THE PENNSYLVANIA STATE UNIVERSITY
SCHREYER HONORS COLLEGE

DEPARTMENT OF CHEMICAL ENGINEERING

METHOD DEVELOPMENT FOR POLYETHYLENE TEREPHTHALATE PYROLYSIS WITH TWO-DIMENSIONAL GAS CHROMATOGRAPHY

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ABSTRACT

The need for a plastic waste solution is becoming evermore dire each year. Plastics use continues to increase without an efficient method of handling the vast waste generated. Pyrolysis has emerged as a promising method to handle the waste and create a circular economy by producing useful chemicals. However, pyrolysis still needs extensive research. Micropyrolysis aims to study the kinetics of converting plastic to its various byproducts. During micropyrolysis experiments, it is paramount to analyze each product. Two-dimensional gas chromatography (GCxGC) may be utilized to separate each analyte but first must be optimized through method development. Method development encompasses every parameter with the GCxGC system and detectors. This study investigated the impact of modulation time and oven program. A modulation time of 4.7 seconds yields the best results, but a 4.5 second modulation should be used, as well, to identify minor products lost in the system. The oven program that provided the best results was a 40 °C hold for 2 minutes, followed by a 3 °C per minute ramp to 300 °C at which the temperature was held for 10 minutes. This method provided the best separation without causing wraparound. With these results, the method may be utilized in micropyrolysis studies.

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Chapter 1

Introduction

1.1 The Recycling of Plastics.

Commercially available plastic has had a relatively short history. Many of the polymers that we use today were unavailable until the 1940s or 50s. Plastic use began due to its several advantages that increase its overall usefulness. Most plastics are thermoplastics which can be heated, molded, and solidified into a specific, rigid shape. Their hard structure result in a reliable, lightweight, and cheap to produce material. Their hydrocarbon backbones also make them waterproof.[1] These attributes increase usability over other materials like wood, metal, glass, or ceramic. Polyethylene terephthalate (PET) is currently the 5th most used plastic and share 5% of total production (behind polypropylene; 16%, low density polyethylene/linear low density polyethylene; 12%, polyvinylchloride; 11%, and high density polyethylene; 10%).[2] PET is typically generated from crude oil or natural gas and is used to produce plastic beverage bottles or textiles.

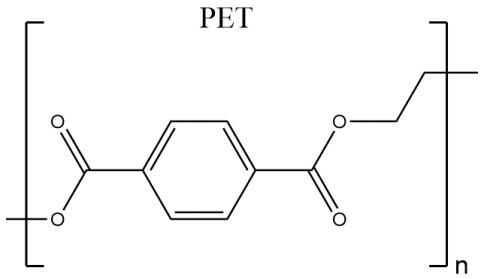


Figure 1. Chemical structure of PET.

Although plastics are a valuable and necessary material, the United States has failed to keep up with the generated waste. As of 2018, 35.68 million tons of plastic waste were generated, making up 12.20% of total municipal solid waste (MSW), third to only food (21.59%) and paper and paperboard (23.05%). In contrast, it is only the fifth most recycled MSW at 3.09 million.[3] The remaining plastic waste ends up landfilled, combusted for energy recovery, or leeched into the environment.

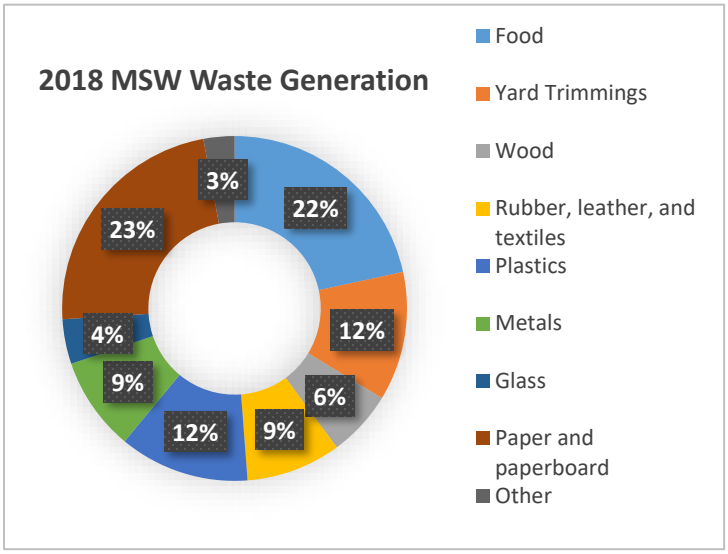


Figure 2. United States 2018 waste generation for each category.[3]

A variety of issues arise from failing to recycle plastic. The most prominent end life for plastic-landfilling- handles 75.59% of plastic waste.[3] However, this method has no advantages. Landfilling requires a vast amount of space and causes microplastic to seep into the surrounding environment. The microplastics may be ingested by animals and humans, and the full extent of consequences are currently unknown. Of the plastic that does remain in landfills, they will require decades-or even centuries-to decompose as millions of tons are added.[4] Combustion with energy recovery serves as the second most popular waste management method handling

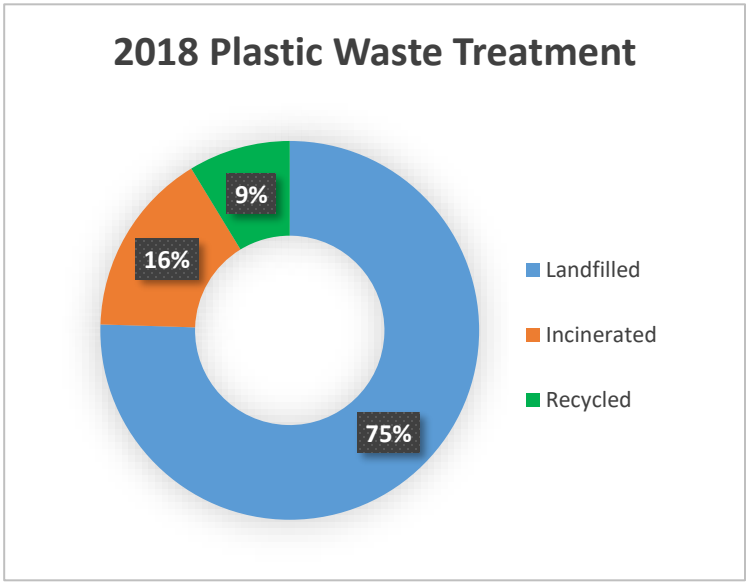


Figure 3. United States plastic end-of-life treatment.[3]

approximately 15.75% of plastic waste.[3] Incineration releases toxic gases-such as dioxins and furans-into the environment.[4] This also contributes to an increase in greenhouse gases due to the release of carbon dioxide. Aside from recycling, the last end of life results from the littering or leeching of plastic into the environment. This poses the same risks to landfilling. Currently, 18.5% of PET generated gets recycled which is slightly higher than the overall rate.[3] However, PET makes up 5% of total microplastic loss and 13% of macroplastic loss to the environment.[2] Because PET is often used for disposable consumer products, the rates of leeching are higher. The only sustainable plastic waste treatment is recycling, so why is it so underused?

Plastic recycling faces many problems which prevent its complete use. When mechanically recycling, the feedstock must be considered to achieve effective recovery rates. Each plastic must be recycled separately to recover the individual monomers. Currently, all plastics are compiled together which requires a laborious and time-intensive separation process and slows recycle rates. Afterwards, the process shreds plastic into small fragments and washes away contaminants to be extruded into new plastic material. The process can often result in lower quality plastic that will eventually end up landfilled or incinerated.[5]

Chemical recycling is the only alternative to mechanical recycling. Chemical methods return the plastic waste back to virgin-grade, and there are several different types currently being investigated: solvolysis, dissolution, and pyrolysis.[5] Solvolysis takes place in a solvent in high excess to break down the chemical structure to obtain the original monomer. The fluid can be sub- or supercritical to increase the reaction efficiency and decrease the need for a catalyst.[6] Challenges of solvolysis include the large amount of solvent required and use of extremely high pressures which increases operating costs.[7] Additionally, only one plastic type may be used per reaction.[5] Dissolution utilizes a solvent to separate polymers in a mixture which can be

advantageous for multilayer packing. The polymer can then be crystallized or precipitated out of the solvent to obtain pure polymer. The downsides include long separation times and the necessary removal of the solvent.[5]

Pyrolysis is defined as the thermal degradation of feedstock in the absence of oxygen. Unlike other chemical recycling methods, plastic can be continuously fed into a reactor with a wider variety feedstock removing the need for time intensive reactions and laborious separation beforehand.[5] Because plastics contain carbon and hydrogen, the pyrolysis oils that are produced which have potential to be used a fuel. Gasoline contains hydrocarbons ranging from C4 to C12 while diesel ranges from C10-C20, both of which are produced.[7] Additionally, gases like methane, ethane, and propane may be generated. Furthermore, the products may be converted into monomers to produce more plastic.

