

# **Gas Chromatography of a Hydrocarbon Mixture at Two Different Temperatures (GCH)**

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CHEM438 - 021L

*I submit this laboratory report as an original document. I assert that all ideas and discussion of data contained herein are my own work, unless otherwise referenced.*

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## ABSTRACT

A mixture containing cyclohexane, toluene, ethyl benzene, para-xylene, and ortho-xylene was to be separated in an isothermally operated gas chromatography. The compounds were eluted one by one, in the same order of their boiling point. At a specific ratio of stationary phase volume to the mobile phase volume ( $V_s/V_m$ ), as the retention time increases, the equilibrium constant also increases. Increasing ( $V_s/V_m$ ) will decrease the equilibrium constant at a specific retention time, with the same decrease in magnitude for all retention time. When the GC is run isothermally and comparison is done at two temperatures, the lower temperature (80°C) yields better resolution of peaks but the higher temperature (120°C) has a lower retention time for each compound, making the process more efficient and data collected quickly.

## INTRODUCTION<sup>1</sup>

To separate mixtures of volatile compounds, gas chromatography (GC) is used. GC incorporates a capillary column. Since volatile compounds were used, the choice of column type is not critical as the compounds were eluted based on their boiling points. In this lab, the effect of the temperature on the elution of compounds is the study of interest. Compounds are in equilibrium with the mobile and stationary phases as they eluted through the column. This is described mathematically as the equilibrium constant  $K$  as the ratio of the equilibrium concentrations of each compound in the stationary phase to the mobile phase.

To separate the mixture of compounds in GC, appropriate separation conditions have to be selected. These include the choice of column type, gas flow rate, temperature, and the method to vary the temperature (temperature gradient or isothermal). A capillary column 30 m long with an inner diameter of 0.25 mm will be used, with a stationary phase consisting of 0.25- $\mu\text{m}$  film of the HP-5 (5%-diphenyl-95%-dimethylsiloxane copolymer inner coating) column.  $\text{H}_2$  gas will be used for the mobile phase as it supports the flame ionization detector.

## PROCEDURE <sup>1</sup>

A mixture of cyclohexane, toluene, ethyl benzene, para-xylene, and ortho-xylene were prepared. Small vials were used to run the gas chromatography of each sample. The column was set to run at two temperatures: 80 and 120°C, with gas inlet pressure of 15 psi. At 80°C, each component was analyzed individually in the column. The results were recorded and the chromatograms were collected. The hydrocarbon mixture was analyzed next at both temperatures and the results and chromatograms were recorded and saved. Proper injection of samples from the vials into the instrument should be practiced and the same person should be doing it to minimize errors from variation in injection technique.

## RESULTS AND DISCUSSION

**Table 1.** Retention time and equilibrium constant for each hydrocarbon.

Compound	<sup>a</sup> $t_R$ (min)	<sup>b</sup> $T_{bp}$ (°C)	<sup>c</sup> $K_1$	<sup>d</sup> $K_2$	<sup>e</sup> $K_3$
Cyclohexane	1.486	80.8	48,600,000	4,860	4.86
Toluene	2.016	110.6	101,600,000	10,160	10.16
Ethyl benzene	2.508	136.2	150,800,000	15,080	15.08
p-xylene	2.585	138.4	158,500,000	15,850	15.85
o-xylene	2.994	144.4	199,400,000	19,940	19.94

