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# Resolution Modeling of Length Tuning in Gas Chromatography

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## **Abstract**

Tunable selectivity provides a relatively simple and inexpensive way to manipulate peak positions and gain resolution in chromatographic separations. Length tuning utilizes two columns of different polarities connected in series. Selectivity is manipulated by changing the relative lengths of the two columns. However, a direct correlation is not seen between relative length and effective contribution due to gas compression effects. Rather, a direct correlation is observed between the carrier gas transport time through a segment of column (relative to the total carrier gas transport time) and the effective contribution of that segment. This relationship has been used to predict retention data for analytes in a target mixture, and to determine the combination of columns that would result in the best resolution overall. Further examination reveals that at a given length fraction, the effective contributions of the columns in series are independent of inlet pressure. The relative resolution, a measure of peak separation independent of peak width, is thus constant. In contrast, the resolution calculated using the Purnell Equation does depend on inlet pressure, in accordance with the plate height measured for each individual column and its fractional contribution to a tandem-column separation. Retention factors, peak widths, and plate heights for aromatic molecules of varying functionality, and homologous series of alkanes and alcohols were measured over a range of pressures using both individual columns and several different tandem-column combinations. Measured values of overall plate height and resolution closely matched theoretical predictions and it was determined that theoretical surface plots could be used to accurately predict optimal length fractions for separation.

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RESOLUTION MODELING OF LENGTH TUNING IN GAS CHROMATOGRAPHY

By

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A Senior Thesis Submitted to the

Eastern Michigan University

Honors College

in Partial Fulfillment of the Requirements for Graduation

with Honors in Chemistry

Approved at Ypsilanti, Michigan, on this date \_\_\_\_\_

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Department Head (Print Name and have signed)

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Honors Director (Print Name and have signed)

*To those who have supported me through this four-year journey.*

## TABLE OF CONTENTS

<b>ABSTRACT</b> .....	<b>4</b>
<b>INTRODUCTION</b> .....	<b>5</b>
GAS CHROMATOGRAPHY .....	5
GENERAL CHROMATOGRAPHY THEORY.....	6
<i>Resolution and Theoretical Plates</i> .....	6
<i>Band Broadening Effects</i> .....	7
SELECTIVITY TUNING .....	9
<b>EXPERIMENTAL METHOD</b> .....	<b>12</b>
THEORETICAL MODEL .....	12
CHROMATOGRAPHIC MEASUREMENTS .....	15
MODELING CALCULATIONS .....	16
<b>RESULTS AND DISCUSSION</b> .....	<b>17</b>
CHROMATOGRAPHIC OBSERVATIONS .....	17
MODEL COMPARISON .....	21
<b>CONCLUSIONS</b> .....	<b>23</b>
EXPERIMENTAL DETERMINATIONS .....	23
FUTURE WORK .....	23
<b>ACKNOWLEDGEMENTS</b> .....	<b>25</b>
<b>REFERENCES</b> .....	<b>26</b>

## **Abstract**

Tunable selectivity provides a relatively simple and inexpensive way to manipulate peak positions and gain resolution in chromatographic separations. Length tuning utilizes two columns of different polarities connected in series. Selectivity is manipulated by changing the relative lengths of the two columns. However, a direct correlation is not seen between relative length and effective contribution due to gas compression effects. Rather, a direct correlation is observed between the carrier gas transport time through a segment of column (relative to the total carrier gas transport time) and the effective contribution of that segment. This relationship has been used to predict retention data for analytes in a target mixture, and to determine the combination of columns that would result in the best resolution overall. Further examination reveals that at a given length fraction, the effective contributions of the columns in series are independent of inlet pressure. The relative resolution, a measure of peak separation independent of peak width, is thus constant. In contrast, the resolution calculated using the Purnell Equation does depend on inlet pressure, in accordance with the plate height measured for each individual column and its fractional contribution to a tandem-column separation. Retention factors, peak widths, and plate heights for aromatic molecules of varying functionality, and homologous series of alkanes and alcohols were measured over a range of pressures using both individual columns and several different tandem-column combinations. Measured values of overall plate height and resolution closely matched theoretical predictions and it was determined that theoretical surface plots could be used to accurately predict optimal length fractions for separation.

## Introduction

### Gas Chromatography

Gas chromatography (GC) is an analytical methodology developed in the mid-20<sup>th</sup> century as an alternative to other separation methods, chiefly liquid chromatography. The use of a gaseous mobile phase for chromatography was first described in 1941 as a way to help improve the efficiency of contact between the components to be separated and the stationary phase.<sup>1</sup> A decade later, further investigation by James and Martin revealed that using gas as the mobile phase allowed for better efficiency (narrower peaks) and thus an easier detectable change in composition for all separations (greater resolution). Additionally, they found that the compressible gaseous mobile phases created mobile phase velocity gradients in the column, in contrast to separations using liquid mobile phases.<sup>2</sup> In the following years, GC developed into a separation tool that is powerful in the detection and quantitation of volatile and semi-volatile organic compounds.