Pyrolysis oil characterization is extremely important for determining each compound present. Currently, gas chromatography paired with mass spectrometry and/or a flame ionization detector (GC-MS/FID) is the most common characterization technique. This method, however, cannot efficiently handle the wide range of pyrolysis products due to similarities in boiling points and polarity between products.[8] Comprehensive two-dimensional gas chromatography (GCxGC), a more recent technology, has been used to result in better product resolution for characterization. GCxGC may also be paired with sulfur and nitrogen chemiluminescence detector (SCD, NCD) to increase sulfur and nitrogen detection.[9] Other characterization methods include Fourier transform infrared spectroscopy (FT-IR) and high-performance liquid chromatography (HPLC).[10,11]

1.2 The Use of Micropyrolysis.

To study pyrolysis pathways and products, micropyrolyzers are utilized. Samples sizes are typically on the order of 50-200 micrograms with particle sizes on the order of microns. The primary pyrolysis reactions refer to the conversion of solid plastic to gaseous products. Secondary reactions result from reactions between the volatiles or between volatiles and remaining solid. Micropyrolysis aims to eliminate secondary reactions by reducing the transport effects from heat and mass transfer. Heating transfer effects arise when the particle size is large enough to create a temperature gradient across each particle. When pyrolyzing, the heating rate must be nearly instantaneous throughout each particle to prevent reactions occurring only at the particle surface. Mass transfer effects cause secondary reactions by the slow release of volatiles from the remaining solid. Increasing convective mass transfer via high carrier gas flowrates minimizes mass transfer limitations. With negligible transport effects, the pyrolysis will be primarily controlled by the reaction kinetics.[12]

The resulting pyrolysis products must be separated before they can be analyzed. For micropyrolysis studies, GC is typically utilized. During the pyrolysis reaction, the evolved gases are carried into a GC oven by use of an inert carrier gas such as helium or nitrogen. The GC oven contains a long, narrow column with a stationary phase coating the internal surface. Compounds interact with the column based off the stationary phase and separate based on their respective polarities (polar separation). The oven ensures the less volatile products will continue through the column.[13] Additionally, the different stationary phase can be used to separate compounds based on boiling points (nonpolar separation). Upon separation, the analytes will enter a detector (a mass spectrometer, flame ionization detector, etc.).

Polymer pyrolysis results in a wide variety of different hydrocarbon molecules which may have similar boiling points or polarities. In this case, a single column (one dimension) will not adequately separate the analytes. In this case, GCxGC must be employed. The analytes will flow through two columns in series to increase separation. Orthogonality describes the column combination (i.e. nonpolar x polar, polar x nonpolar). To connect the two columns, a modulator must be used. The modulator must continuously collect the analytes from the first column and inject them into second dimension column in stages. Two different types of modulators may be used. The first, a thermal modulator, cryogenically cools the analytes then rapidly heats to inject the analytes into the second column. The second, a flow modulator, utilizes an arrangement of valves to allow the analytes from the first column to flow in then switches the flow to inject them into the second column. Fractions of the total analytes are continuously injected into the second dimension, so the flow rate must be much higher relative to the first. A first-dimension time can be on the order of minutes to hours while the second-dimension time is typically only several seconds.[14]

A variety of elements dictate the separation efficiency of GCxGC. To obtain the best separation, method development must be performed. Method development can be viewed as the first step in performing micropyrolysis studies and is an analysis of the column selection, modulator settings, and parameter optimization and their corresponding elements. The first step, column selection, includes the phase, length, internal diameter (ID), film thickness of each column and the orthogonality. The second step, modulator settings, includes the sample loop, bleed line, and the transfer lines to each detector. For the purposes of this experiment, the column selection and modulator setting remained constant. The last step, parameter optimization includes column flow, GCxGC oven settings, detector settings, injector settings, auxiliary

pressure, and modulation time.[15] The description of each investigated parameter is laid out in the Methods and Materials section.

1.3 Gaps in Research

The research into the use of plastic pyrolysis paired with GCxGC is still at a relatively early stage. Recent PET pyrolysis studies include the use of GC-MS for product characterization which, as previously mentioned, fails to separate all products.[16,17] Currently, there is no literature available for PET pyrolysis and subsequent analysis via GCxGC. Method development for GCxGC system has also not been extensively researched. Optimization of GCxGC parameters can be found in a paper from 2021, but it uses various standard chemicals and pine and cedar woodchips as feedstock.[15] The chromatogram of the products obtained from the pyrolysis of polymers needs its own optimization approach, and no method development for GCxGC with flow modulation has been studied until now. An in-depth method development paper for plastics would be useful in future studies as plastic pyrolysis and GCxGC become more popular.

Chapter 2

Methods and Materials

2.1 Materials and Equipment

Chemicals and Materials. The PET was obtained from Goodfellow with an initial particle size of less than 300 microns. The gases used were 5-grade helium (UHP), 5-grade nitrogen (UHP), 5-grade hydrogen (UHP), and ultra-zero air and were obtained from Praxair. Refrigerated Medipure liquid nitrogen was obtained from Linde. Each sample cup contained 4-micron quartz wool acquired from Acros Organics.

Equipment. The samples were prepared in sample cups and measured using a Mettler Toledo microbalance (model XPR56, Mettler Toledo). The samples were placed into an Auto-Shot Sampler (model AS-1020E, Frontier Laboratories) to be selectively inserted into a Tandem μ-Reactor (Rx-3050TR, Frontier Laboratories). The system was also equipped with a Microjet Cryo-Trap (model MJT-1035E, Frontier Laboratories) to improve overall peak shape. The GCxGC analyses were conducted in an Agilent 7890B GC with an Insight flow modulator (Sepsolve) coupled to a BenchTOF mass spectrometer (Markes) and a flame ionization detector (FID). The column combination used in the system is normal phase in which the first-dimension column separates compounds by boiling point (Rtx DHA-50, Restek, 50-meter, 0.20 mm ID), while the second-dimension column separates the analytes by polarity (Rxi-17 Sil MS, Restek, 8-meter, 0.32 mm ID). Before entering the second-dimension column, the analytes entered the flow modulator.

The modulation time, P_M (composed of the flow modulator fill and flush time), describes the overall second-dimension time. During the fill time, analytes enter the flow modulator via the first-dimension column and fill sample loop (Z-8318, SepSolve, 22.665 cm, 0.53 mm ID). Once filled, any additional analytes will leave the system via the bleed column (Z-8311, SepSolve, 2.15 m, 0.10 mm ID). During the flush time, the analytes in the sample loop were sent to the second-dimension column. The percentage of sample loop filled by analytes can be determined via Eq. (1)

$$Percent\ filled = \frac{Q_{1D} * Fill\ Time}{V_{Sample\ loop}} * 100\% \quad (1)$$

Where Q_{1D} and $V_{Sample\ loop}$ refer the flowrate through the first-dimension column and the total volume of the sample loop, respectively. An Insight flow calculator, provided by Markes, suggests a 75% sample loop fill. The flow of columns is calculated using the initial GCxGC oven temperature, all column lengths and IDs, auxiliary pressure (which maintains column flow balances), and carrier gas., A 3 second modulation period would result in a 75% fill. Figure 4 shows the flow modulator calculator provided by Markes.

Insight Flow Calculator	
Column flows and bleed line	
Carrier Gas	Helium
Oven Temp (Deg. C)	40
PCM Pressure (psig)	20.4
Secconary column length (m)	8
Secondary column diameter (mm)	0.32
Bleed line length (m)	2.15
Bleed line diameter (mm)	0.1
2D Effluent Splitter	
X-line to TOF length (m)	1
X-line to TOF diameter (mm)	0.18
X-line to FID length (m)	0.72
X-line to FID diameter (mm)	0.32
Loop Fill and Flush	
Values valid for 0.530 mm ID tubing only. Calculations are for He carrier gas.	
LOOP VOLUME	
Loop Length (cm)	22.665
Loop Internal diameter (mm)	0.53
Volume (µl)	50.00
FILL	
^{1}D Column volumetric flow rate (ml/min, He)	0.76
^{1}D Column Average linear velocity (cm/sec, He)	6.08
Loop fill time by volumetric flow rate (seconds)	3.9476136
Loop fill time by average linear velocity (seconds)	3.7277961
75% capacity fill time (by volume)	2.96
75% capacity fill time (by velocity)	2.80
FLUSH	
^{2}D Column volumetric flow rate (ml/min, He)	20
^{2}D Column Average linear velocity (cm/sec, He)	157.52
Loop flush time by volumetric flow rate (milliseconds)	150.00932
Loop flush time by average linear velocity (milliseconds)	143.88951

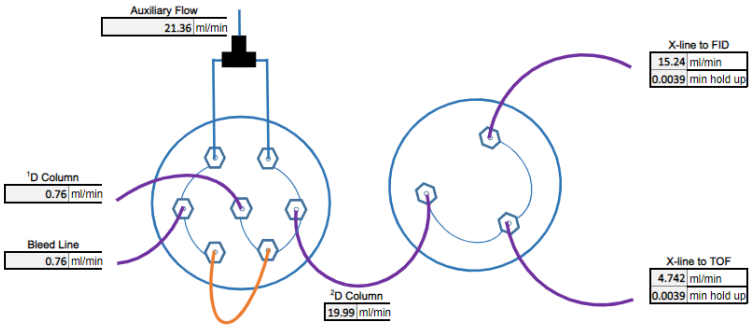


Figure 44. Insight flow calculator and flow modulator/three-way port diagram provided by Markes.