<sup>a</sup> Retention time

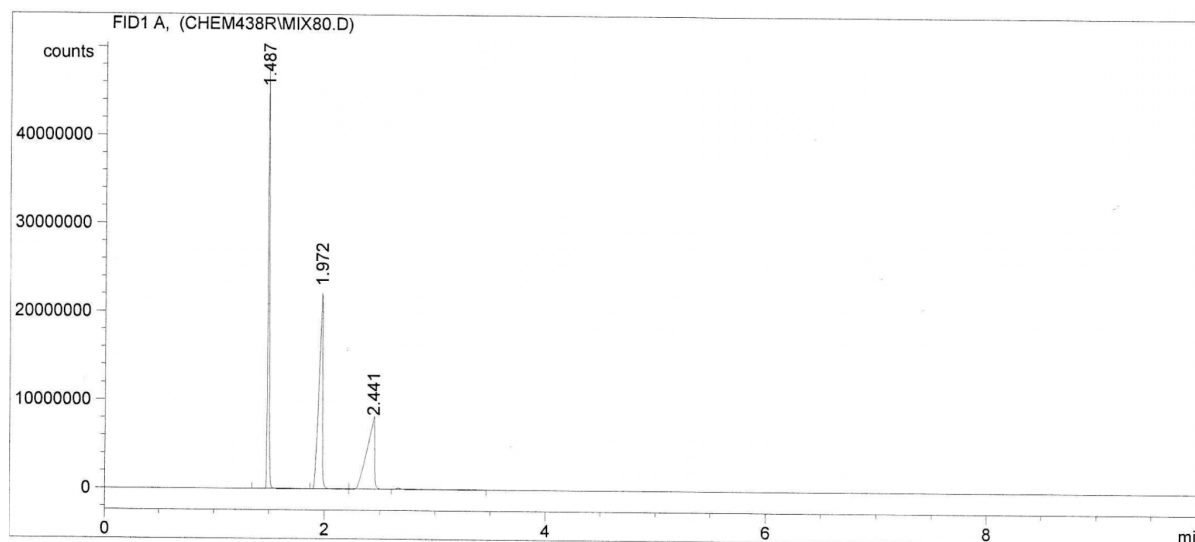
<sup>b</sup> Boiling point

<sup>c</sup> Equilibrium constant at  $V_s/V_m = 10^{-8}$ , at  $t_0 = 1$  min

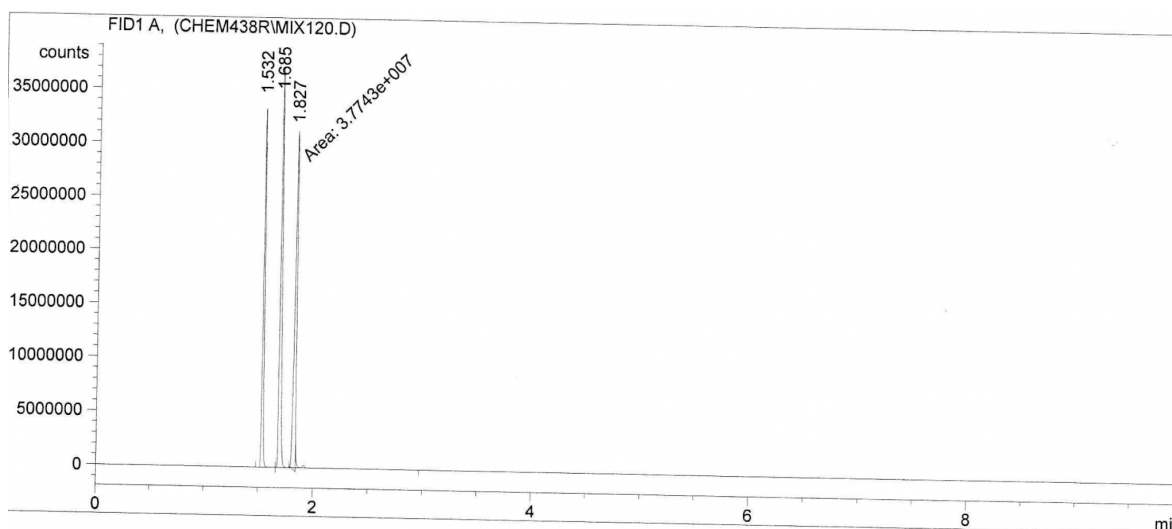
<sup>d</sup> Equilibrium constant at  $V_s/V_m = 10^{-4}$ , at  $t_0 = 1$  min

<sup>e</sup> Equilibrium constant at  $V_s/V_m = 10^{-1}$ , at  $t_0 = 1$  min

Based on the data tabulated in **Table 1** (peaks in **Appendices - Supplemental Figures**), the compounds were eluted in increasing order as their boiling point. This is as expected as the compound with higher boiling point means slower time to be a gas, thus longer retention time in the column. For o-xylene, there is a small peak at  $t_R = 9.654$  min observed. This was ignored in the tabulated data above as it does not represent the presence of pure o-xylene. It could be associated with the elution of the next sample in the instrument, indicating that the measurements were not ensured to be free of the previous elution upon taking the next GC's measurement.