In GC, the mobile phase is a chemically inert gas that can be set at a specific flow rate to vary separation.<sup>3</sup> Samples are injected into a heated inlet port using a small-volume syringe. The injection volume may at this point undergo sample splitting to have a fractional amount of the total volume reach the column. The components injected as a mixture then travel through the column where the differential interactions between the components in the mobile phase and the stationary phase act to separate the components.<sup>3</sup> Finally, the components reach a detector and activate an electric signal that indicates the presence of a compound. Ideal detectors combine high sensitivity with stability, reproducibility, short response time, and a large dynamic range.<sup>3</sup> For mixtures including volatile and semi-volatile organic compounds, flame ionization detectors

tend to be preferred. As components elute from the column into a flame ionization detector (FID), they are pyrolyzed in an air-hydrogen flame, in which  $\text{CHO}^+$  ions produce a current. This current is the electronic signal read by a computer output system, and translated into peaks in a chromatogram.<sup>3</sup>

## **General Chromatography Theory**

### **Resolution and Theoretical Plates**

Separation in a chromatographic column occurs due to chemical equilibration between the stationary and mobile phase. Each equilibration-length in the column is referred to as a theoretical plate in the original description by Martin and Synge.<sup>1</sup> Comparing the method of separation to an equilibration in distillation, nomenclature arose to describe the “height equivalent to one theoretical plate” (referred to as H.E.T.P. or plate height). Pioneers in the field, they were able to show how the plate height in the chromatograph they used was equal to 0.002 cm as opposed to 1 cm for normal distillation columns, yielding an efficiency 500 times greater than contemporary methods. Plate height (H) can be determined as the ratio of column length (L) to the number of theoretical plates in the column (N), as shown in Equation 1.

$$H = \frac{L}{N} \quad [1]$$

The separation of components into narrower zones results from a reduction of plate height.<sup>4</sup> Normally, this is achieved through increasing the number of theoretical plates in a column rather than increasing the column length (which increases the separation time).



Resolution, shown in Equation 2, is a term that is used to describe how well separated two peaks are, and is a function of the number of theoretical plates and the retention factor of the two peaks.<sup>4</sup>

$$R_s = \frac{\sqrt{N}}{4} \left( \frac{\alpha - 1}{\alpha} \right) \left( \frac{k}{k + 1} \right) \quad [2]$$

Here,  $k$  is the average of the retention factors of the two compounds, and  $\alpha$  is the ratio ( $k_2/k_1$ ). Raising the temperature of the column lowers retention factors for all components, and improves efficiency, but also results in a reduction of peak separation.<sup>4</sup>

### **Band Broadening Effects**

Band broadening is a chromatographic effect that causes the thin band of sample to elute as a wider zone, negatively impacting resolution.<sup>4</sup> Small plate heights result in narrow peaks, and thus good resolution. Equation 3 shows the expanded Golay equation, which describes plate height as a function of mobile phase flow rate ( $u$ ).

$$H = A + \frac{B}{u} + (C_g + C_l)u + Du^2 \quad [3]$$

The A-term is a result of the travel of molecules on random paths throughout a packed column, and is not applicable to capillary columns.

Longitudinal diffusion (the B-term) is due to the diffusion of solute molecules in both forward and backward directions. This process occurs as soon as the sample is injected into the column and continues throughout the entire analysis. The most retained bands have more time to diffuse, and thus become broader. This term can further be defined as

$$B = 2D_g f_1 f_2 \quad [4]$$

in which  $D_g$  is the binary gas-phase diffusion coefficient,  $f_1$  is the Giddings-Golay pressure correction factor, and  $f_2$  is the Martin-James pressure correction factor. The binary gas phase diffusion coefficient can be calculated as

$$D_{AB} = \frac{(1 \times 10^{-8})^{1.75} \left( \frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2}}{p \left[ (\sum_A v_i)^{1/3} + (\sum_B v_i)^{1/3} \right]^2} \quad [5]$$

Here,  $T$  is the temperature in K,  $M$  is the molecular mass in g/mol,  $p$  is the pressure in atm, and  $v$  is the atomic diffusion volume. The Giddings-Golay, and Martin-James pressure correction factors are given by Equations 6 and 7, respectively.

$$f_1 = \frac{9(P^4 + 1)(P^2 - 1)}{8(P^3 - 1)^2} \quad [6]$$

$$f_2 = \frac{3(P^2 - 1)}{2(P^3 - 1)} \quad [7]$$

The variable  $P$  is the ratio of inlet to outlet pressure,  $p_i/p_o$ .

The  $C$ -term describes broadening due to mass transport, or equilibration between the mobile and stationary phases. Molecules that interact with the stationary phase are held in place, and are left behind molecules traveling in the mobile phase. As the mobile phase flow rate increases, the stationary molecules are left farther behind, broadening bands significantly. The contribution to  $H$  by mass transport in the stationary phase for partition systems is given by

$$C_L = \frac{2kd_f^2}{3(k+1)^2 D_L} \quad [8]$$

for which  $k$  is the retention factor,  $d_f$  is the stationary phase film thickness, and  $D_L$  is the diffusion coefficient for a molecule through the stationary phase. In capillary chromatography

with thin films, this term is often negligible. The contribution to H by mass transport in the mobile phase is given by

$$C_g = \frac{(11k^2 + 6k + 1)d_c^2 f_1}{96(k + 1)^2 D_g f_2} \quad [9]$$

for which  $d_c$  is the diameter of the column.

The D-term describes the contribution to H from extra-column band broadening, and is given by

$$D = \frac{\Delta t^2}{L(k + 1)^2} \quad [10]$$

for which  $\Delta t$  is the total instrumental dead time. This term is often unknown, and can be difficult to assess. For this reason it is frequently neglected.

One way to decrease band broadening is to optimize the mobile phase flow rate. With an increased flow rate, the sample spends less time in the column and experiences less longitudinal diffusion, resulting in sharper peaks. However, increasing the flow rate too much can result in band broadening due to the mass transfer equilibration.<sup>4</sup> Resolution is optimum when using intermediate flow rates, with the exact value determined experimentally based on the sample and mobile phase.

