution accurately, the density of the stationary phase must be known and taken into account [20].

The column is completely filled with the stationary phase solution and capped on one end. The other end is attached to a round flask which is then evacuated. The column is then opened to the vacuum and the solvent is allowed to dry quiescently. The drying process can take about 100 hours for a standard 30-m column. The disadvantage of this coating method is that it is slow. The significant advantages are that the coating thickness can be predicted and the coating is more likely to be even along the length of the column due to quiescent drying. A problem with this method is that the presence of air bubbles in the filling solution can create areas of thinner
stationary phase, allowing for more interaction between the column surface and analytes being separated.

The static coating method is used by the majority of column manufacturers, followed by proprietary bonding and cross-linking processes to immobilize the stationary phase on the column. The final steps are to rinse the column with an appropriate solvent(s) followed by drying with an inert gas. The column is then cured near its upper temperature limit and monitored for bleeding of the stationary phase. Finally, the column is tested with chemical probes which allow the manufacturer to monitor the column-to-column quality and performance [21].

*The Use of Polyimide as a GC Capillary Column Base Material*

While it is well-known and widely used as a protective coating for the fused-silica glass GC capillary column, the use of a polymeric polyimide capillary as a chromatographic column in its own right has not been studied.

In 1984, J. Balla and M. Balint published their research into the effectiveness of using a polyimide coating over the top of a fused-silica column surface in order to seal off that surface and its associated active sites [22]. They suggested the use of polyimide as a column without the glass support, but the manufacturing methods of that time did not produce capillaries of sufficient length and close tolerances. Instead, Balla and Ballint took a tube-in-tube approach by coating the inside of an untreated glass capillary with polyamic acid solution followed by heat curing to form a polyimide layer.

Balla and Ballint used the same base materials used to produce the polyimide whose DuPont trade name is Kapton®. The dianhydride was pyromellic acid dianhydride (PMDA), the diamine was 4, 4′-diaminodiphenylether (ODA), and the solvents included dimethylformamide, N-methylpyrrolidone and N, N-dimethylacetamide. Kapton® is a very common polyimide and is prized for its excellent mechanical properties, water resistance, low dielectric constant, wear resistance, and inertness to solvents.

In a polar aprotic solvent, the dianhydride and the diamine will form a polyamic acid at ambient temperatures. The mechanism of the polyamic acid formation is a nucleophilic substitution reaction at one of the carbonyl carbon atoms of the dianhydride with diamine. The polyamic acid is dehydrated at temperatures of 250 - 350 °C. The imidization proceeds rapidly at first, and then slows as the polymer starts to become more rigid and sterically hindered. Some
traces of water and solvent may be entrained in the polymer as imidization slows down [23]. The structure of the PMDA-ODA polyimide is shown in Figure 1.2.

Balla and Ballint performed thermal degradation studies on polyimide films and found that degradation began at about 450 °C. They also determined the chemical resistance of the polyimide to solvents, acids, and bases. The polyimide was susceptible to strong acids and bases, but unchanged by 24 hours of exposure to solvents.

Their research showed that a polyimide (PI) layer of 1 – 10 µm formed a continuous, well-adhered layer and was sufficient to minimize the activity of the glass surface. They tested the wettability of 20 stationary phases on 20-µm layers of PI on glass and found that they could wet the PI surface well with all of the phases which were nonpolar to moderately polar, while having less success with the highly polar phases. Because of these findings, they performed thermal tests comparing the adhesion of two highly polar Carbowax PEG stationary phases on PI-coated glass column sections to that of the phases on uncoated glass column sections. In both cases, the PEG/PI/glass adhesion was superior to that of PEG/glass surface. These tests implied that the polyimide coated column would exhibit a lower bleed rate than the bare glass column.

Fourier-transform infrared (FTIR) analysis of the PI layer alone and that of the PI/PEG layer was performed in the wavelength region of 1700 cm\(^{-1}\), the area where the carbonyl peaks should be dominant. As expected, the polyimide film had strong peaks in the region. The PI/PEG film showed less intense peaks, shifted to lower wavelengths in this region, indicating that the PEG had adhered to the PI surface at least partly through hydrogen bonding with the PI surface carbonyl groups.

Balla and Ballint made several PI-coated columns, using a variety of polarities of stationary phases and were able to demonstrate excellent separation of compounds. For example, seven alcohols were separated on two 0.5-mm ID x 20-m L polyimide columns, one coated with 100% methyl silicone stationary phase and the other with Carbowax.

Polyimide capillary tubing is manufactured for medical devices such as coronary and urinary catheters. It is available in a wide range of IDs, including those typically used for capillary GC columns: 0.10, 0.25, 0.32, and 0.53 mm. The tubing is rigid, yet flexible enough to be wound into coils of a few centimeters in diameter. It exhibits excellent chemical resistance and the high purity of modern manufacturing methods has enabled polyimide to be classified for use in human medical devices.
SECTION 1.4: PURPOSE

The purpose of this research study was to explore the use of polymeric polyimide capillary tubing as GC capillary columns, both uncoated and coated with stationary phases of different polarities. Polyimide capillary columns with dimensions of 0.32-mm ID x 3-m L were obtained from two OEM suppliers to the medical device industry. Methods for cleaning and bleed testing the bare polymeric columns were developed.

The selected stationary phases were moderately-polar 50%-PMS (OV-17) and nonpolar 5%-PMS (SE-54). The polyimide columns were coated using the static method followed by conditioning in the GC instrument. The phase thickness was measured by scanning electron microscopy (SEM) after coating and conditioning of the columns.

A method was developed for securing these short columns in the oven of an HP 5890 Series II gas chromatograph. The columns were installed into the GC oven using normal ferrules and column nuts.

A method was developed for conditioning the columns prior to analytical runs. Grob test mixture compounds were purchased and made into standard solutions as test probes for the polyimide columns. These test probes were determined on two sets of uncoated and coated polyimide columns and the results were compared. The separations were performed isothermally using split injection and a flame ionization detector.

A sample mass load study was run to determine the range of sample mass injections which would not result in column overloading. A column reproducibility study was run to verify the reliability of the GC system.

Because the length of the polyimide columns was about 10% of the typical GC capillary column, the column flow rates were too high to perform a van Deemter study of $H$, plate height, vs. $u$, mobile phase velocity, even at a very low column head pressure. A deactivated fused-silica retention gap, 0.25-mm ID x 10-m L, was attached to a 3-m, 5%-PMS coated polyimide column using a zero-dead-volume connector. The retention gap added column length without affecting analyte separation, and reduced column flow over a wide range of column head pressure values. This combination column was installed in the GC and a van Deemter study was performed to determine the minimum $H$ and the optimal $u$ values for the column.
Finally, a 0.32-mm ID x 3-m L portion of a commercial column coated with a 1-µm thickness of 5% PMS was installed in the GC. The Grob test mix standards were run on this column for comparison to the analytical results achieved on the polyimide columns.
Figure 1.1. A Typical van Deemter Curve for a GC Column. Adapted from reference [24]
<table>
<thead>
<tr>
<th>Class</th>
<th>Compound</th>
<th>Boiling Point °C</th>
<th>Purpose of Probe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkanes</td>
<td>n-decane</td>
<td>174</td>
<td>100% recovery of neutral compounds, peak shape</td>
</tr>
<tr>
<td></td>
<td>n-undecane</td>
<td>196</td>
<td></td>
</tr>
<tr>
<td>Fatty Acid</td>
<td>methyl decanoate</td>
<td>224</td>
<td>homologous series, separation efficiency</td>
</tr>
<tr>
<td>Methyl Esters (FAMEs)</td>
<td>methyl undecanoate</td>
<td>241</td>
<td></td>
</tr>
<tr>
<td></td>
<td>methyl dodecanoate</td>
<td>261</td>
<td></td>
</tr>
<tr>
<td>Alcohols</td>
<td>1-octanol</td>
<td>195</td>
<td>adsorption due to hydrogen bonding to silanol groups</td>
</tr>
<tr>
<td></td>
<td>2,3-butanediol</td>
<td>183</td>
<td></td>
</tr>
<tr>
<td>Aldehyde</td>
<td>nonanal</td>
<td>93</td>
<td>adsorption not due to hydrogen bonding</td>
</tr>
<tr>
<td>Acids</td>
<td>2-ethylhexanoic acid</td>
<td>228</td>
<td>adsorption due to hydrogen bonding to silanol groups</td>
</tr>
<tr>
<td></td>
<td>2,6-dimethylphenol</td>
<td>203</td>
<td>or basic stationary phase</td>
</tr>
<tr>
<td>Bases</td>
<td>2,6-dimethylaniline</td>
<td>216</td>
<td>adsorption due to hydrogen bonding to silanol groups</td>
</tr>
<tr>
<td></td>
<td>dicyclohexylamine</td>
<td>256</td>
<td>or acidic stationary phase</td>
</tr>
</tbody>
</table>
Figure 1.2. The Structure of PMDA-ODA Polyimide.
REFERENCES


CHAPTER 2
POLYIMIDE POLYMER GLASS-FREE CAPILLARY COLUMNS
FOR GAS CHROMATOGRAPHY
SECTION 2.1: INTRODUCTION

Gas chromatography is a mature analytical science with a long history of published theoretical and laboratory research. The GC column in widest use today is the open-tubular wall coated (WCOT) capillary column. The typical WCOT column consists of a fused-silica glass capillary core covered with a protective outer layer of polyimide polymer. The inner surface of the fused-silica capillary is coated with a stationary phase selected to match the separation, efficiency, and sensitivity requirements of the application.

