Chem 2219: Exp. #6 Fractional Distillation

Objective: In this experiment you will learn to separate the components of a solvent mixture (two liquids) by distillation. The boiling point (BP) range and refractive index (RI) will be determined for the three fractions. NMR will be used to determine the percent composition and purity of the first fraction. *Gas chromatography might be used if it becomes available in time.

* Gas Chromatography is extremely useful in determining the percent composition/purity of known liquids. Recall the boiling point and refractive index (R.I.) are two useful physical properties of a liquid. They are used for identification purposes. The R.I. is additionally used as a measure of purity of the sample being examined.

Reading Assignment: MTOL, pp. 79-83 (distillation theory), 57-62 (gas chromatography) and:
OCLT, pp. 254-262 (separation theory), 279-281 (fractional distillation),
139-153 (gas chromatography).

Also on **CANVAS** read and answer prelab questions for – **Fractional Distillation**
and (*prelab for next week*) Gas Chromatography

Concepts:

Boiling Point, Condensate, Condensation, Distillate, Distillation, Evaporation, Reflux, Refractive Index, Theoretical Plates, Vaporization

Chemicals:

Cyclohexane, Toluene, p-Xylene

Safety Precautions:

Wear chemical splash-proof goggles and appropriate attire at all times.
Cyclohexane, toluene and p-xylene are flammable liquids.
Hot glassware looks just like cold glassware.
Be careful when working with hot glassware! Do not to touch it!

Materials:

aluminum block, aluminum foil, beaker (50ml), packed air condenser, conical vial (5 ml), disposable pipets & bulbs, disposable vials and lids, finger clamps (2), glass wool batting, Hickman still head, hot plate with magnetic stirrer, labels (3-small), magnetic spin vane (large), ringstand, Teflon septum with hole in the center, and thermometer

Instruments:

Digital Refractometer, Gas Chromatograph (maybe), Magritek desktop NMR

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Background Information:

Distillation is the process of separating two or more compounds based on their boiling points. The compound with a lower boiling point will vaporize first allowing it to be separated from the higher boiling point compound. During distillation, the mixture is placed in a container, the lower boiling point compound vaporizes and the vapor condenses in a separate container. The condensed vapor (***the condensate or distillate***) is then collected from the second container.

Simple distillation involves a single vaporization / condensation cycle. Simple distillation is used to separate compounds with widely differing boiling points (e.g., a solid dissolved in a liquid) where both compounds want to be collected. It can also be used to purify a liquid that contain either nonvolatile impurities (e.g., salts) or very small amounts of another liquid with a widely differing boiling point from the liquid to be purified. If two liquids have a boiling point difference of less than 40-50^{o}C, simple distillation will not be effective at separating them. In this case, fractional distillation must be used.

Fractional distillation is used to separate liquid mixtures where the compounds have similar boiling points and/or they are present in comparable amounts. When a mixture of two compounds with relatively close boiling points is heated, the vapor above the liquid will be composed of both compounds at the boiling point. For example, there is a 50:50 mixture of compounds A and B, where A has a lower boiling point than B. When the mixture starts to boil, the vapor above the liquid will be enriched with compound A, but will still have a significant proportion of B. If the vapor is enriched by 30% of compound A, then the mixture ratio would be 65:35 A:B. As the vapor cools in the condenser, it forms a liquid with the same mixture ratio as the vapor. The collected distillate would then have the ratio 65:35 A:B. At the end of the simple distillation, the liquid remaining in the still pot would likewise be enriched in compound B. To further purify A, the distillate of 65:35 A:B could be added to a new still pot and distilled again. If vapor was again enriched by 30% with compound A, the distillate for the second cycle would be approximately 85:15 A:B. If this process consistently enriches the distillate by 30%, then by the third cycle of this example, the distillate would be pure A. So in order to increase the amount of compound A beyond what is obtained from a simple distillation, a series of vaporization / condensation cycles would be needed. This series of cycles is called a **fractional distillation**.

Fractional distillation can be thought of as a series of simple distillations. However, instead of having multiple still pots and condensers, the vaporization / condensation cycles take place in a single distillation column. In fractional distillation, vapor rises up the column and condenses. It then re-evaporates, rises further up the column and condenses again. With each cycle the vapor becomes enriched in the component with the lower boiling point. In this way, fractional distillation accomplishes in one apparatus what would require several simple distillation setups.