**Figure 1.** GC peaks for mixtures of compounds eluted at 80°C.



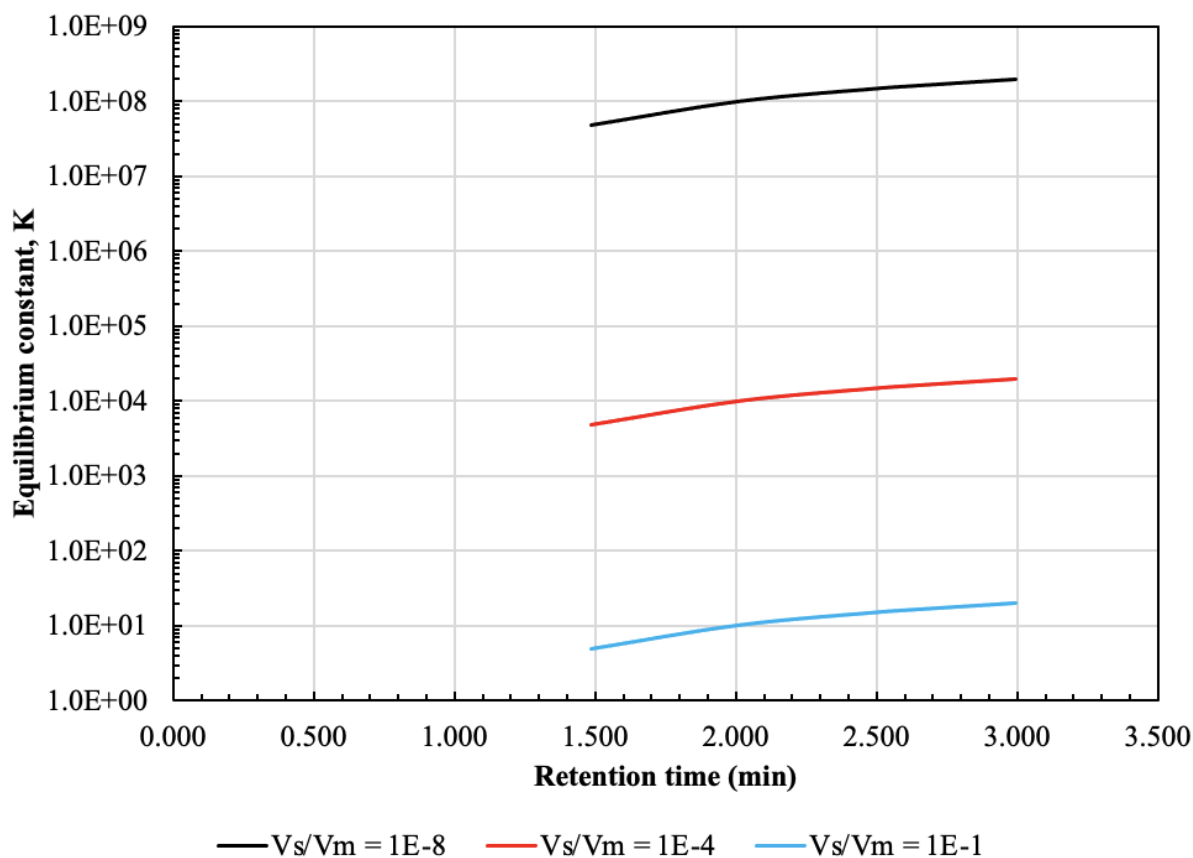
**Figure 2.** GC peaks for mixtures of compounds eluted at 120°C.

**Table 2.** Comparison of peaks at two temperatures.

Peak #	T = 80°C		T = 120°C	
	$t_R$ (min)	Area (counts·s)	$t_R$ (min)	Area (counts·s)
1	1.487	$4.14 \times 10^7$	1.532	$2.84 \times 10^7$
2	1.972	$5.08 \times 10^7$	1.685	$4.13 \times 10^7$
3	2.441	$3.98 \times 10^7$	1.827	$3.77 \times 10^7$

Shown in **Figure 1** and **2** were the peaks generated in GC after eluting the hydrocarbon mixtures at 80 and 120 °C respectively. The data were summarized in **Table 2** above. For each peak, it could be observed that the area decreases as the temperature increases. The area is related to the resolution of the peaks where the smaller the area under the peak, the poorer the resolution is. In this case, increasing the temperature in the GC for elution decreases the resolution of the peaks. Other than that, only 3 peaks were observed, where there are 5 hydrocarbons present in the mixture. This is due to the overlapping in peaks between compounds, associated with poor resolution. As expected, the compounds with similar boiling points have poorer resolution. As predicted in the prelab, the peak of ethyl benzene and p-xylene will have poorer resolution, which is the  $t_R = 2.441$  min.