From the flow calculator, several values including sample loop volume, column flows, fill time, and flush time (shown in grey) were calculated based off input parameters (as shown in orange). Adjusting each parameter has a large impact on the precise balance of flow. Because the system works with set first- and second-dimension column, bleed line, and sample loop parameters, the auxiliary pressure and first-dimension flow rates are the only modifiable parameters. However, both changes would require a change in column lengths to balance the flow in the system. Increasing the auxiliary pressure increases the flow in the second-dimension column. The analytes will travel faster through the column and reduce separation, so a longer column would be needed to reduce the flowrate. The flowrates to the detectors would also increase, but a flowrate greater than 5 mL/min cannot be sent to the TOF-MS. A first-dimension flowrate increase would require a decrease in the bleed column length as the flowrates must be equivalent. Additionally, a chosen modulation time would lead to much more sample loss through the bleed column. The system utilized a 20.4 psig and 0.76 mL/min for the auxiliary pressure and first-dimension flowrates, respectively.

After separation, the analytes were sent to-by use of a 3-way port-the time-of-flight mass spectrometer (TOF-MS) detector for identification and FID detector for quantification. ChomSpace software was used for data acquisition and processing of the TOF-MS and FID data. The GCxGC oven setup can be seen in Figure 5.

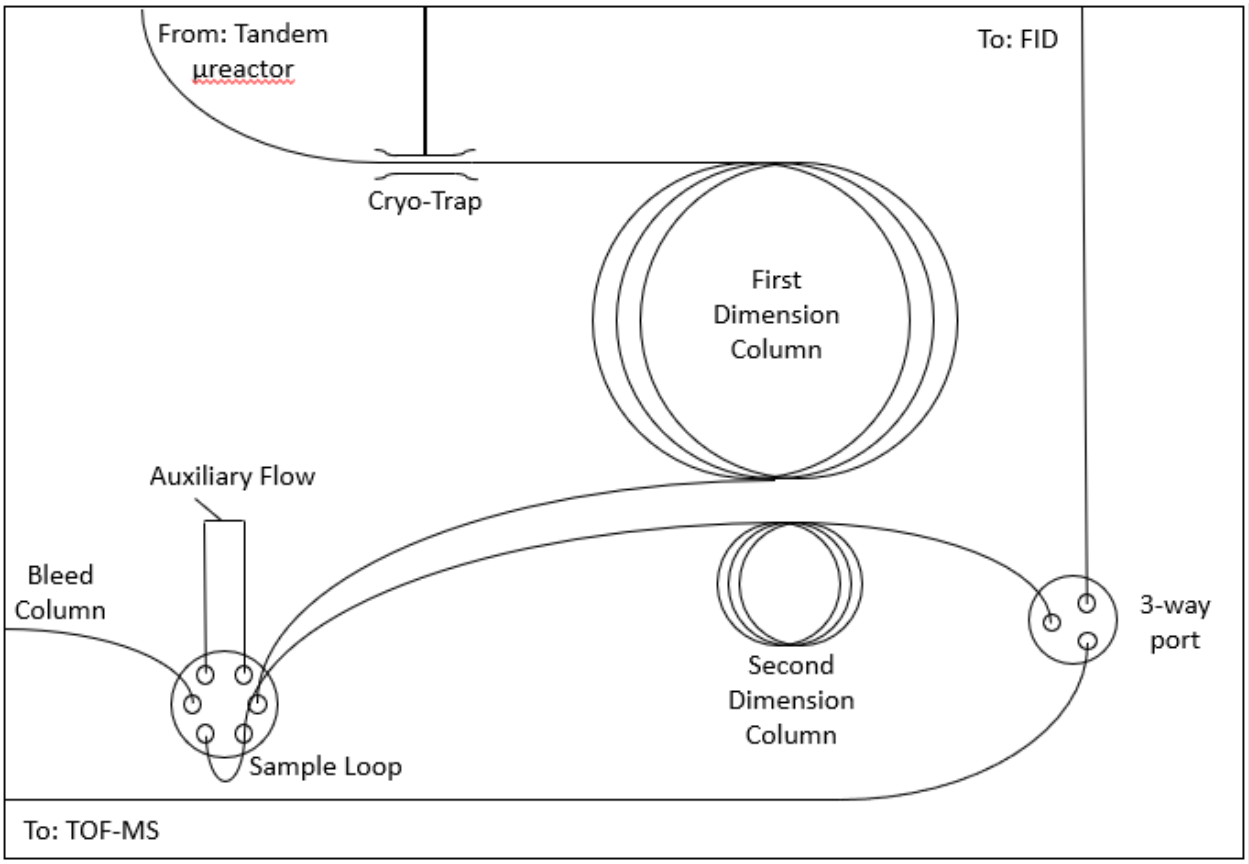


Figure 5. Two-dimensional gas chromatography set-up.

2.2 Methods

Sample Preparation. PET samples were prepared in pre-weighed sample cups using the microbalance and measured to 50 micrograms. Approximately 1 milligram of Quatz wool was placed inside the cup to ensure the PET sample remained in place during transfer and pyrolysis. Once ready, the samples were transferred to the autosampler corresponding to its number determined during the program set up.

GCxGC Settings. The method development involved working with fixed and varied settings. Throughout the experiments, the physical dimensions of each column (first- and second-dimension, sample loop, bleed column, and FID and MS lines) and respective flows were fixed.

Additionally, the pyrolysis temperature and carrier gas flowrate were constant, and each detector operated with a constant scan rate and range. Every fixed parameter and its corresponding value can be seen in Table 1. Varied settings included the oven program and modulation time.

Table 1. GCxGC fixed settings.

Component	Parameter	Value
Tandem µreactor	Temperature	500 °C
	Carrier gas flowrate	196.84 $\frac{mL}{min}$
First dimension column	Flowrate	0.76 $\frac{mL}{min}$
Second dimension column	Flowrate	20 $\frac{mL}{min}$
Bleed column	Flowrate	0.76 $\frac{mL}{min}$
FID detector	Flowrate in	15.24 $\frac{mL}{min}$
	Data acquisition	200 Hz
MS detector	Flowrate in	4.742 $\frac{mL}{min}$
	Scan rate	60 Hz
	Scan range	45-600 Hz

Data Processing. The pyrolysis data processing was completed using ChromSpace software. A chromatogram file was generated for each detector. MS files were converted to dynamic background compensated (DBC) files. The DBC takes an approximate two-dimension width based off typical peak width to reduce chromatogram noise. The FID utilized TopHat which follows the same method as applying DBC. Each peak was analyzed using ChromSpace

peak integration. MS peaks were detected using deconvolution which utilizes the minimum signal required of a peak ion. FID peaks were detected using curve-fitting. The remaining integration settings included adjusting overlap, intensity, and tolerance percentage as well as minimum peak area, height, and width. The low modulation times often causes peaks to be split up across different modulation periods and results in several second-dimension peaks per product. The highest peak in the second dimension is referred to as the main peak, and every other peak is a sub-peak. Overlap percentage specifies the minimum overlap between adjacent sub-peaks. Intensity percentage refers to the minimum height percentage of a sub-peak relatively to the main peak. These parameters must be optimized to ensure background noise is not considered a sub-peak. The minimum peak area, height, and width must be used to ensure background noise is not mistaken as a true compound peak.

The TOF-MS integration compares the peaks to NIST library to identify the compound. Each peak results in a match factor (MF), reverse match factor (RMF), and probability. The MF compares the compound's mass spectrum peaks to peaks in the NIST library's spectra. The RMF compares the peaks in the compound's mass spectrum that do not appear in the library spectra. A MF and RMF of over 900 is excellent, over 800 is good, and over 700 is adequate.[16] Upon product identification, the FID chromatograms were analyzed for to obtain each peak performance descriptor: Resolution, symmetry, peak tailing, and 2D occupation. ChromSpace integration generates a table including all identified peaks and descriptors.