### **Selectivity Tuning**

The idea of trying to optimize the separation of specific components based on selectively tuning specific variables of the chromatographic method was first discussed in 1958. In this year, W. H. McFadden attempted to improve gas chromatographic separations by predicting retention based on the stationary phase used, and investigating the use of mixed stationary

phases.<sup>5</sup> Improving upon this work, it was found that due to a linear relationship between retention factor and the amount of specific stationary phases used, retention factors could be predicted for mixed stationary phases.<sup>6</sup> In 1962, Maier and Karpathy reported work into tuning the inlet pressure and the column length to improve separation.<sup>7</sup> Finally, other variables were studied to see if this chromatographic method could be selectively tuned, including mixed mobile phases, mixed stationary phase packings, and the placement of two different columns into one serial tandem column (including two liquid stationary phases, or one liquid and one solid stationary phase).<sup>8-11</sup>

Once these methods had been established and verified as effective, people began trying to model these effects in an effort to determine the best settings for high-resolution separations. Computerized methods for predicting retention through window diagrams were developed to help save time in optimizing column parameters.<sup>12-13</sup> However, these methods lacked an in-depth investigation into the effects of gaseous mobile phase compression on the contributions of each column fraction in a serially-linked tandem column. It is known that plate height (and therefore resolution) is affected by gas compression within a gas chromatography column.<sup>14</sup> In the 1980's, Purnell and his colleagues published a series of articles that corrected for gas compression effects and then correctly predicted and optimized retention times on tandem-column gas chromatographic systems through window diagrams.<sup>15-22</sup> First, they theoretically discussed how gas compression would change commonly used equations that were used to predict retention. Then, they developed models that would allow them to properly predict retention with the new equations and compared them to experimental data to confirm reliability. The reliability of these changes was confirmed and these equations are still commonly used when attempting to optimize column parameters.

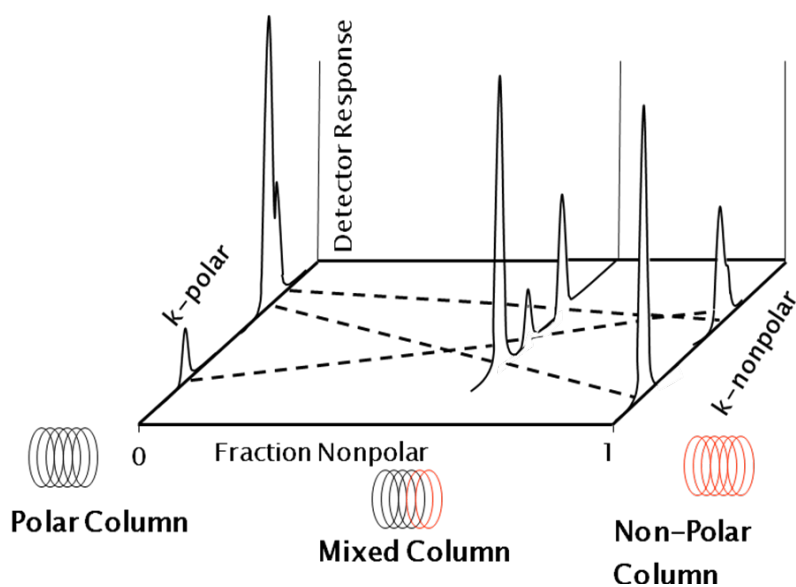
More recently, the focus of selectivity tuning has turned to trying to further tune the use of tandem columns for high-speed separations. In high speed separations, incredibly small bandwidths are necessary to compensate for increased band broadening effects from high inlet pressures and the mass transfer equilibration rate. A variety of inlet systems have been developed to help ensure sufficiently small injection bandwidths.<sup>23-25</sup> Additionally, applications of temperature programming to alter the contributions of each column fraction have been investigated.<sup>26</sup> In-depth analysis has been conducted on controlling the junction pressure between the two columns to affect the fractional contributions, both isothermally<sup>27-29</sup> and taking into account the temperature programming process<sup>30</sup>. Finally, a vector model has been described that gives a full analysis of fractional contributions and optimized separations.<sup>31</sup>

With all of these models that have been developed, none are able to properly predict the actual resolution between peaks in addition to retention. While peak position can be accurately predicted, no attempts have been made to determine the peak shape. When only predicting peak position, peak overlap may not be properly determined. This could make a separation that seems optimal actually not sufficient for quantitative analysis. With a determination of both shape and position, a theoretical chromatogram could be produced, which would ensure full optimization prior to analysis. Because band broadening effects can be calculated based on column parameters and known physical constants, accurate peak widths and shapes should also be accessible through calculations. This project was developed to help create such a model and then experimentally test the predictions to ensure accuracy of the model.

## Experimental Method

### Theoretical Model

Figure 1 shows a conceptual picture of selectivity tuning as it can be used in chromatographic separations, with a nonpolar and polar column linked in tandem. A fraction of 0 represents all polar character, and a fraction of 1 represents all nonpolar character. A fraction of 0.5 indicates equal contributions to the separation from each column. Neither column alone is able to separate the three example components, but a combination of the two results in complete resolution.



**Figure 1.** Visual depiction of the length tuning of two chromatographic columns in an effort to improve separations using a tandem column.

Retention of a compound on a dual-column system is described by the overall retention factor

$$k_{overall} = f_1 k_1 + f_2 k_2 \quad [11]$$

Here,  $f_1$  and  $f_2$  represent the fractional contributions of the first and second column to the separation. The fractional contribution is the ratio of mobile phase transport time ( $t_m$ ) in each segment to the total transport time through the tandem columns (Equation 12).

$$f_1 = \frac{t_{m1}}{t_{m1} + t_{m2}} \quad [12]$$

$$f_2 = \frac{t_{m2}}{t_{m1} + t_{m2}} \quad [13]$$

Because  $f_1$  and  $f_2$  equate to 1, Equation 5 can be expressed using a single fractional contribution.

$$k_{1+2} = (k_2 - k_1) f_2 + k_1 \quad [14]$$

Note that Equation 14 is linear, and is often used to predict retention factors on tandem-columns. The fractional contributions of each column can be calculated using Equation 15, in which the variables are: length  $L$ , column diameter  $d$ , inlet pressure  $p_i$ , and outlet pressure  $p_o$ . The mobile phase viscosity is given by  $\eta$ .