To explain the poorer resolution as the temperature increases, one should understand what is happening in the column at a molecular level. As the temperature increases, the molecules of each compound in the mixture will gain greater total kinetic energy as theorized by Maxwell Boltzmann.<sup>2</sup> Greater fraction of the molecules will elute faster through the column, leading to smaller retention times. However, when one is dealing with several compounds in the mixture, even though the retention time is decreased, it could cause overlapping in peaks. A compound may have a decrease in retention time that is much greater than the rest. When they are observed to be not overlapping at a lower temperature, due to this decrease in retention time, it will result in overlapping of peaks; poor resolutions.



**Figure 3.** Comparison of equilibrium constant at various  $V_s/V_m$  values.

The equilibrium constants at 3 different ratios of volumes of the stationary phase ( $V_s$ ) to the volumes of mobile phase ( $V_m$ ) for all compounds are as tabulated in **Table 1** and plotted in **Figure 3** above. It could be observed that as the retention time increases, the equilibrium constant increases. At the same time, the equilibrium shifted with the same magnitude as the change in  $V_s/V_m$  ratio. Increasing  $V_s/V_m$  decreases the equilibrium constant. Higher ratio of  $V_s/V_m$  indicates that the column is using more of a stationary phase medium. It is expected that the compound to be eluted much slower and prefer to remain with the stationary phase, rather than moving along with the mobile phase. This will lead to smaller equilibrium constant measured for each compound. Capillary column is used because it only requires a small amount of sample injected for the chromatography process.<sup>3</sup> It also gives a higher resolution, which makes the expensive price of the column worth it.

If one wants to rapidly monitor the levels of these compounds in an environment with reasonable accuracy, one has to decide which one takes the utmost priority. If one prefers to monitor the compounds' levels rapidly and quickly, the GC can be run at a higher temperature (120°C). This is because the retention time of each compound is lower, thus eluting through the columns faster. However, if accuracy is more important, the GC has to be run at a lower temperature (80°C) due to higher resolution of the peaks.

## CONCLUSIONS

Volatile compounds in a mixture can be separated in a gas chromatography, separated by their affinity towards the stationary/mobile phase of the column. The trend in elution of the compounds can be predicted based on their boiling points. The higher the boiling point, the greater the retention time will be, the slower it will elute through the column. Performing the GC isothermally at two temperatures is to compare the retention time and the resolution of the peaks. The choice of temperature depends on if the retention time or the resolution matters the most.



## REFERENCES

<sup>1</sup> Cruz, F. *CHEM438 Instrumental Methods Laboratory - Gas chromatography of a Hydrocarbon Mixture at Two Different Temperatures lab*; University of Delaware: Newark, Delaware, 2018; pp 1-3.

<sup>2</sup> Maxwell Distribution. <https://mathworld.wolfram.com/MaxwellDistribution.html> (accessed Nov 20, 2021).

<sup>3</sup> Deepak, D.; Saurabh, D. Why capillary columns are preferred over packed columns in GC. <https://lab-training.com/why-capillary-columns-are-preferred-over-packed-columns-in-gas-chromatography/> (accessed Nov 20, 2021).

# APPENDICES

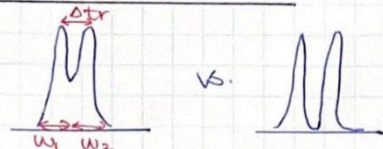
## Lab Notebook

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Exp. No. <u>109</u>	Experiment/Subject <u>CHEM438 (GCH)</u>	Date <u>11/8/2021</u>
Name <u>Abdul Fayed</u>	Lab Partner	Locker/Desk No. <u>021L</u>

### PRELAB Questions

1.



Resolution means the ability to separate the two signals. Peak on the left showed poor resolution as opposed to the peaks on the right.

$$\text{Resolution} = \frac{\Delta t_r}{W_{av}}, \Delta t_r \text{ is the}$$

separation between peaks in unit of time, and  $W_{av}$  is the average width of the two peaks.

$$\frac{W_1 + W_2}{2} = W_{av}$$

2.

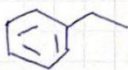
cyclohexane



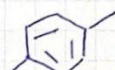
fluorene



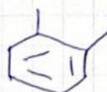
ethyl benzene



para-xylene



ortho-xylene



3.