Performance Descriptors. Resolution is a measure of separation between two identified peaks. Resolution is numerically valued with higher number indicating better resolution. ChromSpace calculates resolution via Eq. (2) and Eq. (3).

$$Rs_{prev} = 1.18\frac{Apex - Apex_{prev}}{FWHM + FWHM_{prev}} \quad (2)$$

$$Rs_{next} = 1.18\frac{Apex - Apex_{next}}{FWHM + FWHM_{next}} \quad (3)$$

Where Apex, $Apex_{prev}$, and $Apex_{next}$ refer to the retention time of the selected peak, previous peak, and next peak, respectively, and FWMH, $FWMH_{prev}$, and $FWMH_{next}$ refer to the width at half maximum peak height of the selected peak, previous peak, and next peak, respectively. ChromSpace compares the two resolutions and returns the lower of the two. A value greater than one indicates suitable separation, but a value greater than 1.5 is preferred. The ChromSpace calculation fails to adequately consider separation in the second dimension. Peaks that have identical first-dimension retention times will return a resolution close to 0 regardless of second dimension separation. To comprehensively study resolution, the procedure involved grouping peaks with similar second dimension times (using ChromSpace stenciling) and integrating separately. For example, alkane and alkenes were group together while phenyl containing compounds were grouped together. This method increases the resolution accuracy. Toraman et al. (2016) resolution calculation allows for the comparison between peaks in separate groups via Eq (4).[17]

$$Rs_{2D} = \sqrt{Rs_1^2 + Rs_2^2} = 2\sqrt{\frac{(\Delta t_{r1})^2}{(\omega_{A1} + \omega_{B1})^2} + \frac{(\Delta t_{r2})^2}{(\omega_{A2} + \omega_{B2})^2}} \quad (4)$$

Where Rs_1 and Rs_2 refer to the first- and second-dimension resolution, respectively. Δt_{r1} and Δt_{r2} refer to the difference in first- and second-dimension retention times between two peaks, respectively. ω_1 and ω_2 refer to the first- and second-dimension peak widths, respectively, and A and B refer to the two peaks being compared. Because the equation considers retention time

differences in the second dimension, it can be used to acquire more accurate resolution values between different compound groups.

Peak symmetry describes the overall shape of each peak. To facilitate identification and quantification, each peak should be completely symmetrical. ChromSpace calculates peak symmetry via Eq. (5).

$$A_S = \frac{peak\ width\ left\ of\ apex}{peak\ width\ right\ of\ apex} * 100 \quad (5)$$

As with resolution, the width is measured at half the maximum peak height. A symmetric peak will yield a factor of 100. A factor greater than 100 indicates the peak is distorted on the left, and a factor less than 100 indicates the peak is distorted on the right. Another peak shape consideration is peak tailing. ChromSpace calculates the tailing factor via Eq. (6).

$$T = \frac{Tailing\ width}{Fronting\ width} \quad (6)$$

The tailing width refers to the right width and fronting width refers to the left width. Both widths are taken at 10% maximum peak height. A tailing factor greater than 1 indicates peak tailing, and a tailing factor less than 1 indicates peak fronting. The fronting factor is simply the inverse of the tailing factor.

The final performance descriptor, 2D occupation, describes the overall peak spread. The 2D occupation must be calculated via Eq. (7).[18]

$$2D\ occupation = \frac{tr_{A1} - tr_{B1}}{Tr_1} * \frac{tr_{C1} - tr_{D1}}{P_M} \quad (7)$$

Where tr_{A1} and tr_{B1} refer to the first-dimension retention times of the first and last eluted peaks, respectively, and tr_{C1} and tr_{D1} refer to the second-dimension retention times of the first and last eluted peaks, respectively. Tr_1 refers to the total first-dimension time, and P_M refers to

the modulation time. A higher 2D occupation indicates better peak spread throughout the 2D chromatogram.

Chapter 3
Results and Discussion

3.1 Modulation Time

The modulation times were chosen based on the sample loop size. The modulation time must be high enough to ensure polar molecules will have enough time flow through the second-dimension column, but low enough to not overfill the sample loop and lose analytes through the bleed line. A fill time of 4 seconds fills the entirety of the sample loop. During the experiments, modulation times of 4, 4.5, 4.7, and 5.0 seconds were tested. The initial oven program was a 40 °C hold for 2 minutes, then a 3 °C ramp, followed by a 10-minute hold at 300 °C.

With a modulation time of 4, the sample loop is approximately 95.6% filled with analytes, larger than the suggested 75%. However, the challenge with any modulation time less than 4 seconds is obtaining proper separation in the second dimension. PET's structure contains oxygens and phenyls which result in very polar molecules. The GCxGC chromatogram can be seen in Figure 6. The use of this modulation period was immediately ruled out due to the bleed line obscuring a peak. When testing the other modulation periods, the peak was found to have an area of $9.6x10^6$ (determined for modulation time of 4.5s) which is third greatest of all peaks. The product's MS spectra is likely not in the NIST library as the MF and RMF are both below 700. The MS spectrum was compared to literature containing several spectra for PET pyrolysis products. The comparison of MS spectra can be seen in Figure 7. The product may be 2-(benzoyloxy)ethyl vinyl terephthalate, bis(2-(benzoyloxy)ethyl) terephthalate, or a similar

compound.[21] Although this modulation time does not cause sample loss, the missing peak must be considered.

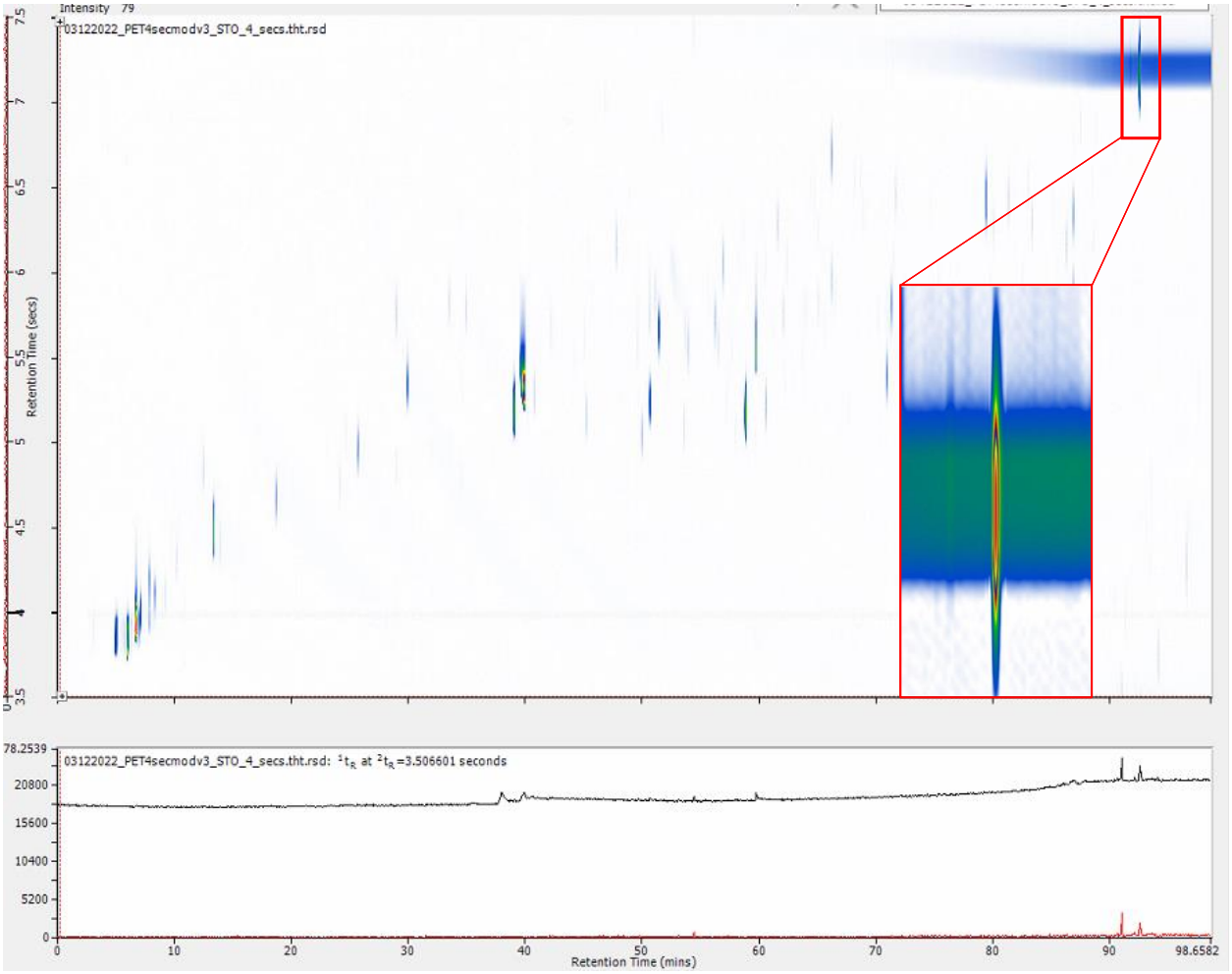
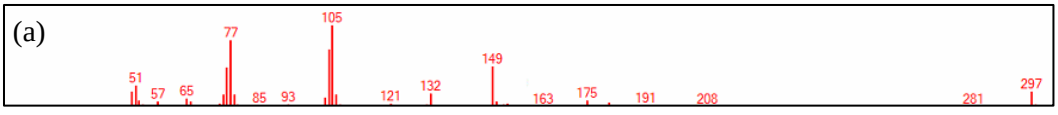
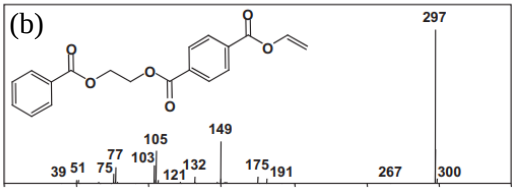


Figure 6. Chromatogram of 4 second modulation time experiment.