$$t_m = \frac{128\eta L^2 \left( -\frac{p_i^3}{p_o^3} - 1 \right)}{3d^2 p_o \left( -\frac{p_i^2}{p_o^2} - 1 \right)^2} \quad [15]$$

For the first column in a tandem-series, the pressure drop is given by  $p_i - p_x$ , where  $p_x$  is the pressure at the junction of the two columns. The pressure drop across the second column in the series is thus given by  $p_x - p_o$ . The junction pressure is given by

$$p_x = \sqrt{p_i^2 - \frac{2L_1(p_i^2 - p_o^2)}{L}} \quad [16]$$

in which  $L_1$  is the length of the first column in the series, and  $L$  is the total length ( $L_1+L_2$ ). Thus, the fractional contribution of the first column in the series is obtained by combining Equations 12 and 15 to get

$$f_1 = \frac{t_{m1}}{t_{m1} + t_{m2}} = \frac{\frac{128\eta L_1^2 \left( -\frac{p_i^3}{p_x^3} - 1 \right)}{3d^2 p_x \left( -\frac{p_i^2}{p_x^2} - 1 \right)^2}}{\frac{128\eta L^2 \left( -\frac{p_i^3}{p_o^3} - 1 \right)}{3d^2 p_o \left( -\frac{p_i^2}{p_o^2} - 1 \right)^2}} \quad [17]$$

Equation 17 simplifies to

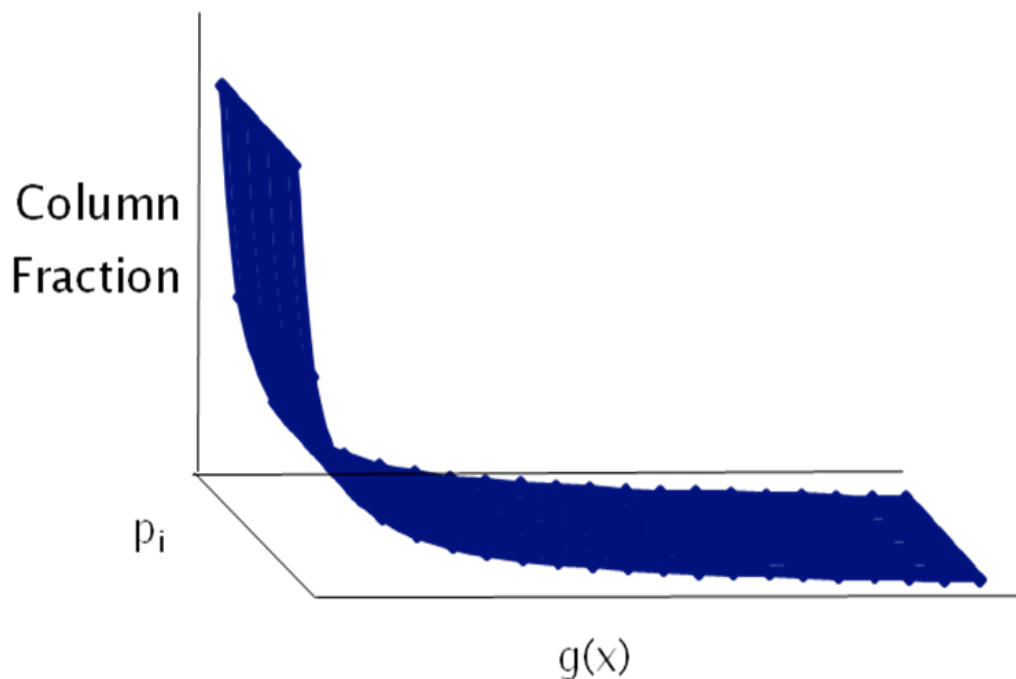
$$f_1 = \frac{t_{m1}}{t_{m1} + t_{m2}} = \left( \frac{L_1}{L} \right)^2 \left( \frac{p_o}{p_x} \right) \frac{\left( -\frac{p_i^3}{p_x^3} - 1 \right)}{\left( -\frac{p_i^2}{p_x^2} - 1 \right)^2} \cdot \frac{\left( -\frac{p_i^2}{p_o^2} - 1 \right)^2}{\left( -\frac{p_i^3}{p_o^3} - 1 \right)} \quad [18]$$

in which the term  $(L_1/L)$  is the length fraction ( $f_L$ ) of the first column in the series relative to the total length. The outlet pressure  $p_o$ , is typically constant for GC separations. The inlet pressure  $p_i$ , is set by the analyst, and the junction pressure  $p_x$ , is dependent on  $f_L$  as shown in Equation 16. It is not clear from Equation 18, that  $f_1$  is invariant with  $p_i$ . For simplicity, Equation 18 can be represented by

$$f_1 = f_L^2 \cdot g(x) \quad [19]$$



Figure 2 shows the dependence of  $f_i$  on  $p_i$  and  $g(x)$ , clearly demonstrating the independence of  $f_i$  on  $p_i$  for any  $g(x)$ . This is significant to optimization of analysis time as well as resolution. Once the analyst has determined the optimum fraction, the inlet pressure may be increased to speed the separation, limited only by band broadening as discussed previously.



**Figure 2.** Surface plot of column fraction vs.  $g(x)$  at a variety of inlet pressures

### **Chromatographic Measurements**

A test mixture consisting of pentane, hexane, heptane, octane, nonane, methanol, ethanol, propanol, butanol, pentanol, *p*-xylene, and 3-chlorotoluene, was used. Chromatograms were obtained using a Shimadzu GC14-A instrument with a flame ionization detector. Samples were all run isothermally at 80° C. Three replicate samples of each functionality group were run, as well as three samples of the complete mixture, at a variety of inlet gauge pressures ranging

from 25 kPa to 275 kPa (at intervals of 25 kPa). From each chromatogram, retention times and peak widths were obtained in order to calculate  $k_f$  and H values.