Because the fused-silica glass core is subject to winding stress, GC capillary columns are typically wound on wire hangers about 20 cm in diameter. Temperature control is a critical factor in chromatographic analyses, and it must be reproducible from run to run to achieve quantitative results. These factors combine to make the oven of the typical lab-based instrument very large. Smaller GC instruments are available for portability and for field use, but winding stress limits the fused-silica capillary column to a winding radius no smaller than 10 cm. The size of the column affects the design of the instrument.

The surface of the fused silica must be treated vigorously to prevent silanol (–SiOH) functional groups on the surface from behaving as active sites while the column is being used for separations. These active sites can affect the retention time of analytes and contribute to band broadening in non-reproducible ways.

Polyimide capillary tubing of very high purity and with a variety of inner diameter (ID) values is manufactured with PMDA-ODA polyimide [1] for use by medical device manufacturers. The polyimide capillaries are manufactured with ID values < 0.5 mm with tolerances of ± .005 mm of nominal ID. They are available in lengths up to 3 m [2]. A fused-silica glass capillary of similar ID will have the same level of ID tolerances [3]. The flexibility of the polyimide capillary allows it to be wound into a coil with a diameter of a few centimeters.

The surface of the PMDA-ODA polyimide polymer has been extensively researched because of its ubiquity in the electronics industry. A characterization of the surface density-of-states performed by ultraviolet photoemission spectroscopy (UPS) determined that the surface chemical bonds are dominated by the C π bonds associated with the aromatic rings, and the 2p non-bonding orbitals of the N and O lone pairs [4]. This study also determined that the intrinsic polyimide surface could not be revealed by UPS until after water, which was entrained at the surface during polymerization, was removed by annealing the polyimide above 250 °C.
Another study characterized the components of surface tension measured on a variety of polyimides using contact angle measurements [5]. For polyimides with ether linkages, such as PMDA-ODA, the polar component of surface tension was much less than the other polyimides tested, and the dispersive component was much larger. The surface was characterized as hydrophobic and dispersive, or less polar, when compared to polyimides where no ether linkages were present. The contact angles measured for polar liquids such as water and glycerol were still below 90°, indicating that the surface was wettable by the liquids.

The dispersive nature of the surface can be explained by the high level of conjugation of the bonds in the PMDA-ODA polyimide. This is one of the reasons that the PMDA-ODA polyimide demonstrates a desirable low dielectric constant and is relatively impervious to chemical attack [6].

Stationary phases for GC have been characterized extensively for the components of intermolecular actions which are responsible for their selectivity in GC separations [7]. The stationary phases used in capillary GC columns have been characterized as having four system constants: $l$, which is related to dispersive effects, or van der Waals forces, of the solvent-solute interaction; $a$, a measure of the hydrogen-bond basicity of the phase; $s$, which measures the ability of the phase to take part in dipole-dipole interactions; and $r$, which measures the ability of the phase to interact with solute n- or π- electron pairs. Values for $l$, the dispersivity constant, are nearly the same for all GC capillary stationary phases.

The stationary phases used in this research are 5%-phenyl methyl silicone (5%-PMS) and 50%-phenyl methyl silicone (50%-PMS). These phases are generally considered to be nonpolar and moderately polar, respectively. When the system constants of these phases are compared, the $a$ constant for the 50%-PMS is somewhat higher, while the $s$ constant is increased two-fold. The 50%-PMS phase, therefore, will have a much higher ability to have dipole-dipole interactions with solutes, which accounts for its polar nature. The $s$ constant for the 50%-PMS is, however, only approximately one-half of those seen for highly polar phases such as polyethylene glycol (PEG). The percentage of the phenyl monomer in the 50%-PMS phase accounts for increased interaction with the n- and π- electrons of solutes, so the $r$ constant is positive for this phase and zero for the 5%-PMS [7].

The characterizations of the polyimide surface and the system constants of the PMS stationary phases are complementary. If it can be assumed that the system constants determined
for interaction between the stationary phase and solutes can be interpreted as indicative of the
tendencies for the stationary phase interaction with the base material of the column, the PMS
stationary phases should wet and adhere to the polyimide surface very well.

Research has been published indicating that a variety of GC stationary phases were
successfully wetted on the surface of PMDA-ODA polyimide films. Some success in making
polyimide tube-in-tube GC capillary columns was demonstrated [8]. If polymeric polyimide
capillary columns can be successfully coated with GC stationary phases, shown to be robust and
able to perform separations, they may be a novel column type to be developed specifically for
use in small GC instruments. A comparison of the sizes of standard GC columns to that of a 3-m
polyimide capillary column wound around a test tube is shown in Figure 2.1.

This research project involved the development of procedures for cleaning and bleed-
testing polyimide capillary columns of the dimensions 0.32-mm ID x 3-m L. After these
preparation steps, polyimide columns were coated with one of the two stationary phases:
50%-PMS or 5%-PMS. The static coating method was employed. Film thickness was measured
by scanning electron microscopy (SEM). Uncoated, polymeric polyimide columns were also
prepared and tested as GC columns.

Grob test mix components with a variety of polarity and acid/base character were used as
chromatographic probes on the polyimide columns. Separations were performed on duplicate
sets of these polyimide columns, prepared and coated months apart, to assess the reproducibility
of the process and of the columns.

The reliability of the GC system was assessed with a column reproducibility study
performed by measuring the relative standard deviation of the retention times and of the peak
areas for a homologous series of solutes. Fatty acid methyl ester (FAME) compounds were
assessed on the polyimide column coated with 5%-PMS. The sample mass load limits of the
column coated with 50%-PMS were determined by performing a column overload study using
n-undecane in a range from 0.15 – 3.0 µg mass load.

For the van Deemter study, a retention gap of deactivated, uncoated fused-silica capillary
column with dimensions of 0.25-mm ID x 10-m L was connected to a 3-m polyimide column
coated with 5%-PMS using a zero-dead-volume connector. This configuration allowed
instrument flow through the column to be controlled in a wide enough range of values to
facilitate the study.
A 3-m length of commercially produced column with a 0.32-mm ID, coated with a 1-µm thickness of 5%-PMS, (DB-5), was installed into the GC. Grob test mix components were analyzed on this shortened commercial column to serve as a basis for comparison with the polyimide column performance.
SECTION 2.2: EXPERIMENTAL

Chemicals and Materials

The stationary phases, 5%-PMS, (SE-54) and 50%-PMS, (OV-17), were purchased from Sigma-Aldrich, St. Louis, MO. A Grob test mixture standard was purchased from Alltech Associates (Grace), Chicago, IL. The individual Grob test components and various solvents were purchased from Fisher Scientific, Chicago, IL, and from Sigma-Aldrich.

The capillary column washer used to clean and coat the polyimide columns, as well as the digital flow check meter were purchased from Alltech Associates. Standard column nuts and graphite ferrules, purchased from a variety of suppliers, were used as column installation supplies for the polyimide columns. A column hanger was fabricated from a standard hanger to accommodate the polyimide column in a coil of about a 6-cm diameter, as shown in Figure 2.2.

The polyimide columns used for the development of cleaning and bleed testing procedures were purchased in dimensions of 0.32-mm ID x 0.76-m L from Small Parts, Inc., Miami Lakes, FL. Polyimide columns in dimensions of 0.32-mm ID x 3-m L, with OD ranging from 0.35 – 0.39 mm, were purchased from MicroLumen, Inc., Tampa, FL, and from RiverTech Medical, Chattanooga, TN. Both of these companies are manufacturers of the polyimide capillaries. Per discussions with both of these companies, 3 m is the longest practical length of capillary polyimide tubing currently available.