Ethyl benzene and para-xylene will be the most difficult to resolve because they have very similar boiling points. (only differ by 2.2°C)

4. At high temperature, the chromatographic peaks will come out earlier.

High temperature causes the solute to elute the column faster, decreasing the retention time.

5. The resolution is expected to degrade at high temperature. As the retention time decreases as the temperature increases, the peaks will start to get closer together. The resolution of the peaks will get poorer.

Signature <u>[Signature]</u>	Date <u>11/8/2021</u>	Witness/TA	Date
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THE HAYDEN-McNEIL STUDENT LAB NOTEBOOK

Note: Insert Divider Under Copy Sheet Before Writing

Exp. No.	9	Experiment/Subject	CHEM438 (GCH)	Date	11/8/2021
Name	Abdul Fayed	Lab Partner		Locker/ Desk No.	Course & Section No. 021L

### Objectives

The purpose of this experiment is to separate mixtures of volatile compounds and quantitate the composition of hydrocarbons in the mixture through gas chromatography at two different temperatures.

### Introduction

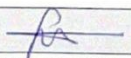
Gas chromatography is used to separate mixtures of volatile compounds. Volatile compounds are in equilibrium with the mobile and stationary phases as they elute the column, which is described by the equilibrium constant. The retention time is directly related to the equilibrium constant. For the experiment, a set of mixture will be analyzed at a constant temperature at two different temperatures.

### Procedure

1. Perform isothermal separation of mixture at 80°C and 120°C at  $P = 1 \text{ atm}$ . Gas mobile phase used is  $\text{H}_2$ .
2. Run the pure compounds of cyclohexane, toluene, ethyl benzene, para-xylene and ortho-xylene in the GC at  $T = 80^\circ\text{C}$ .
3. Run the mixture of the compounds at both temperature.
4. Prepare small vials with samples before running in the GC.
5. Record and print out the chromatograms.

### Conclusion

Gas chromatography can be used to quantitate the compounds in a mixture and to separate them in the column based on their retention time, only for volatile compounds.

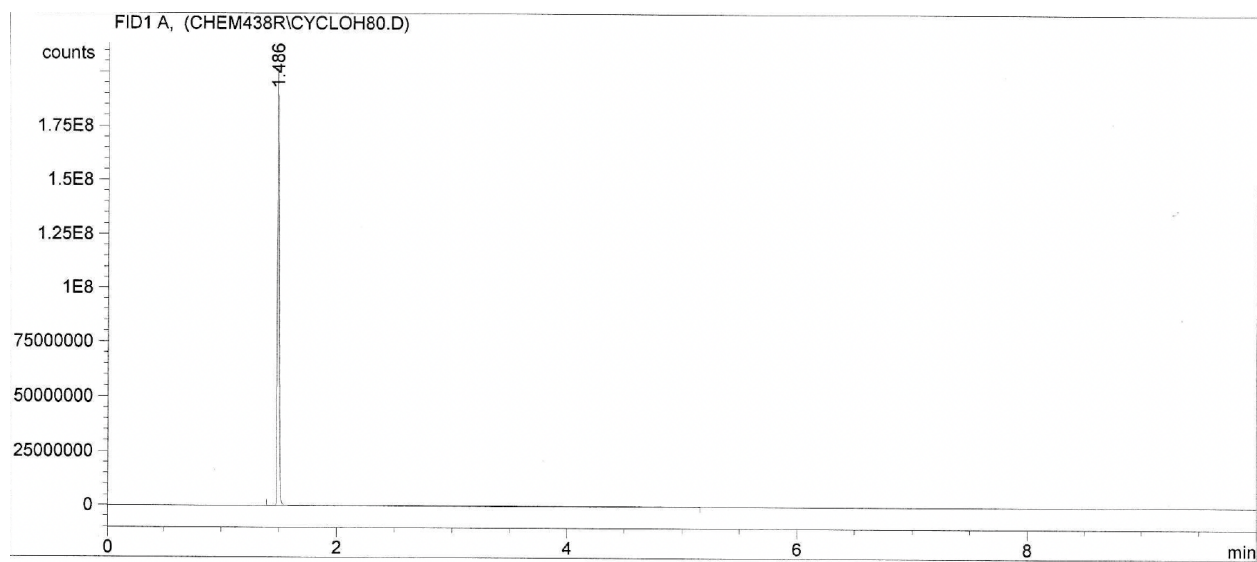
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THE HAYDEN-McNEIL STUDENT LAB NOTEBOOK