In fractional distillation, **"fractionating" columns** are insulated in order to allow multiple vaporization–condensation cycles to occur within a single column. The fractionating column consists of packing material or closely spaced "plates." The more volatile (*lower-boiling*) component vaporizes first. The vapor then condenses on multiple surfaces in the fractionating column, and the resulting liquid vaporizes again. During each step of the vapor / liquid equilibrium, the vapor becomes more enriched in the more volatile component. If there are an adequate number of "theoretical plates," the mixture will distill one component at a time in fractions. With enough plates then, each fraction consists of only a single pure substance.

So the more vaporization / condensation cycles that a mixture goes through, the better the separation. While a fractionating column with greater surface area leads to better separation, it also leads to a longer processing time. Also, when the packing material becomes covered with condensation, any liquid that adheres to the surface or the pores of the packing material will not continue to vaporize stalling the distillation process. This condensation on the surfaces of the column is referred to as **liquid hold-up**. When packing a fractionating column then, it is important to take into consideration both the quality of the separation and the amount of time it takes for the distillation process. For our purposes, we will be using an unpacked column to avoid any liquid hold-up.

During fractional distillation, there is also a **temperature gradient** over the length of the column. The boiling point of a mixture varies with the composition of the mixture. The boiling points of mixtures of known concentrations have been plotted, so the composition of a mixture can be determined by knowing the boiling point of the mixture. (*An example is shown in Figure 3.*) It is easy to see that the higher percentage of the lower boiling point component (*cyclohexane*), the lower the boiling point will be. As the mixture travels up the column, the more concentrated it becomes in the lower boiling point component and the temperature of the column decreases. The temperature on the thermometer will not begin to rise until the distillate reaches the Hickman still head. The temperature on the thermometer corresponds to the boiling point of the vapor condensing on it. (***Recall:*** *The condensation point and the boiling point are the same temperature.*) If the temperature corresponds to the boiling point of the lower boiling compound, then the distilled liquid is pure.

To ensure that only the lower boiling point liquid is distilling, the still pot should be heated slowly in order to create the largest temperature gradient. During the process of refluxing, most of the vapor from the still pot will condense and drip back into the still pot. So it is important to set the temperature of the hot plate high enough that the vapor from the still pot travels up the column and into the still head before condensing. However, when the temperature of the still pot is too high, both of the components of the mixture vaporize and condense in the still head simultaneously. Thus, if the temperature is too high, the separation is not as efficient as it could be. When heating the still pot then, it is again important to take into consideration both the quality of the separation and the amount of time it takes for the distillation process.

Fractional distillation is used not only in organic chemistry labs to purify compounds and to separate the components in a mixture that have similar boiling points, but it is also commonly used in industry for the same reasons. In the petroleum industry, fractional distillation is used for refining crude oil where the components have similar boiling points. Crude oil can be separated by fractional distillation into useful products: liquefied petroleum gas, gasoline, kerosene, jet fuel, diesel oil and fuel oils. The products of crude oil include many items that impact our daily lives - everything from gasoline to plastics to fabrics and even medicine. Without fractional distillation these items would be cost prohibitive.

References:

Flinn Scientific. "Simple Distillation: Separation of a Mixture." Available October 3, 2020 at: https://www.flinnsci.com/api/library/Download/224aed85de4d4fa287d0eceef9a40adc

Northern Virginia Community College. "Fractional Distillation." Available October 3, 2020 at: https://blogs.nvcc.edu/alchm/files/2015/11/45_fractdist.pdf

Wikipedia. "Fractional Distillation." Available October 3, 2020 at: https://en.wikipedia.org/wiki/Fractional_distillation

Fractional Distillation Procedure

You are provided with a 50:50 solution of two volatile liquids (toluene and cyclohexane) which can be distilled readily at a temperature not higher than 120 °C. Your task is to separate the components by distillation, record the boiling point (range) and the refractive index for the distillate fractions, calculate the % error (by comparison with literature values) in the recorded observations, and comment on any similarities or discrepancies.