The uncoated fused-silica retention gap in dimensions of 0.25-mm ID x 10-m L, deactivated for intermediate polarity solvents, was purchased from Restek, Bellefonte, PA. The commercial column of dimensions 0.32-mm ID x 30-m L, coated with 1 µm of 5%-PMS, (DB-5), was manufactured by J&W Scientific (Agilent Technologies, Santa Clara, CA). The DB-5 stationary phase was bonded and cross-linked by a proprietary process.

Instrumentation

A Hewlett-Packard (HP) 5890 Series II gas chromatograph equipped with an HP 7673 autosampler and an Agilent 3396 Series III integrator was used for all analyses. Carrier gas flow on this instrument was controlled by column head pressure. The lowest practical setting for column head pressure, 2 psi, was used for all analyses unless otherwise noted. Column flow on the 3-m polyimide columns averaged 8 – 10 mL/min as measured by the digital flow meter with the oven temperature at 30 °C and the detector at operating temperature, with $u$ values of between 70 - 100 cm/sec. All test mixture separations were performed isothermally with
temperatures indicated in the data tables. Unless otherwise noted, GC instrument parameters were: injector and detector temperatures at 250 °C; attenuation at 2; range at 3. Integrator attenuation was set as required to bring analyte peaks onto scale.

The autosampler injection volume was 1 µL, and analyses were performed in split mode, with the split ratio about 35:1, unless otherwise noted.

*Column Cleaning and Bleed Testing*

After trial runs with the shorter (0.76-m L) polyimide columns, a column cleaning and preparation sequence was developed and applied to all of the 3-m polyimide columns used for GC separations. The columns were washed with a series of solvents of increasing polarity: hexane, 2-propanol, and methanol. The Alltech column washer was connected to a helium carrier gas source, and pressure was controlled by a regulator. The top of the column washer was fitted with a 0.5-mm ID ferrule so that the column could pass through the top and be hand-held while pressure was applied to the solvent inside the column washer tube, as shown in Figure 2.3. The column washer was later used in a similar manner to coat the columns with stationary phase, followed by quiescent vacuum drying, as shown in Figure 2.4.

During the cleaning step, the columns were washed for several minutes with each solvent at a gas pressure of < 5 psi. The columns were dried for several minutes with helium purge after the wash sequence was completed. On the basis of column bleed tests, results to be discussed later, the 3-m columns were individually wound into glass crystallizing dishes and baked in a lab oven at 265 °C for 60 minutes.

Column bleed tests were performed on each of the polyimide columns prior to coating with stationary phase or use as polymeric GC columns. The purpose of the bleed tests was to determine if the polymer would degrade at separation temperatures near the upper limit of the stationary phases planned for use in this study, which was about 350 °C. Bleed is detected by a rise in the baseline signal of the FID. Bleed can cause problems with quantitation and reproducibility.

The column to be bleed-tested was installed into the GC on both the injector and the detector sides. A bleed test temperature ramp program was run: initial temperature (T), 30 °C; ramp rate, 5 °C/min; final T, 300 °C; hold time (at 300 °C), 10 minutes. Graphs of the results of consecutive bleed tests are shown in Figures 2.5 and 2.6.
As mentioned in Section 1.1, it has been reported in the literature [4] that studies of the intrinsic molecular orbital structure of a PMDA-ODA polyimide film, using ultraviolet photoemission spectroscopy (UPS), was unsuccessful until the polyimide film was annealed at temperatures above 250 °C. The evolution of water from the polyimide during annealing was confirmed in the study by mass spectrometry [4]. Another study investigated how to improve the durability of the polyimide outer coating of fused-silica capillary electrophoresis (CE) columns. It was determined that annealing the columns in a GC oven at 300 °C for 200 hours (not optimized) greatly improved the polyimide’s chemical resistance to common CE solvents. This improvement was documented in the study with scanning electron microscopy (SEM) photographs [9].

Column Coating and Conditioning

The static method for column coating was used to coat the stationary phases on the inner surface of the cleaned and bleed-tested polyimide columns [10]. Equations 1.6 and 1.8 show the relationship between the retention factor, \( k \), and phase ratio, \( \beta \):

\[
K_C = k\beta = k \frac{r_c}{2d_f}
\]  
(2.1)

where \( k \) is the retention factor (the ratio of the time the analyte spends in the stationary and mobile phases), \( r_c \) is the column diameter, and \( d_f \) is the stationary phase thickness. Since \( \beta \) and \( k \) are inversely proportional, increasing \( d_f \) will decrease \( \beta \) and increase \( k \). Based on this relationship, it was decided to coat the polyimide columns with a thick stationary phase layer of 5 \( \mu \)m to improve the values of \( k \) by improving retention of the analytes on the column. Typical WCOT stationary phase thickness values range from 0.25 – 1.0 \( \mu \)m. For a column with 0.32-mm ID, the phase ratio range is 320 – 80. The calculated phase ratio for the polyimide columns used in this study, assuming \( d_f = 5 \mu m \), was 16. Actual stationary phase thickness was measured by scanning electron microscopy (SEM) after the columns had been coated, conditioned, and used in separations. SEM scans of both a coated and an uncoated polyimide column are shown in Figure 2.7, along with an SEM scan of a commercial fused-silica capillary column with a cross-linked and bonded 5%-PMS (DB-5) stationary phase.

The concentrations of the solutions for stationary phase coating were calculated two ways. One method was to calculate the volume of the empty capillary tube (\( \pi r^2 L \)) as \( V_1 \). The volume of the capillary inside the coating, \( V_2 \), was then calculated using (\( r - d_f \)) as the radius
corrected for the coating thickness. The volume of the coating, $V_3$, is $(V_1 - V_2)$. The volume percent of the coating in solution is then $(V_3/V_1)$. These calculations were verified using Equation 1.21. Methylene chloride was the solvent for the 50%-PMS, and toluene was the solvent for the 5%-PMS.

The column washer was used to force the stationary phase through the capillary. After allowing the solution to flow for several minutes to assure that the column had time to wet completely and to avoid entrained bubbles, the column was completely filled with the solution and one end was capped. The other end was installed in an open, ferruled Swagelok fitting and was attached to the vacuum drying apparatus shown in Figure 2.4. The round-bottom flask was evacuated to 25-in Hg several times. Finally, the column was opened to the vacuum and allowed to dry quiescently for several days.

The coated column was trimmed on both ends and was installed into the GC on the injector side to facilitate column conditioning. The unattached end of the column was immobilized on the floor of the GC oven. Carrier gas flow through the column was confirmed by bubbling it into a small beaker of methanol.

A conditioning program was run as follows: initial temperature, $T$, 30 °C; ramp rate, 5 °C/min; final $T$, 100 °C; hold time, 120 min. The purpose of this procedure was to allow the column to completely dry without sending any evolved solvent through the detector. The column was then installed into the detector side of the instrument, and a high temperature conditioning program was run as follows: initial $T$, 40 °C; ramp rate, 20 °C/min; final $T$, 200 °C; hold time, 15 min. This high temperature conditioning step was performed well above the operating temperature of the columns (100 °C, typically) and well below the temperature limit of the stationary phases (about 350 °C). FID signals ranged from about 4000 – 8000 pA at 200 °C and then stabilized at around 5 – 6 pA at 40 °C.

The columns were conditioned before daily use by raising the oven temperature to 130 °C with a hold time of 30 min. The uncoated polyimide columns were cleaned, baked out, bleed tested, and conditioned in the same manner.

**Analysis of Grob Test Mix Components**

Grob test mix components, as listed in Table 1.1, were purchased, and standards were made using carbon tetrachloride, CCl₄, as the solvent for the alkanes and methylene chloride, CH₂Cl₂, for the other components. Two sets of polyimide columns were prepared and tested.
These columns were from two different manufacturers and were prepared many months apart for a good test of the reproducibility of the process as well as the columns.

The chromatograms are presented as, where applicable, from the duplicate columns in Figures 2.8 – 2.15, 2.17, 2.19 and 2.21. The data are presented in Tables 2.1 – 2.11. For comparison purposes, a separation of the FAME compounds was performed using the retention gap and 5%-PMS column combination as described above. The data are shown in Figure 2.23 and in Table 2.11.

**Comparison Study to 3-m Commercial Column**

A 3-m section of a commercially produced fused-silica capillary column, coated with 5%-PMS, with \( d_f = 1 \mu m \), was obtained from a 30-m column. The 3-m column was coiled on a standard wire hanger, secured with heat-proof string, and installed into the GC. The column was conditioned with the daily conditioning program described above. The Grob test components were determined on the column, and the results were calculated. The graphs of the chromatograms are presented in Figures 2.16, 2.18, 2.20 and 2.22. The data are presented in Tables 2.8 – 2.11.