All samples were run on four different columns, each 15 meters in length. First, a non-polar column, a DB-5 5%-phenyl polydimethyl siloxane stationary phase was used with a 1  $\mu\text{m}$  film thickness and 0.25 mm inner column diameter. A polar column with a Wax (polyethylene glycol) stationary phase was used with a 0.5  $\mu\text{m}$  film thickness and 0.25 mm inner column diameter. In addition to the two individual columns, a combination of 12 meters of Wax and 3 meters of DB-5 was used twice (once with each stationary phase being placed first in the series).

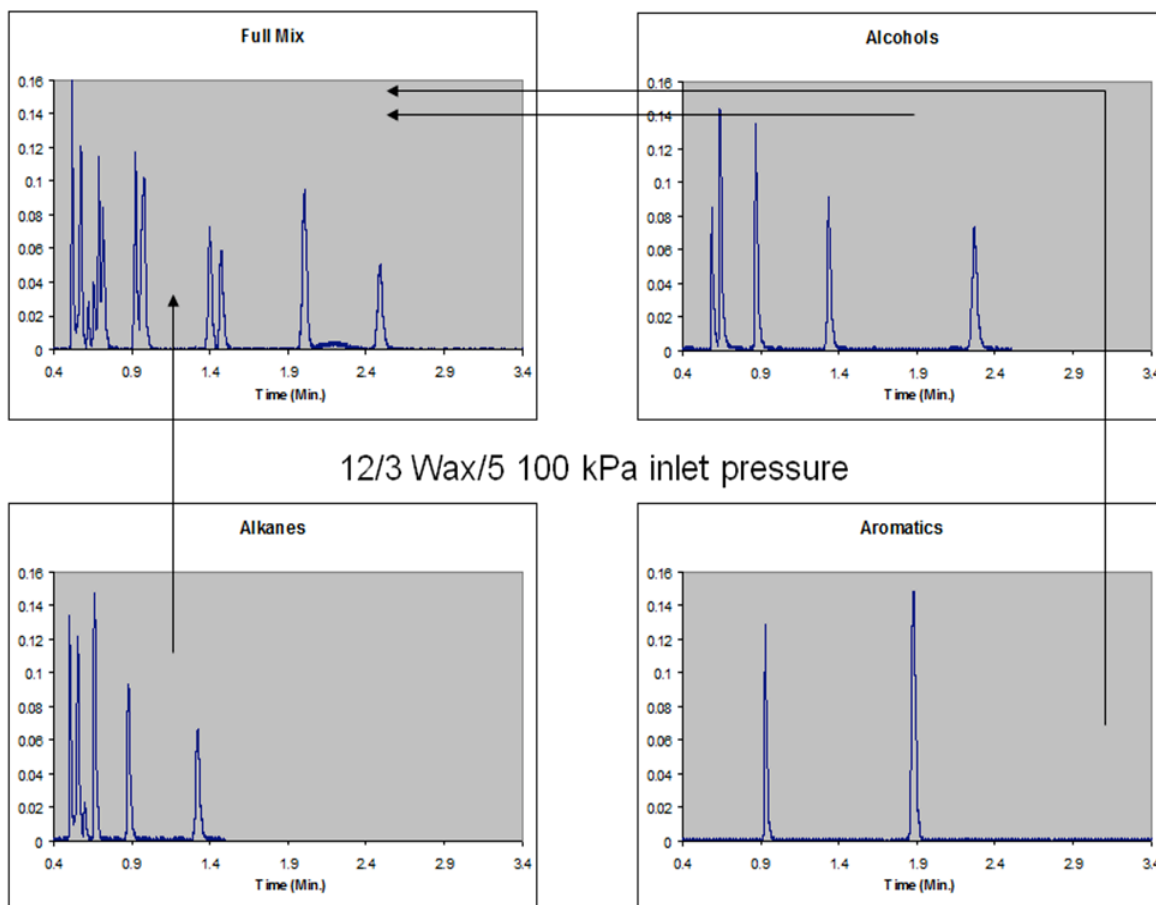
### **Modeling Calculations**

Measured retention factors for C5-C9 n-alkanes, and C1-C5 n-alcohols were used to construct a plot of overall retention factor vs.  $f_{\text{polar}}$ , as well as H values at each fraction, using Microsoft Excel. Calculated values were included corrections for gas compression effects in order to obtain results that reflected the actual contribution of each column to the separation. For each compound, the atomic makeup of the molecule was used to correct for band broadening effects. To confirm the reliability of the model, results from the model were then compared to those from actual experiments.