1. Preheat the hot plate and Al block at a heat setting of ~170 °C while you assemble your glassware.
2. Put together a fractional distillation set-up.*
   (See Figure 1 to the right).

***Note:** Verify that there is an o-ring in each of the black caps before attaching the conical vial to the packed air condenser and the air condenser to the Hickman still head. Verify that the arm of the Claisen head has a cap with a septum in it attached and that the septum does not have holes in it. If there is a sidearm on the Hickman still, verify the arm is capped. **Do not lower empty glassware into the Al block; it will cause the glassware to crack.** Do not worry about adjusting thermometer height until glassware has been lowered into the Al block.

3. Acquire sample from the hood. Record physical properties of unknown in lab report.
4. Transfer sample solution to a 5-ml conical vial, filling it within ½ inch below the cap. Record the volume to the nearest 0.1 ml.
5. Add the large (~ $^{5}/_{8}$”) magnetic stir bar to the vial (*to regulate boiling and avoid bumping*). Attach the packed air condenser and Hickman still head as shown. Wait to add the thermometer until after the apparatus has been properly insulated. Lower the apparatus into the Al block.

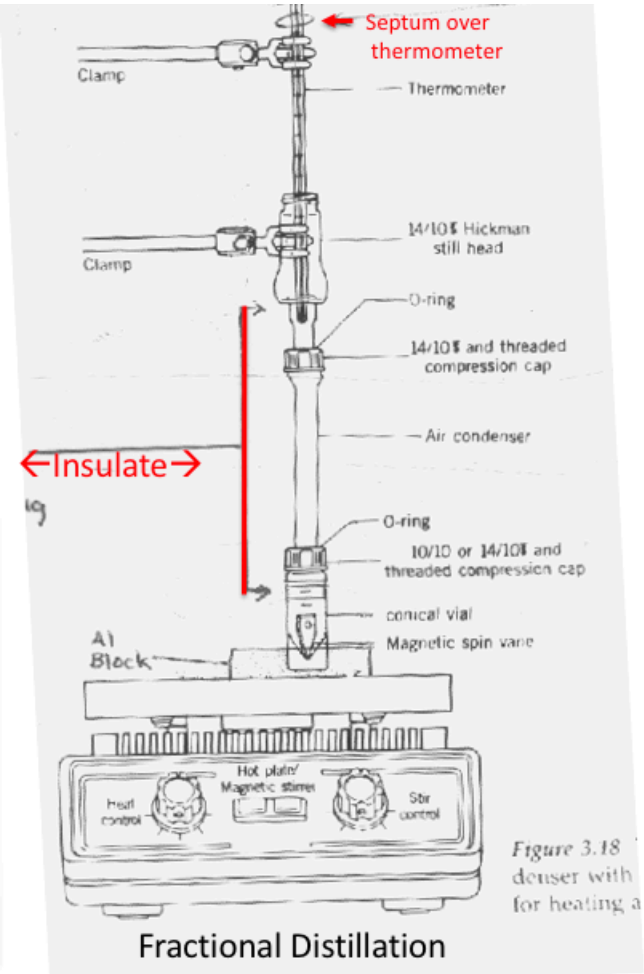

Figure 1: Fractional Distillation Setup

6. Obtain glass wool to insulate the apparatus.* Cover the apparatus from just below the bottom black cap on the 5 ml conical vial to the top of the neck of the Hickman still. Make sure the glass wool is tight against the glassware, pinching it as close as possible to the condenser using the test tube clamps.

***Note:** It is important that no glass be exposed from the conical vial to the base of the Hickman still in order to avoid heat loss to the environment which will slow down or prevent sample from collecting in the Hickman still.

7. Add the thermometer* with the attached Teflon circle. Adjust the height of the thermometer such that the bulb of the thermometer is in the top of the neck of the Hickman still.

***Note:** Be sure to add a Teflon circle with a hole in it around the thermometer. The circle goes above the clamp to keep the thermometer from sliding into the vial and breaking. Do not clamp the thermometer tightly as it might break. Make sure the clamp is tight enough that the thermometer does not tilt and fall over. The bulb of the thermometer should be positioned so that the bulb is completely in the neck. The top of the bulb should be at the top of the neck.

8. Adjust the temperature* of the hotplate in order to regulate the boiling rate so that a smooth slow distillation is attained.