2-(benzoyloxy)ethyl vinyl terephthalate



bis(2-(benzoyloxy)ethyl) terephthalate

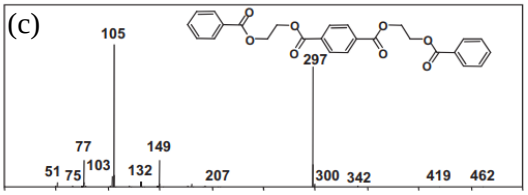


Figure 7. Comparison of MS spectra from experiment (A) to literature (B and C)[21]

The remaining modulation times were compared to determine which results in the best performance descriptors. The integration settings were optimized using the chromatogram from the 4.5 second modulation time. The integration settings were adjusted specific to each stencil region. Figure depicts the stencil used for the chromatogram.

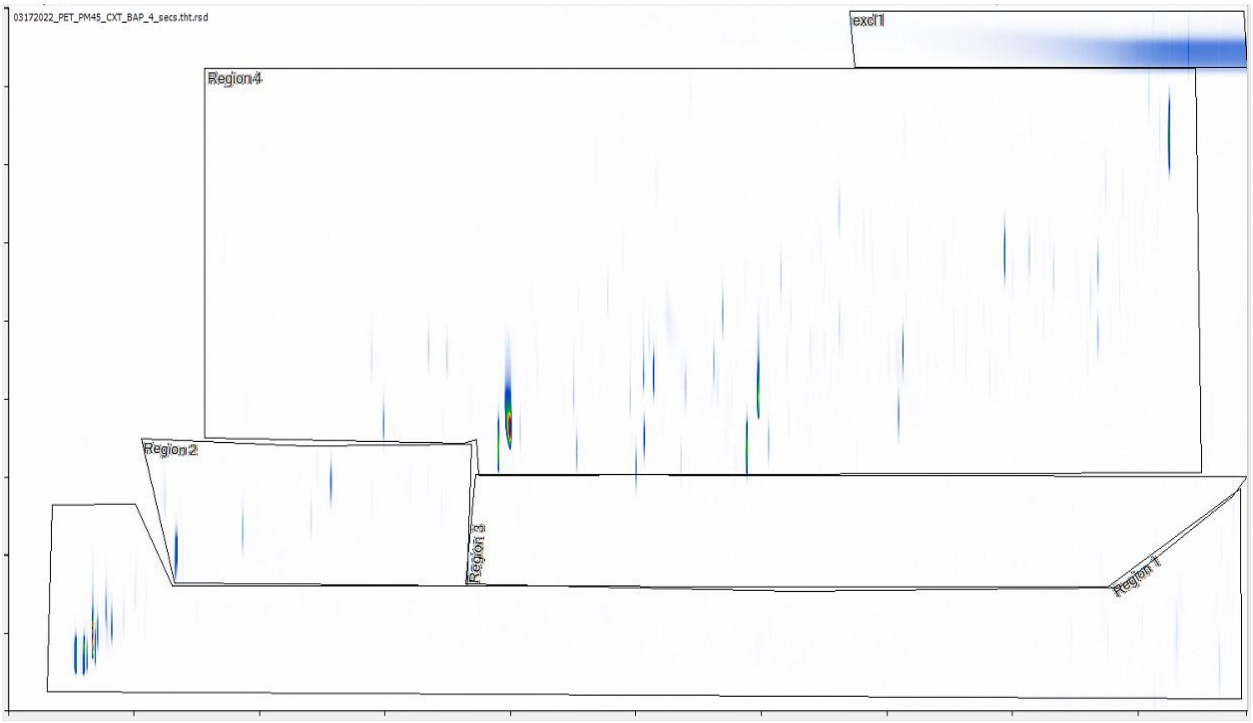


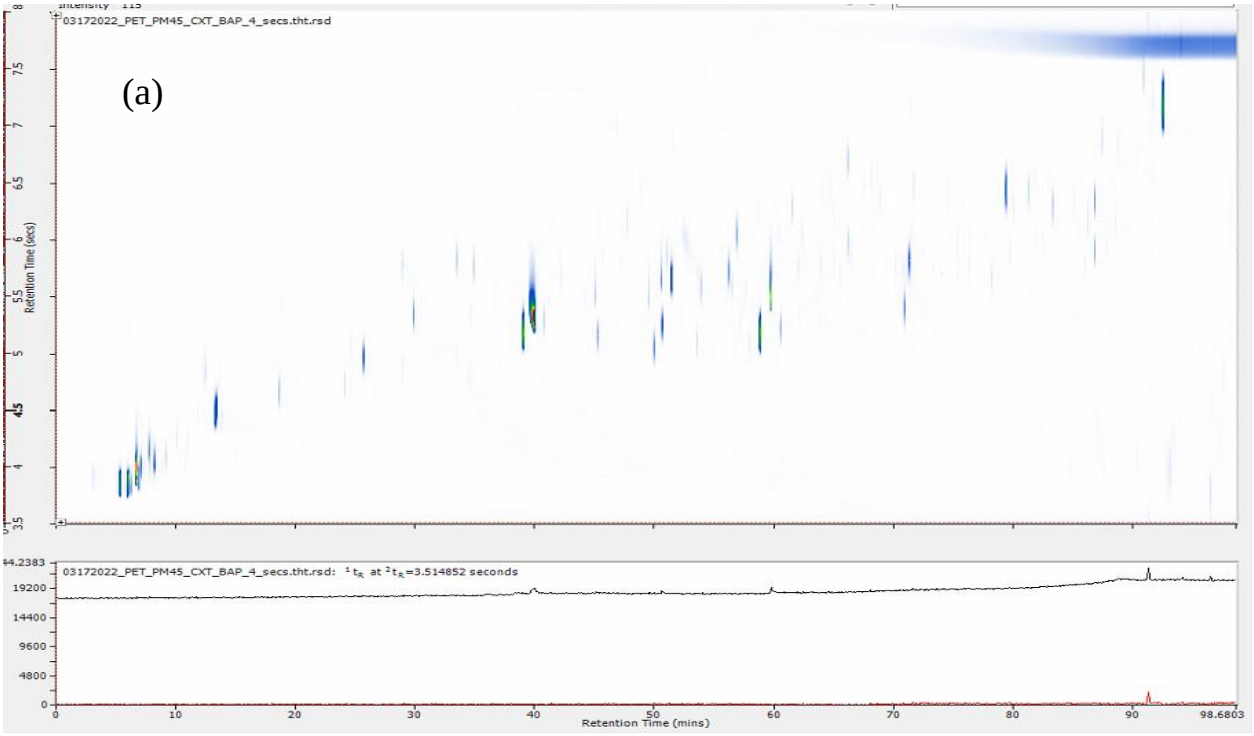
Figure 8. Representation of chromatogram stencil used for each integration.

The first-dimension retention time increases with increasing analyte boiling point and second-dimension retention time increases with increasing analyte polarity. Region 1 (as shown in figure 9) contains molecules with low polarity such as alkanes and alkenes. Region 2 and 3 contains molecules that contain an oxygen atom or a phenyl group which increase the polarity. Finally, region 4 contains compounds that may have several oxygen atoms and/or phenyl groups. Peak quantification was done separately for each region. The integration settings for each region can be seen in Table 2.

Table 2. Summary of integration settings used in each region

Region	Overlap %	Intensity %	Tolerance %	Minimum Height	Minimum Area	Minimum Width
1	25	15	15	700	700	0.00007
2	50	10	10	300	300	0.00003
3	50	5	2	300	300	0.00003
4	50	5	5	400	400	0.00004

4.5 second modulation time yields 244 peaks, 4.7 seconds yields 224 peaks, and 5 seconds yields 215 peaks. As expected, the larger modulation times lead to sample loss through the bleed line. The lower concentrated peaks will either not appear or be inseparable from chromatogram noise. The lost products cannot be accurately identified due to the low MFs and RMFs Figure 8 shows the chromatograms for each modulation time.