## Results and Discussion

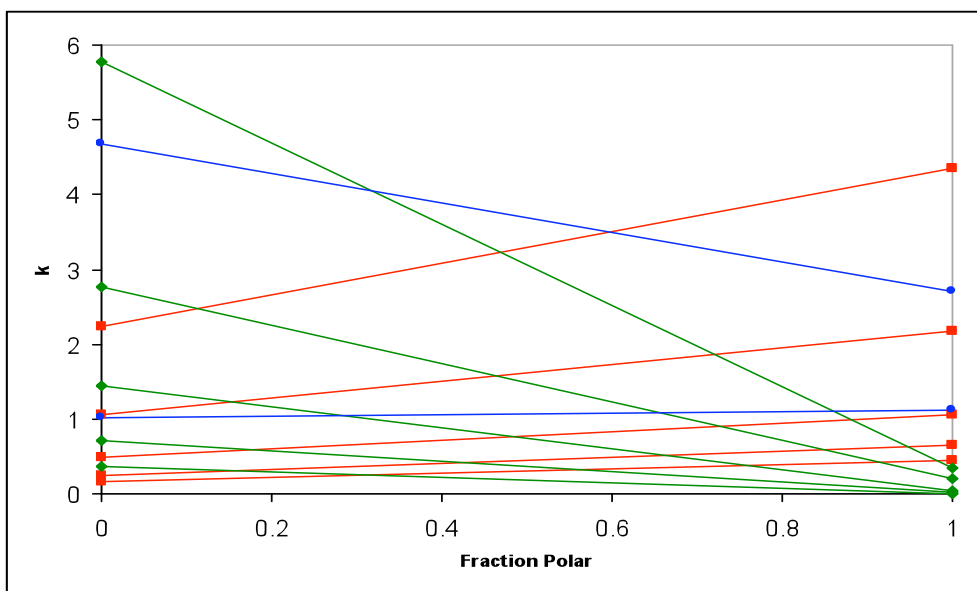
### Chromatographic Observations

Figure 3 shows example chromatograms. Subsets of the full mixture were used to determine accurate retention times and peak widths, as many coelutions occurred in the chromatograms containing all components. At all pressures, peak widths and retention times were measured for comparison to theoretical calculations.

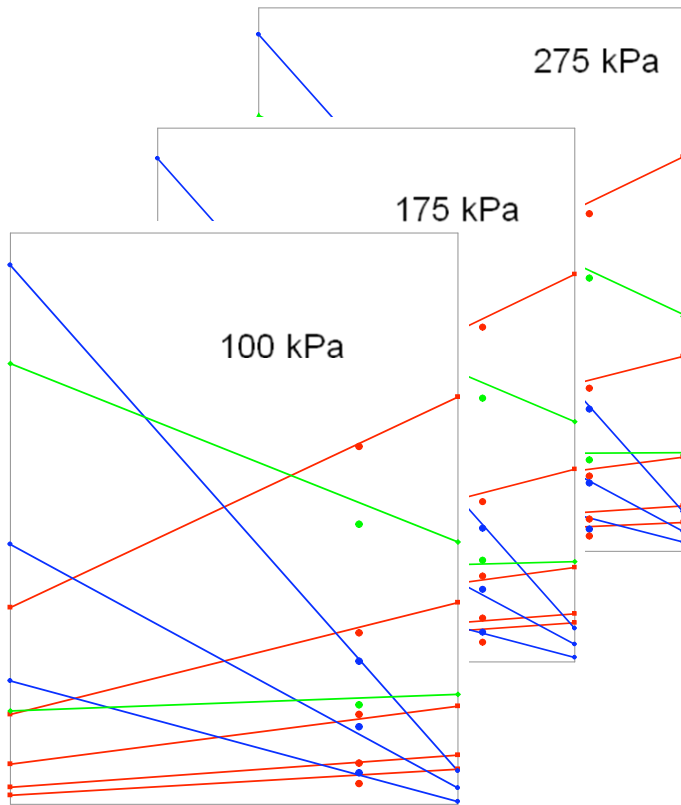


**Figure 3.** Combination of homologous series chromatograms into the full mixture chromatogram on a length tuned column at 100 kPa inlet pressure.

Figure 4 shows a plot of overall retention factor vs. contribution of the polar column ( $f_{\text{polar}}$ ). It was determined that due to compression effects, the actual polar length fraction of 0.8 was 0.82 when the Wax column was placed first and 0.78 when the DB-5 column was placed first. Retention patterns from the  $k_f$  plot seemed to correlate well with retention factors measured using the length tuned columns, an example of which is shown in Figure 5.



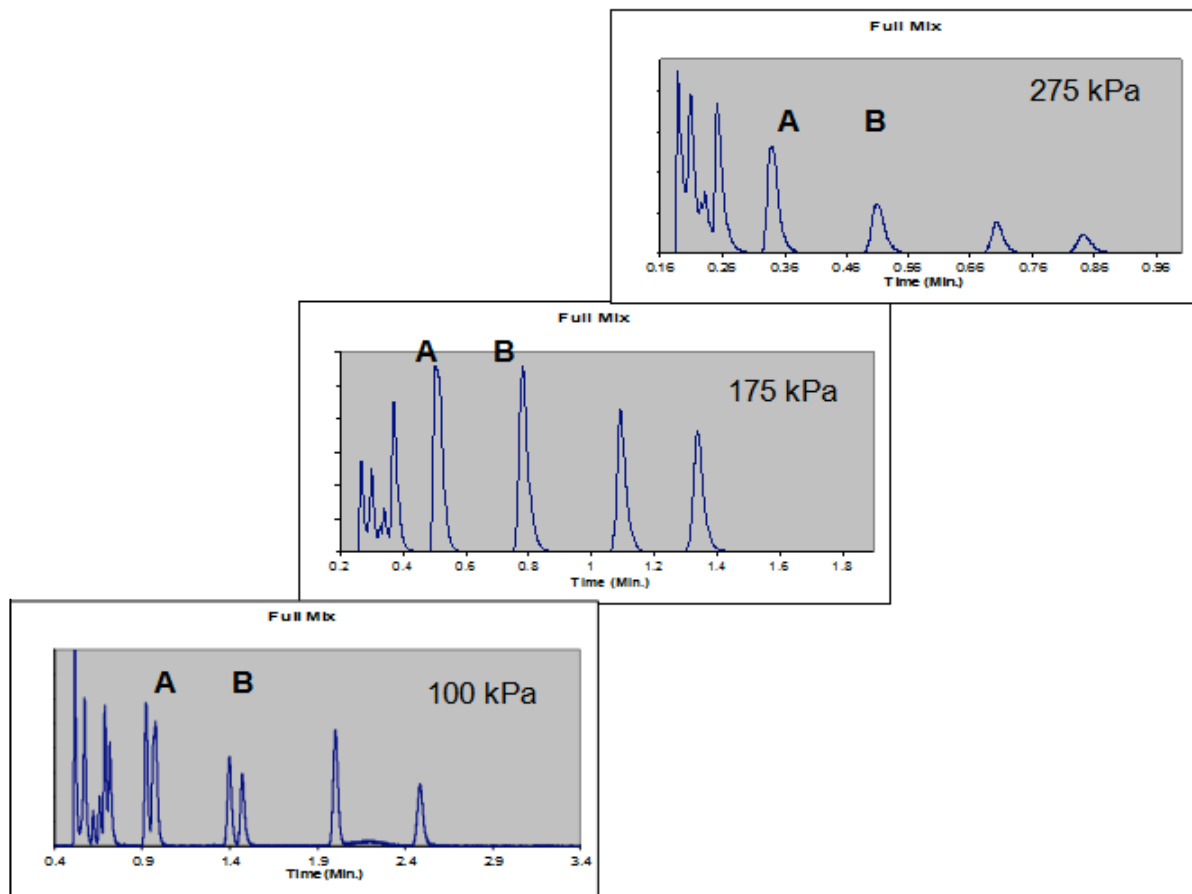
**Figure 4.**  $k_f$  plot for components measured at 100 kPa inlet pressure. Aromatic compounds are displayed in blue, alkanes in green, and alcohols in red.