The following parameters were calculated for each chromatogram as appropriate: from Equation 1.9, the adjusted retention time, \( t'_{R} \), and the retention factor, \( k \); from Equation 1.10, the relative retention factor, \( \alpha \); from Equation 1.13, the plate number, \( N \); from Equation 1.18, the plate height, \( H \); from Equation 1.15, resolution, \( R_S \). In addition, the mobile phase velocity, \( u \), in cm/sec, is calculated as follows:

\[
u = \frac{L}{t_M}
\]

where \( L \) is the length of the column in cm and \( t_M \) is the retention time of an unretained compound in seconds.

**Column Reproducibility Study**

A series of five sequential injections and separations was performed on a polyimide column coated with 5%-PMS. A standard containing 32 ppm each of the three FAME probes, methyl decanoate, methyl undecanoate, and methyl dodecanoate, was analyzed isothermally at 60 °C. The split ratio was 35:1. The mean and standard deviations of the retention times and the peak areas were calculated. The data are presented in Table 2.12.
Column Mass Load Study

A series of standards was prepared with n-undecane in a range from 0.15 – 3.0 µg mass injected in a 1-µL injection with a split ratio of 34:1. The standards were determined in random order on a 5%-PMS coated polyimide column. The values of column efficiency or plate number, \( N \), were calculated according to Equation 1.13. These values were graphed against sample mass load. The top of the graph is characterized by a broad, flat region within which the sample mass load will not overload the column. Once column overload begins, the values of \( N \) are seen to decline because column efficiency is reduced. The graph of this study is presented in Figure 2.24.

The van Deemter Study

The HP 5890 Series II GC used for this research project controlled column flow by column head pressure. Due to the short length of the column, flow rates could not be reduced to values low enough to run the van Deemter study. To accomplish a reduced flow to the 5%-PMS polyimide column used in the study, it was connected on the injection side to an uncoated, deactivated fused-silica retention gap with dimensions of 0.25-mm ID x 10-m L. The retention gap was installed on the injection side of the GC, and the polyimide column was installed on the detector side. A 20-cm wire hanger was placed in the oven in front of the polyimide column hanger, and the retention gap was coiled around it and secured to it with heat-proof string.

A program called FlowCalc 2.05 was downloaded from the Agilent Technologies website [11]. This program allows the analyst to enter various column dimensions, column flows or column head pressures and calculate the effect on the other parameters. This program was used to estimate the flow rates, mobile phase velocities, \( u \), and holdup times, \( t_M \), for an unretained species on the 13-m combined column used in the van Deemter study. The FlowCalc values for flow rates and \( u \) have been included for reference in the data in Table 2.13.

A 50 ppm standard of n-undecane was used in the study. Column head pressures ranging from 2 – 20 psi were used, with \( u \) values ranging from 14 – 82 cm/sec. The graph of the study results is presented in Figure 2.25.
SECTION 2.3: RESULTS AND DISCUSSION

Column Cleaning and Bleed Tests

The column cleaning and bleed-testing procedures were performed on polyimide columns of different lengths from three vendors. The results were consistent on all of the columns.

A graph of the results of the first bleed test performed on a short polyimide column is shown in Figure 2.4. The FID signal increased from 14 pA at 40 °C to over 900 pA at 260 °C, then fell to 34 pA after holding the temperature at 300 °C for 10 minutes. The results of a second and third bleed test on the same column are graphed in Figure 2.5. In the second test, the signal started at 5.4 pA, an acceptable baseline signal, and only increased to 18.5 pA at 300 °C before falling to 14.1 pA after being held at 300 °C for 10 minutes. A third bleed test demonstrated that the column did not produce a signal above 12 pA over the entire temperature range of the test.

The column bleed tests performed for this study demonstrated that the polyimide annealed at about 265 °C and, after annealing, did not contribute significantly to the FID signal in subsequent bleed tests. The annealing process is most likely the evolution of water molecules which had been entrained near the polyimide surface during polymerization.

Column Coating and Conditioning

The 50%-PMS (OV-17 in methylene chloride) flowed through the columns readily and all solvent appeared to have dried under vacuum when the columns were conditioned after coating. The 5%-PMS (SE-54 in toluene) was much more viscous than the 50%-PMS solution and required a higher gas pressure to push it through the capillary during coating. There was still solvent in both of the 5%-PMS columns when they were put into use, and they were dried with helium flow in the GC oven at ambient temperatures for about 30 min prior to conditioning.

The columns were first conditioned at the anticipated operating temperature, 100 °C for 120 min, and then at a temperature exceeding analytical range, ramping from 40 – 200 °C, with a final hold time 15 min. A daily conditioning program, 130 °C held for 30 min, typically resulted in a signal of < 10 pA at 130 °C, and a signal of < 6 pA after cooling back down to 30 °C. These results were confirmed by the observation of a stable baseline in all chromatograms. Normal baseline signal for these columns was < 6 pA.

The actual coating thickness on both sets of the polyimide columns was measured by SEM. The thickness measurements ranged from 0.5 – 2 µm, with an observed mean value near
1 µm. The measurements may have varied within the observed range due to distortion caused by the cutting process, since the stationary phase is a viscous semi-liquid.

Figure 2.7 (a.) is an SEM of an uncoated polyimide column. The regularity of the wall thickness and the smooth inner surface of the capillary can be observed.

Figure 2.7 (b.) is an SEM of the 50%-PMS stationary phase coating as was seen around the entire surface of the polyimide capillary column in a smooth, continuous layer, and which appeared to be well-adhered to the polyimide surface. The presence of silicon in the observed stationary phase layer was confirmed by energy dispersive X-ray spectroscopy (EDS). EDS was performed to ensure that the layer observed in the SEM image was, in fact, the stationary phase layer on the inner diameter of the polyimide capillary.

Figure 2.7 (c.) is an SEM scan of the cross-linked and bonded 5%-PMS (DB-5) coating on the fused-silica commercial column. This stationary phase appeared to be denser than the PMS phases coated on the polyimide columns, with a smooth, highly uniform surface. Coating thickness was determined to be near 0.8 µm.

The apparent loss of stationary phase coating thickness between the coating process and the SEM measurements on the polyimide columns may have occurred during the conditioning steps. Some of the stationary phase thickness may have been lost from the 5%-PMS columns when the excess solvent was dried with helium flowing through the columns.

For future work, the drying procedure should include a re-drawing of the vacuum on a regular basis as well as thermostating of the column above room temperature to facilitate complete drying. A study should be performed with the stationary phase coating thicknesses measured at all stages of coating and conditioning, as well as during use for separations in order to monitor any changes in thickness.

**Analysis of Grob Test Mix Components**

The use of the Grob test mix components in this research study was not intended to assess the columns with the classical application (Section 1.2). Since this group of probes has been in use for many years with fused-silica columns, it was thought that they would be a diverse and instructive set of probes for observing and assessing the column—solute interactions in the polyimide columns.

Good chromatographic data will show consistent values of $k$, $\alpha$, $H$, $N$, and $R_S$. Since $\alpha$ is the ratio of the $k$ values of a pair of eluting peaks, it should remain consistent from column to
column with the same phase ratio, $\beta$. If the values of $\alpha$ are consistent, the separation of the peaks can be said to be happening in a reproducible way between the columns. The terms which measure column efficiency, $N$ and $H$, should also be consistent between duplicate columns operated under the same conditions. All of the separations were performed isothermally at temperatures determined experimentally to balance $k$, $\alpha$, and $R_S$.

Peak asymmetry was assessed at $w_{0.10}$, the peak width at 10% of peak height. This value for the peak width is used when the tailing factor, $TF$, of the peak is measured as:

$$TF = \frac{b}{a} \quad (2.2)$$

where $a$ is the peak width on the left side of a line drawn from the apex of the peak to the $w_{0.10}$ baseline, and $b$ is the width to the right of the line [12].

The uncoated polymeric polyimide columns demonstrated a minimal ability to separate and resolve some of the compounds in the test mixes under the analytical conditions used. A few examples of the results of these determinations have been included in the data.

Figure 2.8 and Table 2.1 show the result of the separation of the alkanes $n$-decane and $n$-undecane on the uncoated columns. These neutral compounds lack a functional group and are retained primarily with dispersive forces. They were nearly unretained on the uncoated columns, with very low $k$ values calculated at 0.5 and 1.0, respectively, although some resolution did occur.

Figure 2.9 and Table 2.2 show the results of the elution of the aldehyde, nonanal, on the uncoated columns. This compound had a $k$ value < 2 on the columns and the values of $N$, although very low, were reasonably consistent. Since the polyimide is not considered to be conducive to dipole-dipole interactions, the retention is probably due to dispersive forces with the long hydrocarbon chain of the molecule.