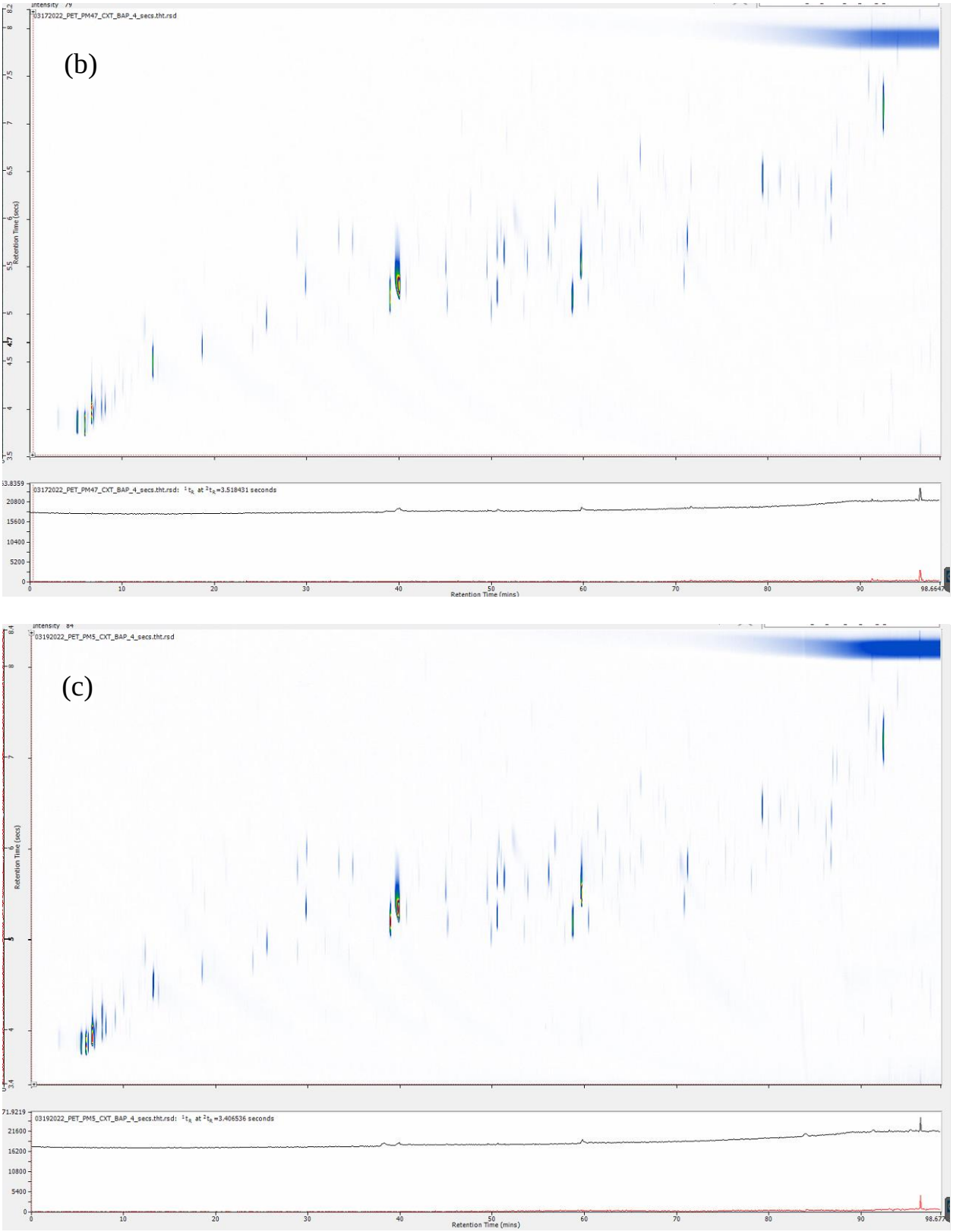


Figure 9. Chromatograms of modulation periods 4.5s (a), 4.7s (b), and 5s (c).

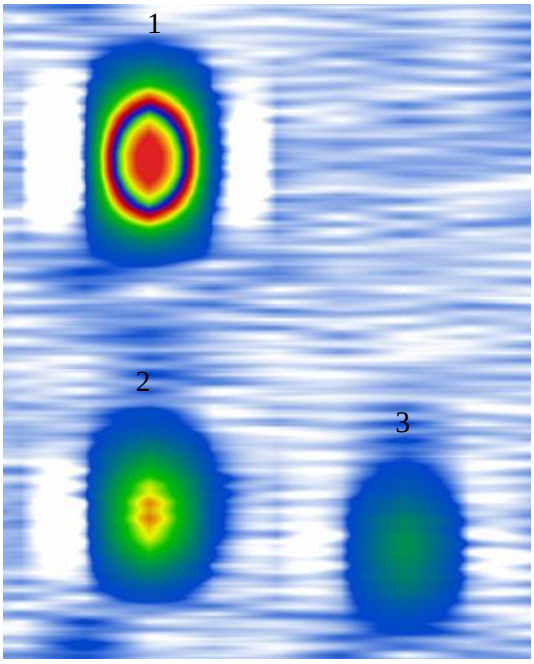


Figure 10. Representation of good versus bad separation according to ChromSpace software.

The first performance descriptor investigated was resolution. Higher resolution increases peak identification and quantification accuracy. The resolution was first calculated via ChromSpace software for each peak. The wide product polarity range result in low resolution values, especially in region 4. For example, in Figure 9, the separation between 2 and 3 yields a resolution of 1.9917, but peaks 1 and 2 yields a resolution of 0.08820. All peaks with resolution less than 1 were investigated for separation in the second dimension, and resolution was recalculated using Eq. 4. For peaks 1 and 2, the resolution was calculated to be 1.3406. Because Eq. 4 considers the second-dimension retention time, it is not necessary to have separation in the first dimension. A resolution value greater than 1 can still be obtained when the peaks are separated by at least 0.55s in the second dimension. The resolution in each region for each modulation time is summarized in Table 3.

Table 3. Resolution in each region for the varying modulation times.

	Peaks with resolution greater than 1 for each region (%)				
Modulation time (s)	Region 1	Region 2	Region 3	Region 4	Overall
4.5	70.97	88.89	100	45.60	52.05
4.7	69.70	84.21	100	61.99	65.18
5	75	76.19	100	67.88	69.77

Between modulation times 4.5 to 4.7, the resolution in regions 1, 2, and 3 remain relatively the same. The similar number of peaks are detected for each indicating little product loss. However, modulation time 5 has a much lower resolution for region 2. The lower concentrated peaks in region 2 do not appear for a modulation time of 5, and the majority of these peaks had a good resolution for modulation time of 4.5. The absence of peaks in modulation time 5 brings down the percentage as the lower resolution peaks remain. The biggest discrepancy is in region 4. Region 4 contains the most peaks of all the regions (approximately 75% of all peaks). Many of the peaks are tightly packed together as shown in Figure 10. Because a modulation time of 4.5 loses the least sample (108% fill compared to 121% at modulation time of 5s), it results in the most peaks. The increased peak number causes the resolution to drop drastically. In contrast, a modulation time of 5 loses the most sample and has fewer peaks to compare.

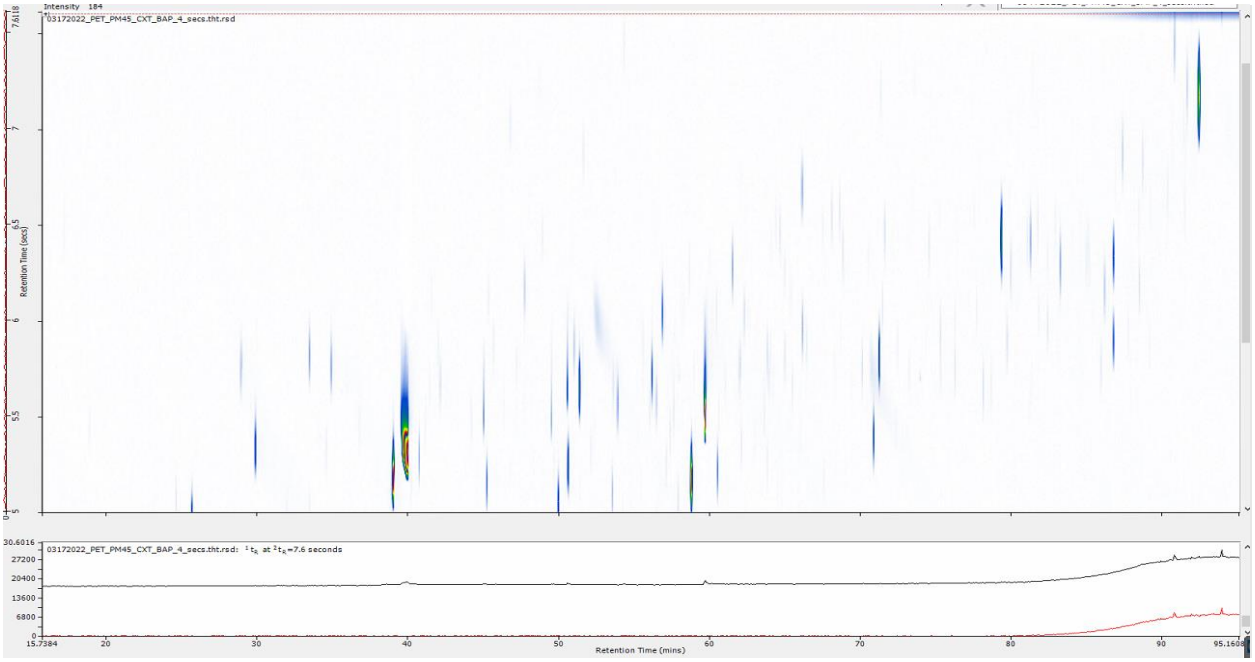


Figure 11. Region 4 of 4.5s modulation time chromatogram.