Note:** Adjust the temperature on the hotplate to regulate the heat so that a smooth slow distillation is attained. **Do <u>not</u> set the temperature too high or else you will boil both the cyclohexane and the toluene.** ***Recall: *Your objective is to separate them.*

9. Acquire from the supply cart, <u>3</u> disposable vials with caps, <u>3</u> small labels, <u>3</u> disposable pipets and <u>1</u> pipet bulb. Label vials #1, #2 and #3. Place the vials in a 50 ml beaker so they stand upright and do not tip over.

10. Record the temperature when the distillate first starts to condense in the Hickman still. (This is the beginning of your boiling point (BP) range for sample #1.)

Note: The expected boiling point ranges for the fractions are in the range of ~75-82 ^{o}C, ~85-95 ^{o}C, >100 ^{o}C corresponding the cyclohexane, BP=81 C and toluene, BP 110 C. However, the actual ranges may differ from the expected ranges – especially if you are not using a mercury thermometer.

Note: ***Exact ranges may differ from one experimenter to the next. There may also be some overlap of the ranges.*** **<u>Record the values that you actually observe for your fractions.</u>**

11. Allow the distillate to accumulate in the Hickman still head until the well is at least half full. Record the temperature. (This is the top of the BP range for sample #1.)

12. Then using a clean pipet, transfer this accumulated first fraction to the 1-mL disposable vial labeled "#1" and cap it.

Note: About ¼" of liquid in the vial is an adequate sample. Make sure and cap the vial. If you need to wait for more liquid to accumulate so that you can add to the sample, leave the cap on until you are ready to add more sample. If possible, completely remove distillate from the still head for the determined temperature range. Keep the vials in a 50ml beaker to prevent them from tipping over.

13. Record the temperature when the distillate first starts to condense again in the Hickman still. (*There may be a slight temperature drop after the removal of the first sample*.) Allow the distillate to accumulate in the Hickman still head. Record the final temperature for the BP range of sample #2. Continue the distillation of most of the remaining material until no more distillate collects. This will probably correspond to a significant temperature drop (≥ 10 ^{o}C) in the still head which indicates the end of the distillation.

14. When the volume in the conical vial is less than half of the initial volume, remove the distillation apparatus from the heat source. Keeping the apparatus clamped to the ring stand, lower the apparatus until the vial is standing on the desktop. Do not place the vial on the metal ringstand. Allow the apparatus to cool down to room temperature. Then using a clean pipet, the final sample (#3) can be taken from the still pot/conical vial. Record the temperature range for sample #3 as greater than the highest temperature for sample #2. For example, if sample #2 is 82-93 ^{o}C, then sample #3 is >93 ^{o}C.

Note: Percent composition may be determined for sample #1 using GC while the distillation apparatus cools. Or take a sample filled to > 3 cm in an NMR tube to room 140(?) to be run.

15. Determine the refractive indices of all 3 fractions on the Abbe or digital refractometer. Place a 1" watch glass over the lens of the digital refractomer to prevent differential evaporation of the sample during measurement of RI. Record the brand/type of which refractometer you used and your results. Record the temperature of the refractometer cooling water in order to do the RI corrections for temperature. *Consult handout for operating directions.*

16. Determine the Percent Composition in your results via the desktop NMR. Calculations are explained in the powerpoint. Record the brand/model of the NMR used. Include your NMR spectra printout and calculations in your lab report submitted to Canvas.

17. Dispose of chemicals appropriately. Clean and return all glassware and equipment.

Post Lab: (*Directions for how to do the calculations are on the next page*.)

1. Show calculations for RI corrections and the % error for your reported BP and corrected RI. Tabulate the literature values, actual values and % error observations.

Note: Samples #1 & #2 should be compared to cyclohexane and Sample #3 should be compared to toluene if it is taken from the vial and cyclohexane if it is taken from the Hickman still.

2. Determine the composition of the distillates based on the corrected RI values using Figure 2. Compare the percent composition based on the RI to the one based on NMR and calculate the % error using the RI value as the theoretical value and the NMR as the observed value.

3. Calculate the number of theoretical plates for the first fraction using a BP vs composition diagram (Figure 3). Include this graph with the markings to show how the theoretical plates were determined. The initial composition was a 50:50 mix.