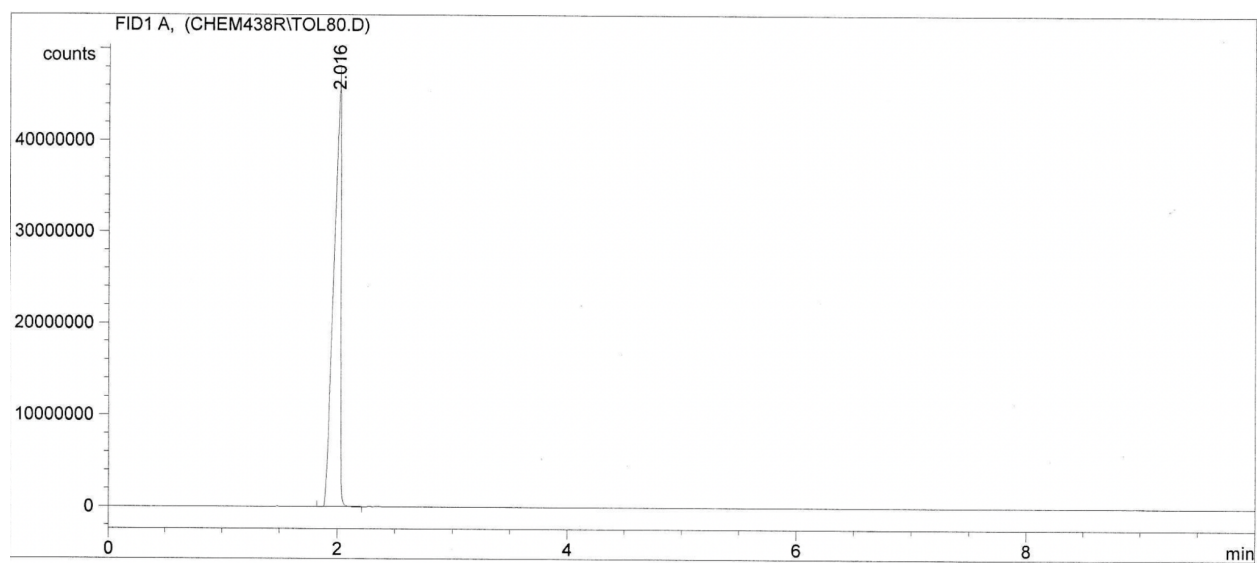
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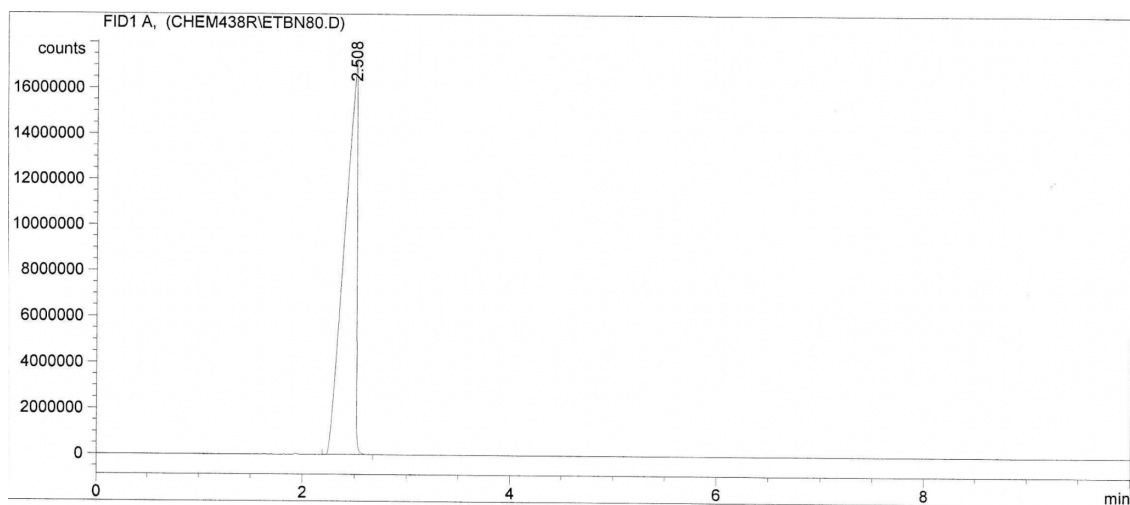
## Supplemental Figures