The symmetry was investigated next. The symmetry accounts for the spreading of compounds across multiple modulation periods. A symmetry value of 100 indicates the peak follows a Gaussian shape. In Figure 11, peak 1, benzoic acid (845 MF and 870 RMF), and peak 2, 1-phenyl-1,2-propandione (900 MF and 912 RMF), have symmetry factors of 32.2917 and 100, respectively. The poor shape of peak 1 can be seen in the sub-peaks. As shown in Figure 12, the main peak is peak six out of seven. After the main peak, the sub-peaks should follow the same trend as the preceding sub-peaks to result in a Gaussian shape.

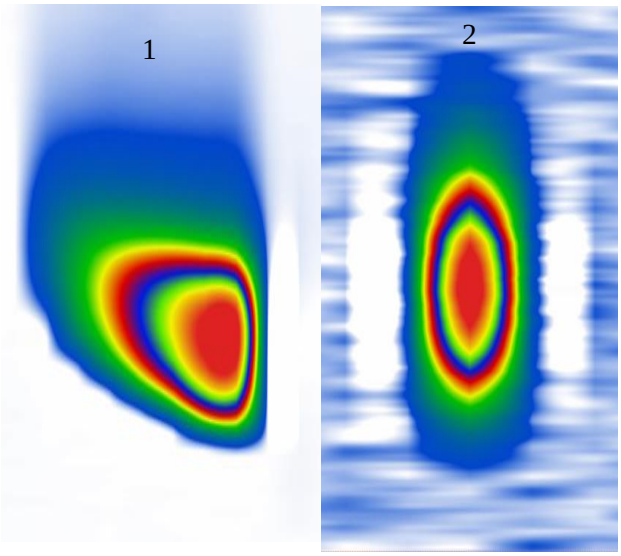


Figure 12. Good versus poor peak symmetry.

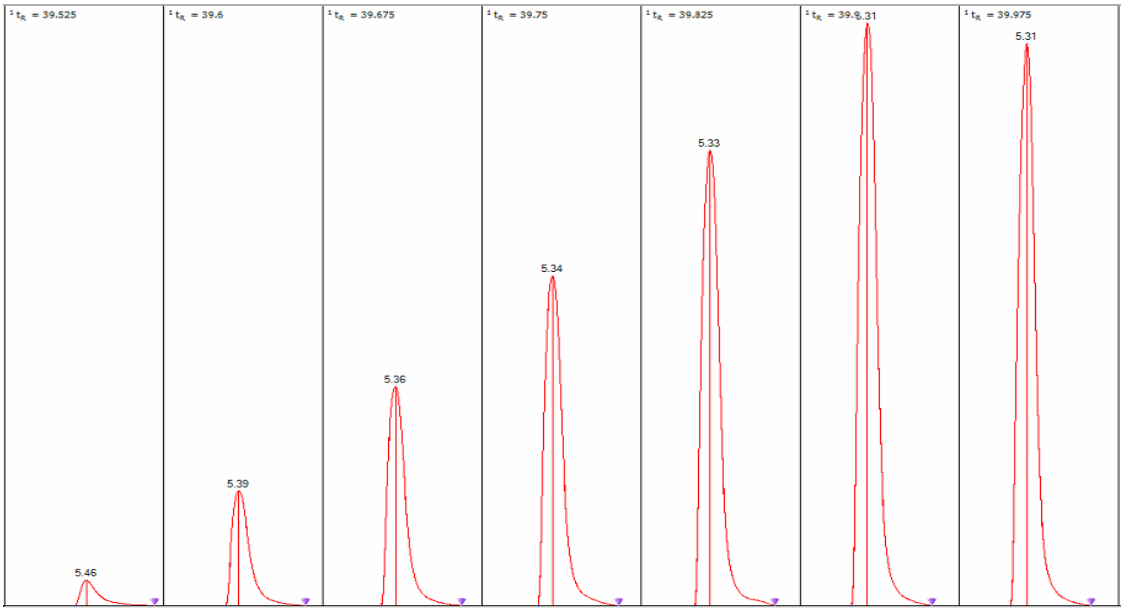


Figure 13. Sub-peak viewer for benzoic acid.

A suitable symmetry was chosen to be in the range of 80-120. The percentage of peaks to fall within that range for modulation times 4.5, 4.7, and 5 were 36.07%, 32.14%, and 38.60%. The asymmetry does not seem to follow a trend with modulation time. Although the percentages are low, peaks outside of the chosen range may still be suitable for identification and quantification.

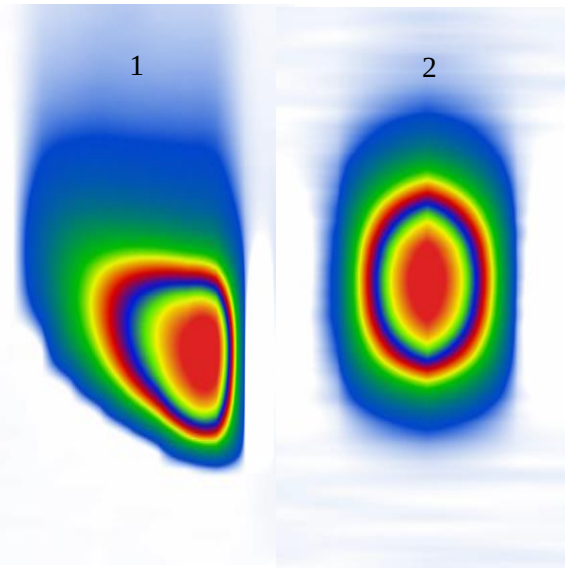


Figure 14. Good versus poor peak tailing.

The peak tailing was also considered alongside the symmetry analysis. Tailing considers peak differences at a much lower height and is another measure of deviations from a Gaussian peak shape. As the peak tailing factor increases above 1, the latter half of the peak stretches over time. A tailing factor below 1 indicates peak fronting which has the same quantification issues as peak tailing. As shown in Figure 13, peak 1, benzoic acid, and peak 2, biphenyl (909 MF and 922 RMF) yield tailing factors of 0.312 and 0.9258, respectively. Peak 1 fails to have an ideal shape which can impact overall quantification. Similarly to asymmetry, a suitable range was chosen to be 0.8-1.2. The percentage of all peaks to fall within the suitable range for modulation times 4.5, 4.7, and 5 were 36.89%, 37.95%, and 42.79%, respectively. The increase in modulation has a slight impact on tailing. However, this is likely due to the loss of low intensity peaks through the bleed line with higher modulation times. The low intensity peaks typically had a worse tailing value compared to high intensity peaks. Additionally, peaks just outside the chosen tailing range may still be suitable.

The final performance descriptor, 2D occupation, was calculated for each modulation time. 2D occupation serves as a measure of chromatogram space efficiency rather than a direct measurement for each peak. The closer to 1, the more space that is utilized by the entire peak spread. The 2D occupation for the 4.5, 4.7, and 5 second modulation times were 0.7621, 0.7267, and 0.6462, respectively. This trend was expected as all of the peaks were able to travel through the second-dimension column within 4.5 seconds. The 4.5 modulation time is likely the most optimal with respect to 2D occupation because it allows all peaks to elute without overlap with column bleed. The performance descriptors for each modulation time can be seen in Table 4.

Table 4. Summary of performance descriptors for each modulation time.