Figure 2.10 and Table 2.3 show the results of the separation of the base compounds, 2,6-dimethylaniline and dicyclohexylamine, on the uncoated columns. The conformation of the peaks shown in the overlay was somewhat reproducible, and two overloaded compound peaks were seen. The values of $k$ and $\alpha$ were fairly consistent, with $R_S$ calculated above the baseline value of 1.5. The values of $N$ and $H$ were poor. The retention and separation of these compounds on the uncoated polyimide is remarkable. Interaction between the n- and $\pi$-electrons of the polymer and those of the 2,6-dimethylaniline and with the n-electrons of the dicyclohexylamine,
as well as dispersive effects, may explain the ability of the uncoated polyimide to retain the bases.

Figure 2.11 and Table 2.4 show the results for the separation of the alkanes, n-decane and n-undecane, on the polyimide columns coated with 50%-PMS. Symmetrical peaks were seen with no tailing observed above \( w_{0.10} \). Retention on the columns was good, with \( k \) values averaging 4.0 for n-decane, the earliest eluting peak. The values for \( \alpha \) were consistent between the columns. The values for \( N \) and \( H \) were more consistent between the peaks on Column B, averaging near 710 and 4.3 mm, respectively. Resolution was excellent on both columns, averaging above 5.0. The integrated peak areas for the alkanes were very close, indicating that both compounds were well recovered in the separations.

Figure 2.12 and Table 2.5 show the results of the elution of the aldehyde, nonanal, on the polyimide columns coated with 50%-PMS. The peaks were sharp, with minimal tailing observed above \( w_{0.10} \), although some fronting was apparent in the peak shape, indicating that sample overload was beginning to occur. The values of \( w_h \) for both elutions were very close. The compound was retained somewhat longer on Column B, resulting in higher calculated values for \( k \) and \( N \), and lower values for \( H \).

Figure 2.13 and Table 2.6 show the results of the separation of the bases, 2,6-dimethylamine and dicyclohexylamine, on the polyimide columns coated with 50%-PMS. Peak conformation on the two columns was very similar, indicating that the compounds were recovered reproducibly in both separations. The \( k \) and \( \alpha \) values were very close between the columns, which was expected given the peak conformation. The better values of \( N \) and \( H \) calculated for the second peak in both analyses are probably overstated due to peak shape. In these cases, the fronting and the tailing tend to counteract each other, minimizing \( TF \). Resolution of the bases is excellent and consistent between the columns, averaging above 6.0.

Figure 2.14 and Table 2.7 show the results of the separation of the FAMEs, methyl decanoate, methyl undecanoate, and methyl dodecanoate, on the polyimide columns coated with 50%-PMS. These compounds consist of a long nonpolar hydrocarbon chain with a polar ester functional group on one end of the molecule. These characteristics combine to make these compounds amenable to separation on stationary phases with a range of system constants. Peak conformation is reproduced well for peaks 1 and 2, but peak 3 is larger and sharper on Column A, indicating that it was better recovered during separation on that column. Values for \( k \) and \( \alpha \)
were nearly identical for each peak on both columns, indicating that the separation processes were reproducible on each column. Slightly longer retention times and slightly narrower peak widths improved the values for N and H on Column A. Resolution was consistent between the peak sets on each of the columns, averaging 5.6 on Column A and about 4.0 on Column B.

Figures 2.15 and Table 2.8 show the results of the separation of the alkanes, n-decane and n-undecane, on the polyimide columns coated with 5%-PMS. This column is less polar than the 50%-PMS phase, and since the alkanes are also nonpolar, they were retained much longer on the 5%-PMS phase. The values for k were essentially doubled on these columns due to the longer retention times. However, the values for α were nearly identical among all four columns, indicating that the mechanism of the separation of these compounds were reproducible in all cases. Peaks were symmetric, although the peaks for Column A showed some distortion, probably due to overload conditions. This also resulted in larger peak widths on Column A, lowering values for N and raising values for H. Resolution was above baseline values and was consistent between these columns, averaging 3.5.

Figure 2.16 and Table 2.8 show the results for the separation of the alkanes on the commercial fused-silica column cross-linked with 5%-PMS, the DB-5 column. Peaks were sharp and symmetric. Retention times were about 3 times longer on the DB-5 column when compared to the 5%-PMS polyimide column, with k values increased accordingly. Most notably, the α value for this column was identical to those of the polyimide columns, indicating that separation was reproducible among them. The increase in retention time was not achieved at the expense of peak width, so calculated values of N and H were much improved over the polyimide columns, averaging 2610 and 1.2 mm, respectively. Resolution was improved by a factor of 2, to 7.5.

Figures 2.17 and Table 2.9 show the results of the elution of the aldehyde, nonanal, on the polyimide Column B coated with 5%-PMS. The peak shape, peak width, and retention time of the aldehyde on this column were very similar to those of the 50%-PMS columns. The compound was well retained and k values were comparable. The consistency of these values between the PMS stationary phases indicates that the aldehyde was most likely retained on the PMS columns by dispersive effects rather than by dipole-dipole interaction with the functional group. Values for H and N were also fairly consistent among the three columns tested. This elution was inadvertently omitted from the determinations performed on Column A.
Figure 2.18 and Table 2.9 show the results for the elution of the aldehyde on the commercial fused-silica column cross-linked with 5%-PMS, the DB-5 column. The peak was symmetric. The retention time was more than 4 times longer than that of the 5%-PMS polyimide column with peak width less than doubled. Accordingly, the $k$ value was proportionally increased, and the values for $N$ and $H$ were much improved over the polyimide column and were comparable to those measured with the alkane separations.

Figures 2.19 and Table 2.10 show the results of the separation of the bases, 2,6-dimethylaniline and dicyclohexylamine, on the polyimide columns coated with 5%-PMS. The bases were not retained as long on this less polar column, but peaks were sharp and conformation was reproduced between the columns. The $k$ values were consistent between these columns and were lower than those on the 50%-PMS columns due to their shorter retention times. The values for $\alpha$ were consistent between the 5%-PMS columns and were observed to be higher than those for the 50%-PMS. This variance in $\alpha$ indicates that there is a difference in the separation mechanism for one or more of these compounds. The $k$ value of the 2,6-dimethylaniline was higher on the 50%-PMS columns, indicating enhanced retention. This difference may be caused by the ability of the 50%-PMS phase to interact with the n- and $\pi$-electrons of the 2,6-dimethylaniline, resulting in a longer retention time on those columns. Values for $N$, $H$ and $R_S$ were more consistent among the 5%-PMS columns than among the 50%-PMS, probably due to improved peak shape.

Figures 2.20 and Table 2.10 show the results of the separation of the bases on the commercial fused-silica column cross-linked with 5%-PMS, the DB-5 column. The peaks were sharp and symmetric. Compared to the 5%-PMS columns, retention times were more than 3 times longer on the DB-5 column, but peak widths were comparable. The values for $k$ were larger, as would be expected with longer retention times. The $\alpha$ values were very close to those of the 5%-PMS polyimide columns, indicating reproducible separations took place. The observed differences in the $\alpha$ values when compared to the 50%-PMS, as discussed above, were reproduced on this column. Enhanced values for $N$, $H$, and $R_S$ were seen to be consistent with the other DB-5 determinations.

Figures 2.21 and Table 2.11 show the results of the separation of the FAMEs, methyl decanoate, methyl undecanoate, and methyl dodecanoate, on the polyimide columns coated with 5%-PMS. As a group, the peak conformations were well-reproduced between these columns,
although the determination on Column A was probably over-attenuated, reducing peak height and area. These compounds exhibited shorter retention time on the 5%-PMS phase, but $k$ values were consistent among all of the columns. The $\alpha$ values were identical among all of the columns, indicating reproducibility in the separation processes. Peak widths were consistent, resulting in consistent values for $N$ and $H$. Resolution was reproduced at about 2.8 for all of the peak pairs.

Figures 2.22 and Table 2.11 show the results of the separation of the FAMEs on the commercial fused-silica column cross-linked with 5%-PMS, the DB-5 column. Peaks were sharp and symmetric. As has been seen with the previous solutes, retention times averaged about 3 times longer on this column, with the resultant increase in $k$ values. The $\alpha$ values were identical with the 5%-PMS and the 50%-PMS columns, indicating reproducibility in the separations on each of the phases. Peak widths were approximately double the values for the 5%-PMS separations, but the longer retention times resulted in the values of $N$ and $H$ being much improved in comparison. Resolution was also higher on this column at about 8.6.