4. In your conclusion, discuss the following:
    a. How you determined the percent composition of each sample.
    b. Whether or not the distillation increased the purity of the sample.
        1. Did the distillate samples have a greater than 50% cyclohexane composition?
        2. If Sample #3 was from the still pot did it have a greater than 50% composition of toluene?
    c. How could you improve the process to get a more pure product?

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Fractional Distillation Calculations

From the PowerPoint: "Fractions will be collected for temperature ranges: ~75-82 ºC, ~85-95 ºC, >100 ºC." (*These values may differ from what you observe.* Record what you actually observe.)

Most of the thermocouples/thermometers were reading lower than these values, so it isn't possible to determine the % composition of the mixture and theoretical plates from the boiling points. Instead you will need to determine the % composition from the corrected Refractive Index data using the equation and the graph shown in figure 2 on page 3 of your directions.

For each of the 3 samples, you should have refractive index data. You will need to do a temperature correction for each of the RI values. For the sample that you also ran on the NMR, you will need to determine the percent composition from the RI and calculate % Errors.

For example,

Sample 1 (65-72 ºC)	1.435	23.5 ºC	
Sample 2 (72-88 ºC)	1.428	23.5 ºC	
Sample 3 (> 88 ºC)	1.493	23.5 ºC	*(Your values will vary.)*

Let's say Sample 1 was used for the GC. The corrected RI is

$$n^{20} = 1.435 + 0.00045\,(23.5 - 20\ {}^{o}\mathrm{C}) = 1.436$$

To Calculate Percent Composition based on the Refractive Index:

Look at Figure 2 below, draw a horizontal line at the corrected value. Here: 1.436. Where the horizontal line crosses the diagonal line, draw a vertical line. The vertical line will give you the percent composition for the mixture at that refractive index. Here approximately (*the scale is difficult to read, just make your best guess*) 85% Cyclohexane and 15% Toluene.

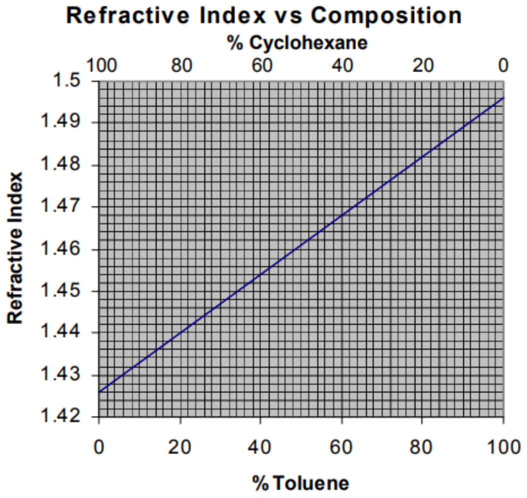
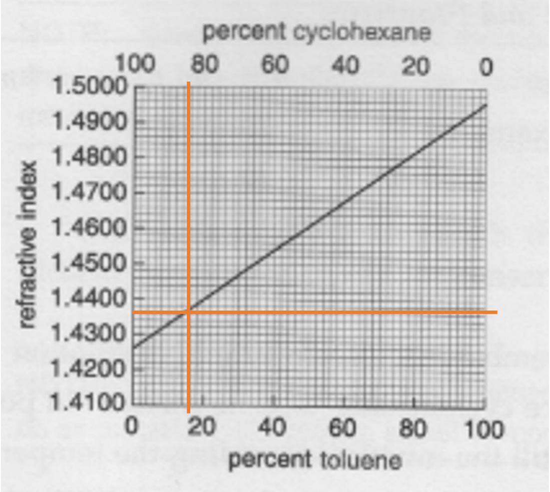


Figure 2: Used to determine Percent Composition based on Refractive Index.



Example of how to draw the lines.

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To Calculate Theoretical Plates:

Normally, the number of theoretical plates would be determined by using a straight edge to draw a horizontal line at the highest boiling point.

If your highest boiling point is between 82 and 110 °C, then draw a horizontal line across at that temperature (similar to the AB line show in the example). Where the line crosses the liquid curve is your percent composition based on boiling point. Where the line crosses the vapor curve, drop a vertical line to the liquid curve. From this point draw a horizontal line to the vapor curve. Repeat until the curves meet.