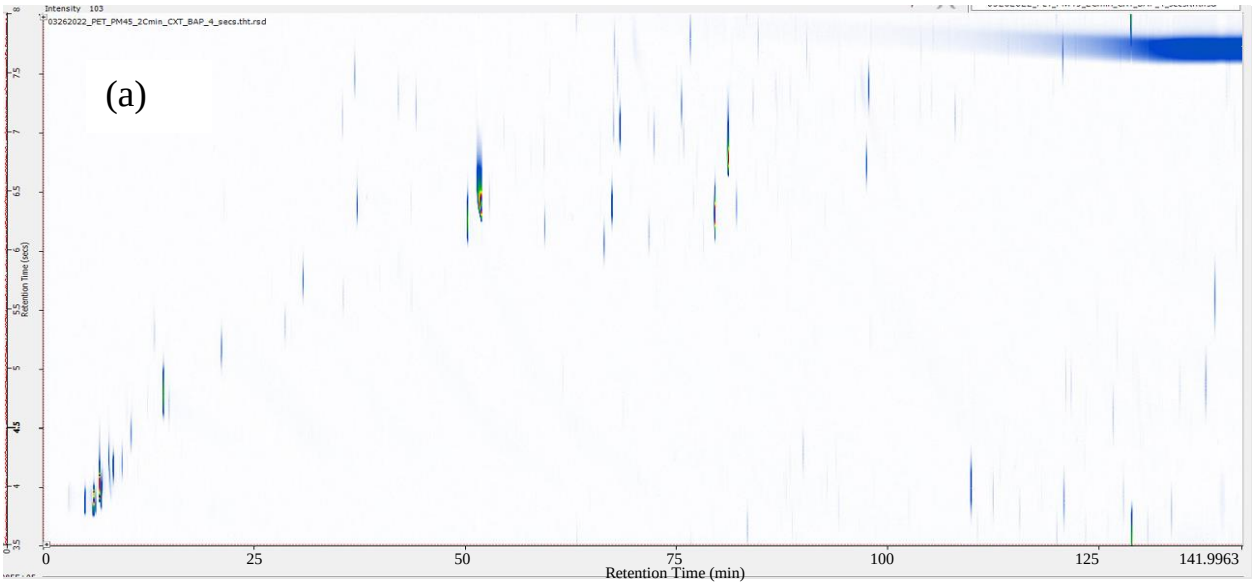
Modulation time (s)	Total Peaks	Peaks with resolution greater than 1 (%)	Peaks with tailing factor between 0.8 to 1.2 (%)	Peaks with asymmetry between 80 and 120 (%)	2D Occupation
4.5	244	52.05	36.89	36.07	0.7621
4.7	224	65.18	37.95	32.14	0.7267
5	215	69.77	42.79	38.60	0.6462

Varying the modulation times gave insight into the peak appearance and separation. Peak tailing and asymmetry only slightly varied between the different times indicating little correlation. However, this was untrue for resolution, the most important performance descriptor. A modulation time of 4.5 seconds yields the most products, but just under half the peaks have an unsuitable resolution. Increasing the modulation time to 4.7 seconds greatly improves the percentage of peaks with suitable resolution. However, it comes at the expense of losing 20 peaks. The 4% increase from 4.7 to 5 seconds does not justify losing even more products. The

next step of method development involved oven program optimization. Both modulation times 4.5 and 4.7 were used to determine if the performance descriptors could be improved.

3.2 Oven Program

With the chosen modulation times, the oven program was modified. The columns utilized had a suggested maximum temperature of 300 °C. The main focus was on improving separation in region 4 which corresponds to the oven ramp. The first-dimension separation can be improved by decreasing the oven ramp.[15] This causes the analytes with a specific boiling point to have more time flowing through the column before the next analytes-those with a higher boiling point-begin to flow. The experiments were performed with a 2 °C per minute ramp instead of 3 °C per minute. The respective chromatograms for the two modulation times can be seen in Figure 14.



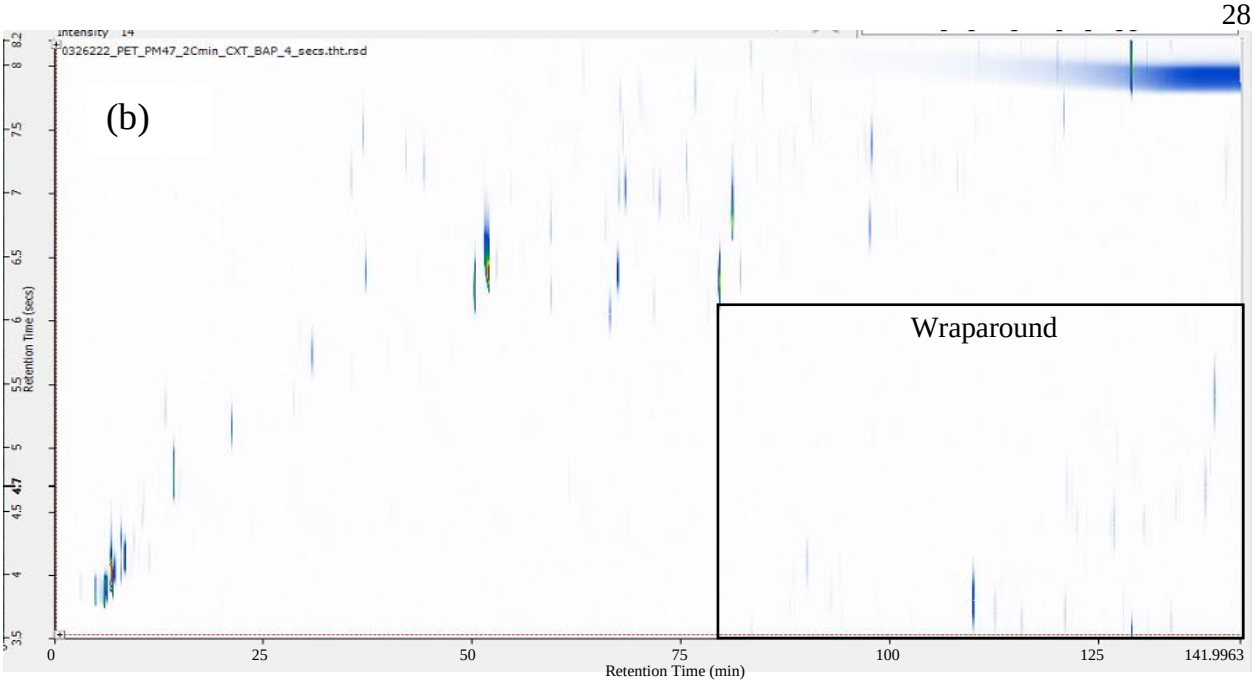


Figure 15. Chromatograms for modulation times 4.5s (a) and 4.7s (b) with 2 °C/min ramp rate.

Lowering the oven ramp resulted in wraparound for both modulation times. Wraparound occurs when a product cannot move through the second-dimension column within the modulation time.[22] When wraparound is observed, different peaks may overlap. In this case, many peaks in both chromatograms become obscured by the column bleed, and thus, cannot be analyzed. The optimal ramp time would be the original 3 °C per minute. Attempting to use a higher ramp rate will cause the peak spread to decrease.

Chapter 4

Conclusions

The method development yielded a chromatogram that may be suitable for micropyrolysis studies. A modulation time of 4.7 seconds yielded the best performance descriptors without losing too many products. However, it will be important to continue to consider the 4.5 second modulation time to analyze as many products as possible. Future studies can utilize both modulation times to maximize both peaks identified and peak performance descriptors. Further method develop could investigate the impact of the MS scanning ranges on the appearance of peaks. The scanning lower bound of the scanning range could be switched to 35 m/z from 45 m/z to analyze more lighter gases. However, attempting to go below 35 m/z will cause oxygen, nitrogen, and water to appear. Additionally, a more detailed examination of MS chromatograms should be performed to accurately determine each peak.

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Education

The Pennsylvania State University — **University Park, PA**
Schreyer Honors College; College of Engineering — **August 2018 to May 2022**
Bachelor of Science, Chemical Engineering

Research Experience

Toraman Research Lab — **University Park, PA**
Undergraduate Research Assistant — **February 2021 to Present**

- Perform PA6 and PET polymer pyrolysis experiments to facilitate understanding of reaction kinetics
- Collaborate with group members to develop experimental plan and analyze TOF-MS and FID data
- Conduct literature reviews of alternative pyrolysis methods
- Transcribed over 800 experimental data points from nearly 70 different sources.

Professional Experience

Penn State Residential Dining — **University Park, PA**
Crew Leader and Student Trainer — **November 2019 to February 2021**

- Operated multiple dining venues which includes preparing orders and customer service.
- Trained and encourage new employees in completing daily station tasks and customer interactions.
- Collaborated with managers to develop the best day-to-day plan for efficiently running each station.
- Stocked and maintained supplies in the station.

Home City Ice – Bridgeport Division — **Bridgeport, OH**
Office Assistant — **May 2018 to May 2020**

- Optimized delivery routes by analyzing customer sales, inventories, and local events.
- Accommodated over 500 businesses by providing delivery updates and plans for new merchandisers.
- Compiled and evaluated daily factory production and sales
- Calculated employee commission using employee hours and each shift's productivity.
- Maintained and repaired factory machinery to preserve production
- Served on route delivery by aiding drivers in greeting customers and supplying ice.

Extracurriculars

Club Ultimate Frisbee

- Collaborate with teammates through practice to improve team chemistry
- Instruct new players in how to perform drills and apply strategy while in game

Relevant Coursework

- Material Balances
- Chemical Engineering Thermodynamics
- Computational Tools for Chemical Engineering
- Process Fluid Mechanics
- Phase and Chemical Equilibrium

- Process Heat Transfer
- Chemical Reaction Engineering
- Mass Transfer
- Chemical Process Safety