**Figure 5.**  $k_f$  plots at ranging inlet pressures with overlapping measured data points confirming prediction of observed peak overlaps.

Two sets of critical components were found when running samples at higher pressures on the length-tuned column. At lower pressures, there was a degree of separation between peaks for propanol, octane, and *p*-xylene as well as for butanol and nonane. However, as inlet pressure increased, retention factors became closer and the small separations coupled with peak broadening led to two overlapping sets (See Figure 6). When a comparison to  $k_f$  plots is made, the separation between these peaks is seen to grow smaller with the increased pressures. Additionally, the measured values are relatively close to the predicted values from the linear

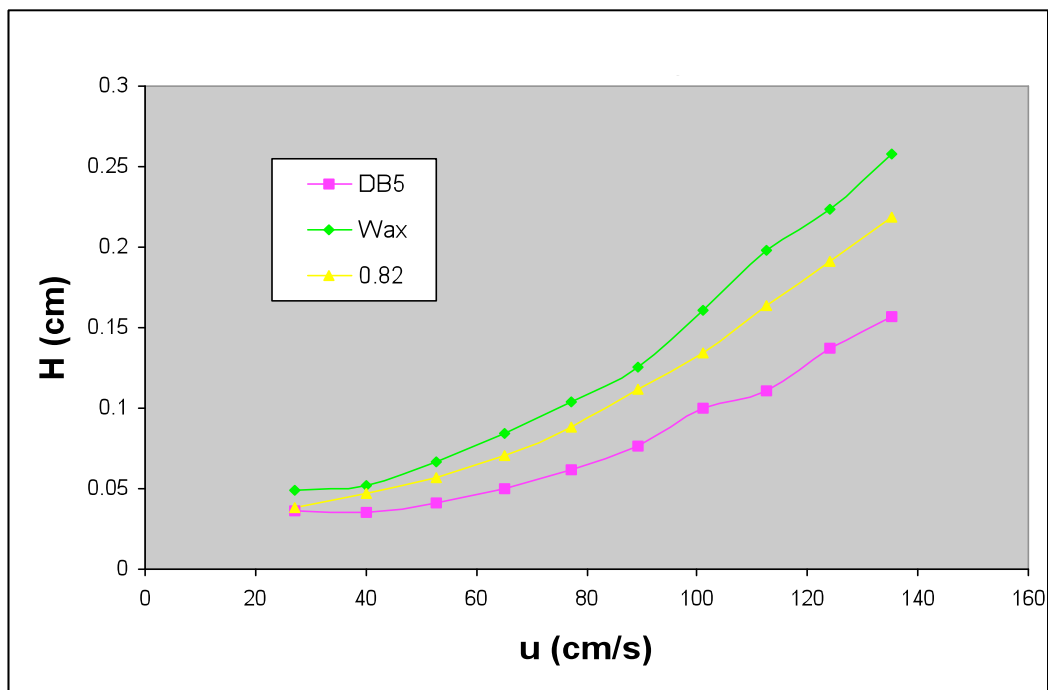
combinations when plotted at the 0.82 calculated length fraction and confirms the reliability of the calculated retention factors to the measured retention factors (See Figure 5).



**Figure 6.** Observation of critical set overlaps for propanol, octane, and *p*-xylene (Set A) and butanol and nonane (Set B) based on increasing inlet pressures.

The effects of flow rate on compound separations in terms of H are observed in Golay plots, as previously discussed. In order to ensure that optimum resolution is obtained, a measurement of band broadening effects through a Golay plot is necessary. Most compounds showed predicted behavior in terms of increasing plate height as flow rate increases (following a minimum reached after infinitely high plate heights at infinitely low flow rates), as seen in Figure 7. Because changing the inlet pressure (and as such, the flow rate) does not affect column

fraction, a linear relationship can be found between H and column fraction, which can then be used in resolution predictions similar to a  $k_f$  plot for retention.