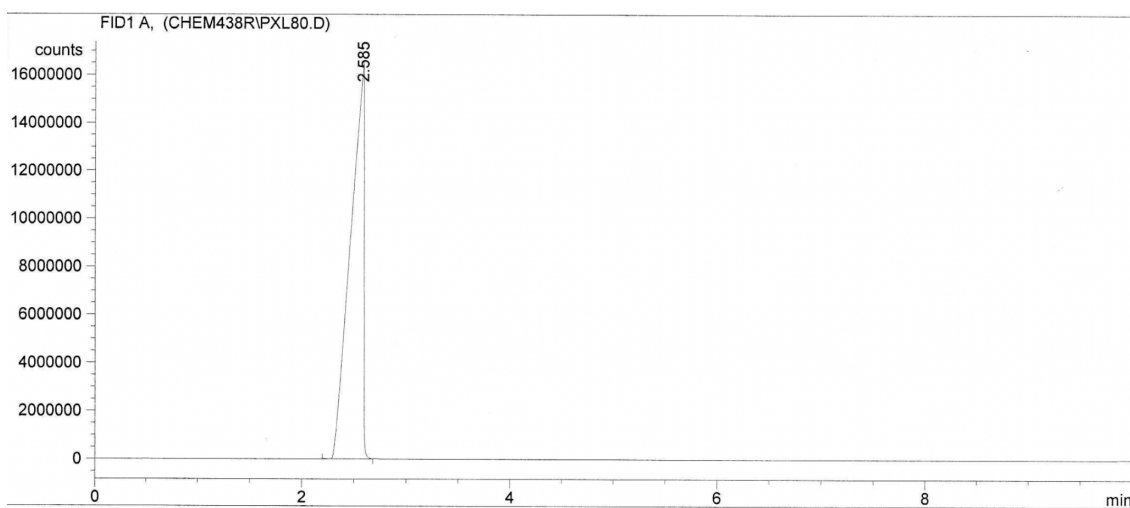
**Figure A.** GC peaks for pure cyclohexane eluted at 80°C.



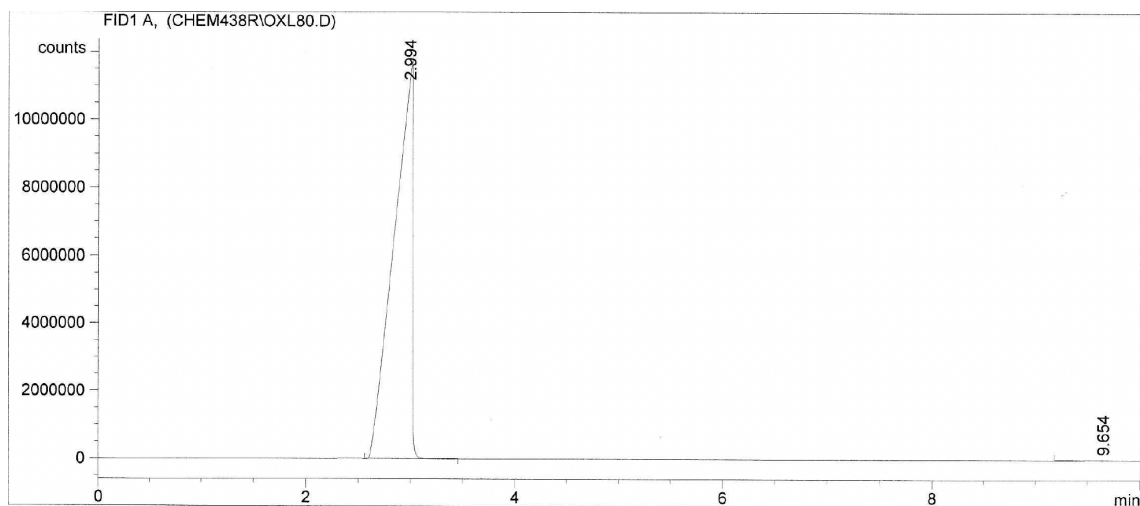
**Figure B.** GC peaks for pure toluene eluted at 80°C.



**Figure C.** GC peaks for pure ethyl benzene eluted at 80°C.



**Figure D.** GC peaks for pure p-xylene eluted at 80°C.



**Figure E.** GC peaks for pure o-xylene eluted at 80°C.