Figures 2.23 and Table 2.11 show the results of the separation of the FAMEs on the combination column used for the van Deemter study. This column had a 10-m deactivated fused-silica retention gap attached to a 5%-PMS coated polyimide column. Separation was performed at optimal flow conditions, near 30 cm/s, as determined in the van Deemter study to be discussed later. The retention times of these peaks were significantly longer than on the polyimide column alone, more comparable to those on the DB-5 column. Significant tailing was seen, most likely due to extra-column effects related to the connection of the two columns. The tailing affected peak shape, the baseline between the peaks, and the integration of the peaks. Due to these problems, the measurements for peak width, $w_h$, were performed manually. These values are included in Table 2.11. The values for $k$ were smaller than those for the 5%-PMS polyimide columns without the retention gap due to the larger measured retention time of the tailing solvent peak ($t_M$). The $k$ values do increase proportionally for each compound. The $\alpha$ values were identical to those of all of the other columns, including the DB-5. The more optimal flow conditions improved the values of $N$ and $H$, to about 2600 and 1.0 mm, respectively. Resolution was twice the value seen on the 5%-PMS columns without the retention gap, at 5.5. The values for $N$, $H$ and $R_S$ approached those of the DB-5 column.

The retention times for the analytes separated on the commercial column were consistently longer when compared to those on the 5%-PMS polyimide columns, and this was
somewhat unexpected. How the proprietary, cross-linked DB-5 stationary phase may affect partitioning of the analytes is unclear. Comparison of the SEM scans of the 50%-PMS coated on the polyimide column and that of the cross-linked and bonded DB-5 phase on the fused-silica column shown in Figure 2.7 (b.) and (c.), respectively, shows an apparent difference in stationary phase density and surface uniformity. The retention time results may indicate that the thickness of the stationary phase on the 5%-PMS coated polyimide columns (not shown in Figure 2.7) was more variable than that of the commercial column.

The coated polyimide columns were not able to separate and resolve the alcohols 1-octanol and 2,3-butanediol. Injections of the individual components revealed that the 2,3-butanediol was not retained on the column. On nonpolar to moderately polar columns, this is the first compound to elute in the classical Grob test [13], so it was most likely unretained and came off the columns in the solvent peak.

The columns were also unable to separate and resolve the acids, 2,6-dimethylphenol and 2-ethylhexanoic acid. The 2,6-dimethylphenol peak was not seen when injected individually or in the acid group standards. The absence of this compound could be an indication of irreversible adsorption on the PMS phases, which are basic with respect to hydrogen bonding. There could also have been active sites in the injection liner of the instrument where adsorption could occur.

The alcohols and acids would be better separated on more polar phases since they all have functional groups with hydrogen bonding capability.

Other Studies

The reproducibility study results are shown in Table 2.12. Average retention times and peak areas for each of the three FAME peaks were determined. The standard deviation ($\sigma_{n-1}$) was determined and % relative standard deviation (%RSD) was calculated. For the peak retention times, the %RSD ranged from 0.46 – 0.52. The %RSD of the peak areas were also consistent, ranging from 2.3 – 2.8. An accepted value for the %RSD of an optimized GC instrument is $\pm 1\%$, with repeatability of the GC method at $\pm 2\%$ [14]. This study looked at the precision of the instrument retention times and at the repeatability of the separation ability of the column. The determined values were reasonable.

The sample mass load study graph, Figure 2.24, showed that the efficiency of the column, $N$, measured at close to 300, was not degraded significantly until the sample mass load exceeded 1 µg. This broad mass load range is a benefit of using a medium-bore column with a relatively
thick stationary phase of 1μm. Considering a 1-μL injection and the average split ratio of 34:1, the sample mass injected in most of the determinations in this research was below 100 ng.

The van Deemter study required the use of the retention gap in front of the coated polyimide column to slow the column flow down enough to run the study at low flow rates. This approach was effective, as shown in Figure 2.25 and Table 2.13. The graphed values moved through a minimum of $H = 1.0$ mm and $N = 2867$. The minimum of the curve occurred at about 30 cm/s, which is consistent with that determined for longer capillary columns and He carrier gas. Efficiency, $N$, for the polyimide column was improved by one order of magnitude under optimal flow conditions. The value was close to 1000 plates/m, consistent with that observed for the probe, n-undecane, on the commercially produced DB-5 column, as shown in Table 2.8.
SECTION 2.4: CONCLUSIONS

To the author's knowledge, this is the first research study to investigate polymeric capillary polyimide columns for use in GC separations. The result of the study is that the polyimide columns coated with the PMS stationary phases were shown to be capable of performing reasonable and reproducible separations on three classes of volatile organic probes: alkanes, bases, and FAMEs. They were also able to retain and elute individual aldehydes, alcohols, and acids, though it was not determined what separation ability these columns have for a range of these compounds.

The column cleaning, annealing, and bleed testing worked reproducibly on all columns. No column bleed was observed for the coated columns during isothermal separations run as high as 100 °C. The static coating process did coat the columns completely and reproducibly. The discrepancy between the calculated value for film thickness and that measured by SEM should be investigated in further work. The drying process for the coated columns should be optimized, especially for viscous coating solutions.

The polyimide columns were robust enough to be installed in the GC oven with standard ferrules and column nuts. The columns were taken in and out of the instrument on several occasions and, after running the normal conditioning program, were found to perform reproducibly with previous determinations.

The low efficiency observed for the columns, $N$ values averaging around 300 - 400, was demonstrated to be much improved when flow conditions in the instrument were optimized. Normal column flow for the instrument during separations was about 60 cm/s above the optimum, which was determined to be 30 cm/s by the van Deemter study. When these conditions were achieved with the use of a deactivated retention gap, the efficiency improved to about 2800. This value was comparable to that seen on the 3-m commercial DB-5 column. Although the optimal $u$ value was not determined for the DB-5 column, it was likely tested under sub-optimal flow conditions. Future development of these columns should be performed with a column restrictor or a retention gap in place in order to achieve and maintain optimal flow conditions.

There are many interesting avenues for further development of these columns. One of these would involve development of improved bonding of the polyimide with stationary phases, perhaps enhanced by chemical treatment of the polyimide surface. Developing methods for cross-linking the stationary phase surface would improve the ability of the columns to be used at
higher temperatures without bleed. The better retention times and peak symmetry on the DB-5 column are likely the result of a well-engineered stationary phase which is bonded and cross-linked using a proprietary process.

The guiding purpose behind this research was the development of a robust, flexible GC column which could be used with normal analytical protocols in a small GC design. The next step towards this goal would be to design and build the small GC instrument, incorporating this column technology in the design. This could involve the development of a reproducible electrostatic heating device for column temperature control since the column can be wound into a coil a few centimeters in diameter.

The design and construction of such an instrument has been proposed using the polyimide capillaries to produce monolithic columns of porous methacrylate rather than using WCOT technology [15]. The purpose of the monolithic column design is to increase column sample capacity and peak resolution with the high surface area of the monolithic phase. This phase would also provide greater flow resistance, and would operate at higher column head pressures.

A possible commercial application for the use of the WCOT polyimide columns in a newly-designed small GC would be to monitor solvent vapor emissions during clearcoat paint manufacturing and/or application [15]. Future work would include investigating the ability of the polyimide columns to retain and separate components of the paint vapors, utilizing headspace injection techniques.
Figure 2.1. Size Comparison of a Polyimide Column and Standard GC Columns. A 3-m polyimide capillary column is wound around a test tube with a 1.5 cm outer diameter.

Figure 2.2. The Polyimide Column Installed in the GC Oven. Installation was performed with standard ferrules and column nuts.
Figure 2.3. The Column Washer Used to Clean and Coat the Polyimide Columns.

Figure 2.4. The Vacuum Apparatus Used to Dry the Coated Polyimide Columns.
**Figure 2.5.** Initial Bleed Test Results on an Uncoated Polymeric Polyimide Column.