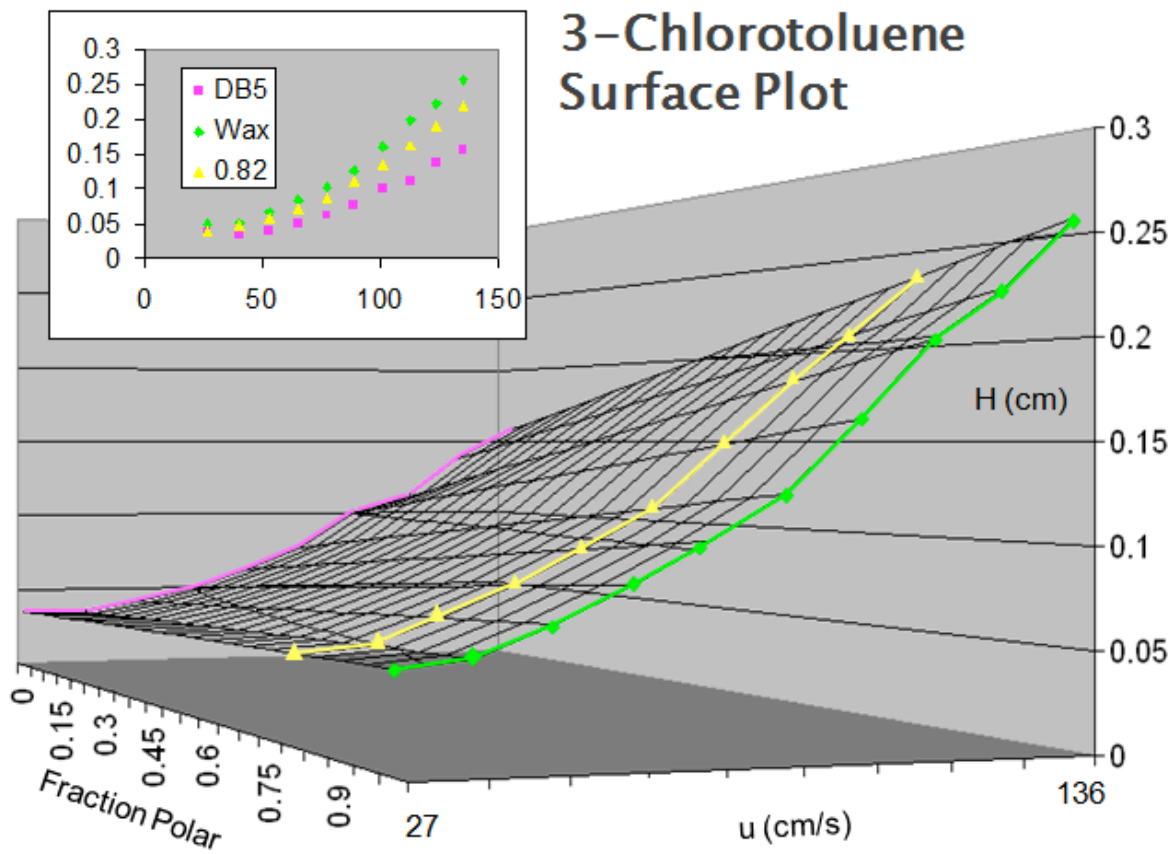


**Figure 7.** Representative Golay plot for 3-chlorotoluene on three columns.

### **Model Comparison**

Because of the linear relationships between length fraction and H, a surface plot can be developed to help properly predict resolution and retention. (See Figure 8) From this surface plot, an H value can be determined at any length fraction and inlet pressure. By only measuring the endpoint Golay plots, all values in-between can be accurately predicted, as confirmed by the experimental data overlaid on the plot. By combining this value with the predicted retention

factor, both peak position and width can be accurately determined for any compound, allowing the calculation of resolution.



**Figure 8.** Surface plot for 3-chlorotoluene giving Golay plot relationships.



## **Conclusions**

### **Experimental Determinations**

This experiment confirmed the reliability of the equations that were used to construct the model, and as such, the reliability of the model in predicting retention, and resolution between peaks. This means that entire chromatograms for any length fraction of two columns can be constructed for any given inlet pressure if retention times and peak widths are calculated on the two individual columns at the same inlet pressure. As such, the large amount of time necessary to optimize separation parameters can be reduced through modeling. By measuring a complex mixture on two columns, the optimal length fraction can be determined and more separations can then be conducted.

### **Future Work**

Although resolution can be increased with the use of two fractions, a third fraction of a polarity different from the first two could provide resolution to otherwise inseparable components. Additionally, applying this method to the pressure tuning methods described earlier would increase the applicability of the method to a number of mixtures. Electronic pressure controls allow for high-precision tuning that can increase critical pair separation in an automated method. By placing tunable pressure valves at two different junctions, more separation between critical pairs could occur at higher speeds.

Another application of the length tuning model involves the setup of two-dimensional gas chromatography (2DGC). This system allows for sufficient separation of multi-component

mixtures, but the instrumentation is not readily available commercially, it is not simple to construct, and the quantification of samples is a difficult process. To reduce these drawbacks, a type of multidimensional gas chromatography (MDGC) known as heart-cutting has been developed to allow the use of overlapped peaks to be further separated on a second column.<sup>32</sup> Instead of further separating every set of critical pairs in 2DGC, the use of heart-cutting to target the analysis for specific target compounds greatly improves the speed of separation.<sup>33</sup> To apply our model, the various columns used in the heart-cutting technique could be length-tuned to maximize separation for a number of critical pairs in a mixture with many compounds. There is no limit to the number of multiple columns that could be used in this setup and the only addition to the existing instrumentation would be a flow-switching valve and the extra columns. This simple modification, when combined with the use of length tuning, would allow for a much greater resolution in chromatograms.

The model developed here focused on isothermal separations. As discussed previously, temperature programming methods can be used to reduce band broadening effects on highly retained compounds and reduce overall separation times. A band trajectory model has been developed to accurately predict peak position in serially coupled columns with pressure junction tuning.<sup>34</sup> By combining the resolution modeling predictions developed here with the trajectory model, chromatograms that use temperature programming during separation would also be able to be accurately predicted.

## **Acknowledgements**

Work on this project was assisted by varying members of the Holmes research team and their help is greatly appreciated. Various funding grants and fellowships from the EMU Honors College, the EMU College of Arts and Sciences, and the EMU Undergraduate Symposium allowed for the purchase of many of the required chemicals and supplies, as well as travel assistance. Thank you to the EMU Chemistry Department for their support of various parts of the project and for use of various facilities and instrumentation. Special thanks to Brian Samuels for all of his technical expertise that was utilized several times throughout the duration of this project.

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