**Figure 2.6.** Results of Additional Bleed Tests on an Uncoated Polymeric Polyimide Column.
Figure 2.7. SEM Scans on Capillary GC Columns.
(a.) the smooth inner surface of an uncoated polyimide column
(b.) the coating thickness of 50%-PMS on a polyimide column measured between Pa1 and PaR1
(c.) the coating thickness of cross-linked and bonded 5%-PMS (DB-5) on a fused-silica column measured between Pa1 and Pb1 and Pa2 and Pb2

(SEM performed by Matt Duley, Miami University, Oxford, Ohio.)
Figure 2.8. Overlay of Alkane Separation on Uncoated Polymeric Polyimide Columns. Probes: n-decane, n-undecane. Conditions: Isothermal 40 °C
Table 2.1. Peak Data for Alkanes Separation on Uncoated Polymeric Polyimide Capillary Columns

Stationary Phase: None
Probes: n-decane, n-undecane
Temperature: Isothermal 40 °C

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<th>t'_R (min)</th>
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<th>w_h (min)</th>
<th>α</th>
<th>N (mm)</th>
<th>L (mm)</th>
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Figure 2.9. Overlay of Aldehyde Elution on Uncoated Polymeric Polyimide Columns. Probe: nonanal. Conditions: Isothermal 40 °C
Table 2.2. Peak Data for Aldehyde Elution on Uncoated Polymeric Polyimide Capillary Columns

Stationary Phase: None
Probe: nonanal
Temperature: Isothermal 40 °C

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<th>t_R (min)</th>
<th>t'_R (min)</th>
<th>k</th>
<th>w_h (min)</th>
<th>α</th>
<th>N (mm)</th>
<th>L (mm)</th>
<th>H (mm)</th>
<th>u (cm/s)</th>
<th>R_S</th>
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<tbody>
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<td>Polyimide A</td>
<td>0.049</td>
<td>0.135</td>
<td>0.086</td>
<td>1.8</td>
<td>0.040</td>
<td></td>
<td>63</td>
<td>3000</td>
<td>47.5</td>
<td>102.0</td>
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</tr>
<tr>
<td>Polyimide B</td>
<td>0.051</td>
<td>0.115</td>
<td>0.064</td>
<td>1.3</td>
<td>0.031</td>
<td></td>
<td>76</td>
<td>3000</td>
<td>39.3</td>
<td>98.0</td>
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</table>
Figure 2.10. Overlay of Bases Separation on Uncoated Polymeric Polyimide Columns. Probes: 2,6-dimethylaniline; dicyclohexylamine. Conditions: Isothermal 60 °C
Table 2.3. Peak Data for Bases Separation on Uncoated Polymeric Polyimide Capillary Columns

Stationary Phase: None
Probes: 2,6-dimethylanine, dicyclohexylamine
Temperature: Isothermal 60 °C

<table>
<thead>
<tr>
<th>Column</th>
<th>t_M (min)</th>
<th>t_R (min)</th>
<th>t'_R (min)</th>
<th>k</th>
<th>w_h (min)</th>
<th>α</th>
<th>N (mm)</th>
<th>L (mm)</th>
<th>H (mm)</th>
<th>u (cm/s)</th>
<th>R_S</th>
</tr>
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<tbody>
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<td>Polyimide A</td>
<td>0.050</td>
<td>0.119</td>
<td>0.069</td>
<td>1.4</td>
<td>0.026</td>
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<td>0.050</td>
<td>0.247</td>
<td>0.197</td>
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<td>0.059</td>
<td>97</td>
<td>3000</td>
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<td>Polyimide B</td>
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<td>0.037</td>
<td>205</td>
<td>3000</td>
<td>14.6</td>
<td>94.3</td>
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</table>
Figure 2.11. Overlay of Alkanes Separation on 50%-PMS Coated Polyimide Columns. Probes: (1) n-decane, (2) n-undecane. Conditions: Isothermal 40 °C
Table 2.4. Peak Data for Alkanes Separation on 50%-PMS Coated Polyimide Capillary Columns

Stationary Phase: \( d_f: 1 \, \mu m \)
Probes: \( n\)-decane, \( n\)-undecane
Temperature: Isothermal 40 °C

<table>
<thead>
<tr>
<th>Column</th>
<th>( t_M ) (min)</th>
<th>( t_R ) (min)</th>
<th>( t_R' ) (min)</th>
<th>( k )</th>
<th>( w_h ) (min)</th>
<th>( \alpha )</th>
<th>( N ) (mm)</th>
<th>( L ) (mm)</th>
<th>( H ) (mm)</th>
<th>( u ) (cm/s)</th>
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<tr>
<td>Polyimide A</td>
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<td>76.9</td>
<td>6.4</td>
</tr>
<tr>
<td>Polyimide B</td>
<td>0.075</td>
<td>0.327</td>
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<td>0.029</td>
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<td>704</td>
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Figure 2.12 Overlay of Aldehyde Elution on 50%-PMS Coated Polyimide Columns. Probes: nonanal. Conditions: Isothermal 40 °C
Table 2.5. Peak Data for Aldehyde Elution on 50%-PMS Coated Polyimide Capillary Columns

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<td>Probe:</td>
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</tr>
<tr>
<td>Temperature:</td>
<td>Isothermal 40 °C</td>
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</table>

<table>
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<tr>
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<th>t_M (min)</th>
<th>t_R (min)</th>
<th>t'_R (min)</th>
<th>k</th>
<th>w_h (min)</th>
<th>α</th>
<th>N (mm)</th>
<th>L (mm)</th>
<th>H (mm)</th>
<th>u (cm/s)</th>
<th>R_s</th>
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</thead>
<tbody>
<tr>
<td>Polyimide A</td>
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<td>1.345</td>
<td>1.284</td>
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<td>Polyimide B</td>
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<td>1.679</td>
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<td>0.136</td>
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<td>905</td>
<td>3000</td>
<td>3.3</td>
<td>84.7</td>
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</table>
Figure 2.13. Overlay of Bases Separation on 50%-PMS Coated Polyimide Columns. Probes: (1) 2,6-dimethylaniline; (2) dicyclohexylamine. Conditions: Isothermal 100 °C
Table 2.6. Peak Data for Bases Separation on 50%-PMS Coated Polyimide Capillary Columns

Stationary Phase: \( d_f: 1 \mu m \)
Probes: 2,6-dimethylaniline, dicyclohexylamine
Temperature: Isothermal 100 °C

<table>
<thead>
<tr>
<th>Column</th>
<th>( t_M ) (min)</th>
<th>( t_R ) (min)</th>
<th>( t'_R ) (min)</th>
<th>( k )</th>
<th>( w_h ) (min)</th>
<th>( \alpha )</th>
<th>( N ) (mm)</th>
<th>( L ) (mm)</th>
<th>( H ) (mm)</th>
<th>( u ) (cm/s)</th>
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<tbody>
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<td>0.314</td>
<td>0.251</td>
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Figure 2.14. Overlay of FAMEs Separation on 50%-PMS Coated Polyimide Columns. Probes: (1) methyl decanoate; (2) methyl undecanoate; (3) methyl dodecanoate. Conditions: Isothermal 100 °C
Table 2.7. Peak Data for FAMEs Separation on 50\% -PMS Coated Polyimide Capillary Columns

Stationary Phase: \(d_f: 1\ \mu m\)
Probes: methyl decanoate, methyl undecanoate, methyl dodecanoate
Temperature: Isothermal 100 °C

<table>
<thead>
<tr>
<th>Column</th>
<th>(t_M) (min)</th>
<th>(t_R) (min)</th>
<th>(t'_R) (min)</th>
<th>(k)</th>
<th>(w_h) (min)</th>
<th>(\alpha)</th>
<th>(N) (mm)</th>
<th>(L) (mm)</th>
<th>(H) (mm)</th>
<th>(u) (cm/s)</th>
<th>(R_S)</th>
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<tr>
<td>Polyimide A</td>
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<td>0.812</td>
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<td>80.6</td>
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<td>1.530</td>
<td>1.468</td>
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<td>90.9</td>
<td>4.1</td>
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</table>
Figure 2.15. Overlay of Alkanes Separation on 5%-PMS Coated Polyimide Columns. Probes: (1) n-decane, (2) n-undecane. Conditions: Isothermal 40 °C

Figure 2.16. Alkanes Separation on 5%-PMS Coated Fused-Silica Commercial Column. Probes: (1) n-decane, (2) n-undecane. Conditions: Isothermal 40 °C
Table 2.8. Peak Data for Alkanes Separation on 5%-PMS Coated Polyimide Capillary Columns

Stationary Phase:  \( d_f: 1 \, \mu m \)  
Probes:  \( n\)-decane, \( n\)-undecane  
Temperature:  Isothermal 40 °C

<table>
<thead>
<tr>
<th>Column</th>
<th>( t_M ) (min)</th>
<th>( t_R ) (min)</th>
<th>( t'_R ) (min)</th>
<th>( k )</th>
<th>( w_h ) (min)</th>
<th>( \alpha )</th>
<th>( N ) (mm)</th>
<th>( L ) (mm)</th>
<th>( H ) (cm/s)</th>
<th>( u )</th>
<th>( R_S )</th>
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</thead>
<tbody>
<tr>
<td>Polyimide A</td>
<td>0.075</td>
<td>0.712</td>
<td>0.637</td>
<td>8.5</td>
<td>0.113</td>
<td>220</td>
<td>3000</td>
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<td>66.7</td>
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<td></td>
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<tr>
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<td>0.075</td>
<td>1.710</td>
<td>1.635</td>
<td>21.8</td>
<td>0.270</td>
<td>222</td>
<td>3000</td>
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<td>66.7</td>
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<tr>
<td>Polyimide B</td>
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<td>0.505</td>
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<td>3000</td>
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<td>3000</td>
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<td>69.4</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>0.120</td>
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<td>3000</td>
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<td>64.9</td>
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<td>6.442</td>
<td>83.7</td>
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<td>7.5</td>
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</table>
**Figure 2.17.** Aldehyde Elution on 5%-PMS Coated Polyimide Column.  
Probe: nonanal. Conditions: Isothermal 40 °C

**Figure 2.18.** Aldehyde Elution on 5%-PMS Coated Fused-Silica Commercial Column.  
Probe: nonanal. Conditions: Isothermal 40 °C
Table 2.9. Peak Data for Aldehyde Elution on 5%-PMS Coated Polyimide Capillary Columns

Stationary Phase: \( d_f: 1 \mu m \)
Probe: nonanal
Temperature: Isothermal 40 °C

| Column                  | \( t_M \) (min) | \( t_R \) (min) | \( t'_R \) (min) | \( k \) | \( w_h \) (min) | \( \alpha \) | \( N \) (mm) | \( L \) (mm) | \( H \) (mm) | \( u \) (cm/s) | \( R_S \) |
|------------------------|----------------|----------------|----------------|------|----------------|--------|---------|---------|---------|---------|---------|-------|
| Polyimide B            | 0.051          | 1.460          | 1.409          | 27.6 | 0.170          |        | 409     | 3000    | 7.3     | 98.0    |        |
| Commercial Fused-Silica Column; \( d_f: 1 \mu m \) | | | | | | | | | | | |
| J&W DB-5               | 0.083          | 6.417          | 6.334          | 76.3 | .300           |        | 2535    | 3000    | 1.2     | 60.2    |        |
Figure 2.19. Overlay of Bases Separation on 5%-PMS Coated Polyimide Columns. Probes: (1) 2,6-dimethylaniline; (2) dicyclohexylamine. Conditions: Isothermal 100 °C

Figure 2.20. Bases Separation on 5%-PMS Coated Commercial Fused-Silica Column. Probes: (1) 2,6-dimethylaniline; (2) dicyclohexylamine. Conditions: Isothermal 100 °C
Table 2.10. Peak Data for Bases Separation on 5%-PMS Coated Polyimide Capillary Columns

Stationary Phase: \( d_f: 1 \mu m \)
Probes: 2,6-dimethylaniline, dicyclohexylamine
Temperature: Isothermal 100 °C

<table>
<thead>
<tr>
<th>Column</th>
<th>( t_M ) (min)</th>
<th>( t_R ) (min)</th>
<th>( t_R' ) (min)</th>
<th>( k )</th>
<th>( w_h ) (min)</th>
<th>( \alpha )</th>
<th>( N ) (mm)</th>
<th>( L ) (mm)</th>
<th>( H ) (mm)</th>
<th>( u ) (cm/s)</th>
<th>( R_S )</th>
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<tbody>
<tr>
<td>Polyimide A</td>
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<td>0.199</td>
<td>0.148</td>
<td>2.9</td>
<td>0.027</td>
<td></td>
<td>301</td>
<td>3000</td>
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<td>98.0</td>
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<tr>
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<td>0.051</td>
<td>0.673</td>
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<td>3000</td>
<td>9.0</td>
<td>98.0</td>
<td>4.9</td>
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<td>Polyimide B</td>
<td>0.049</td>
<td>0.179</td>
<td>0.130</td>
<td>2.7</td>
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<td>403</td>
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<td>0.049</td>
<td>0.580</td>
<td>0.531</td>
<td>10.8</td>
<td>0.062</td>
<td>4.1</td>
<td>485</td>
<td>3000</td>
<td>6.2</td>
<td>102.0</td>
<td>5.7</td>
</tr>
</tbody>
</table>
| Commercial Fused-Silica Column; \( df: 1 \mu m \)
| J&W DB-5     | 0.065           | 0.642           | 0.577           | 8.9    | 0.026          |        | 3378     | 3000     | 0.9      | 76.9       |        |
|              | 0.065           | 2.666           | 2.601           | 40.0   | 0.101          | 4.5    | 3860     | 3000     | 0.8      | 76.9       | 18.8   |
Figure 2.21. Overlay of FAMEs Separation on 5%-PMS Coated Polyimide Columns. Probes: (1) methyl decanoate; (2) methyl undecanoate; (3) methyl dodecanoate. Conditions: Isothermal 100 °C

Figure 2.22. FAMEs Separation on 5%-PMS Coated Commercial Fused-Silica Column. Probes: (1) methyl decanoate; (2) methyl undecanoate; (3) methyl dodecanoate. Conditions: Isothermal 100 °C
Figure 2.23. FAMEs Separation on Deactivated Fused-Silica Retention Gap and 5%-PMS Coated Polyimide Column.
Probes: (1) methyl decanoate; (2) methyl undecanoate; (3) methyl dodecanoate.
Conditions: Isothermal 100 °C; mobile phase velocity at optimum \( u \), about 30 cm/s
Table 2.11. Peak Data for FAMEs Separation on 5%-PMS Coated Polyimide Capillary Columns

<table>
<thead>
<tr>
<th>Stationary Phase:</th>
<th>d&lt;sub&gt;f&lt;/sub&gt;: 1 µm</th>
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<tbody>
<tr>
<td>Probes:</td>
<td>methyl decanoate, methyl undecanoate, methyl dodecanoate</td>
</tr>
<tr>
<td>Temperature:</td>
<td>Isothermal 100 °C</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Column</th>
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<th>t&lt;sub&gt;R&lt;/sub&gt; (min)</th>
<th>t&lt;sup&gt;'&lt;/sup&gt;&lt;sub&gt;R&lt;/sub&gt; (min)</th>
<th>k</th>
<th>w&lt;sub&gt;h&lt;/sub&gt; (min)</th>
<th>α</th>
<th>N   (mm)</th>
<th>L   (mm)</th>
<th>H   (mm)</th>
<th>u   (cm/s)</th>
<th>R&lt;sub&gt;S&lt;/sub&gt;</th>
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<tbody>
<tr>
<td>Polyimide A</td>
<td>0.051</td>
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Table 2.12. Reproducibility Study on 5%-PMS Coated Polyimide Column

Stationary Phase: $d_f$: 1 $\mu$m  
Probes: methyl decanoate, methyl undecanoate, methyl dodecanoate  
Temperature: Isothermal 100 $^\circ$C

<table>
<thead>
<tr>
<th>Injection Number, $n$</th>
<th>$t_R$ 1 (min)</th>
<th>$t_R$ 2 (min)</th>
<th>$t_R$ 3 (min)</th>
<th>Area 1</th>
<th>Area 2</th>
<th>Area 3</th>
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<tbody>
<tr>
<td>1</td>
<td>0.375</td>
<td>0.665</td>
<td>1.210</td>
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<td>1284983</td>
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<td>0.374</td>
<td>0.664</td>
<td>1.206</td>
<td>1302418</td>
<td>1380348</td>
<td>1344171</td>
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<tr>
<td>3</td>
<td>0.372</td>
<td>0.661</td>
<td>1.203</td>
<td>1249913</td>
<td>1313812</td>
<td>1279812</td>
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<td>0.660</td>
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<td>5</td>
<td>0.370</td>
<td>0.657</td>
<td>1.195</td>
<td>1242371</td>
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<td>1243119</td>
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<td>Mean, $\bar{x}$</td>
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<td>1326966</td>
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</table>

Standard Deviation, $\sigma_{n-1}$:  

|                | 0.002 | 0.003 | 0.006 | 29509 | 30644 | 36294 |

% Relative Standard Deviation:  

|                | 0.52  | 0.49  | 0.46  | 2.4   | 2.3   | 2.8   |
Figure 2.24. Sample Mass Load Study on Polyimide Column Coated with 1 µm 5%-PMS
Figure 2.25. van Deemter Curve
Table 2.13. Peak Calculations for van Deemter Study on WCOT Polyimide Column with 1 µm 5%-PMS

Probe: n-undecane in CCl₄ (unretained)
Temperature: Isothermal 100 °C

<table>
<thead>
<tr>
<th>Pressure psi</th>
<th>t_M (min)</th>
<th>t_R (min)</th>
<th>t'_R (min)</th>
<th>k</th>
<th>w_h (min)</th>
<th>N (mm)</th>
<th>L (mm)</th>
<th>H (mm)</th>
<th>Column flow ** (mL/min)</th>
<th>u (cm/s)</th>
<th>u ** (cm/s)</th>
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</thead>
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* Optimum conditions
**Predicted by FlowCalc 2.05 software [11]
REFERENCES