If your highest boiling point is below 82 °C, then used the Percent Composition that you determined from the Refractive Index to determine your number of theoretical plates. To do this, draw a vertical line at that composition from the x-axis to the lower (liquid) curve. From there, draw a horizontal line to the upper/left (vapor) curve. Where the horizontal line meets the vapor curve, drop a vertical line to the liquid curve. Repeat until the curves meet.

For the example data from Sample 1, it will be similar to the graph above, or 1 to 2 plates.

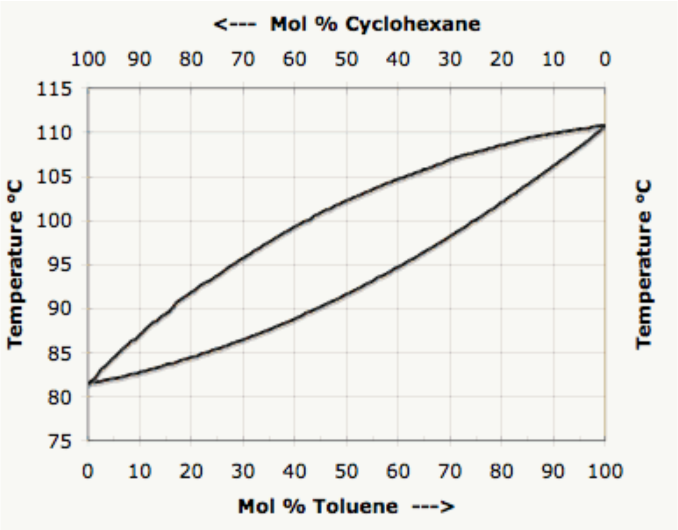
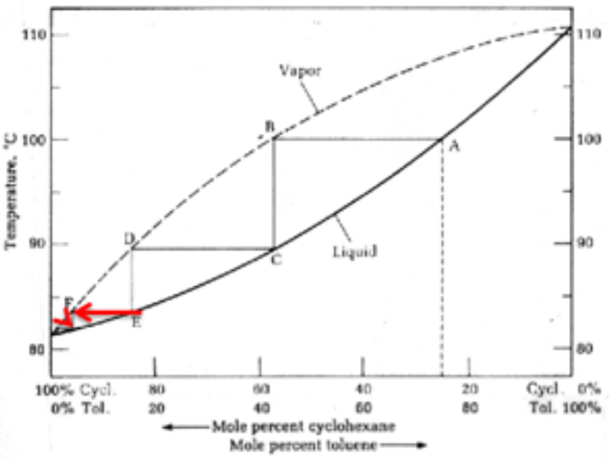


Figure 3: Used to determine Theoretical Plates. (Initial Composition 50:50.)



Examples: If BP was 100 oC, then theoretical plates would start at A an progress down the steps to the left. The hand drawn arrows, show theoretical plates based on the 85% composition determined from the RI.

To calculate the % Error for RI:

Use the RI literature value for cyclohexane for the first two samples and the RI literature value for toluene for the third sample if it was taken from the vial rather than the Hickman still head. (If all 3 samples were taken from the Hickman still head, use the RI value for cyclohexane for all 3.)

% Error RI = [(theoretical – observed) / theoretical] x 100

Literature RI value for cyclohexane: 1.427 (*Theoretical value*)
Corrected RI value for Sample 1: 1.436 (*Observed value*)

% Error RI = [(1.427 – 1.436) / 1.427] x 100 = -0.63% (***the absolute value also acceptable***)

To calculate the % Error for Percent Composition: *(Your values will vary.)*

NMR value for % Cyclohexane (1st peak on chromatogram): 78% (*Observed value*)
RI value for % Cyclohexane: 85% (*Theoretical value*)

% Error %C = [(85-78) / 85] x 100 = 8.24%

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To Calculate Percent Composition based on the NMR Data Using Distillate Sample:

Note: *An example of how to do the calculation is provided on pp 52-53 of the 8-2219 Gas Chromatography PowerPoint.*

1. Using the NMR data (example shown below) for the distillate calculate the percent composition of cyclohexane to toluene. The peak on the far right of the spectrum corresponds to the 12 protons of cyclohexane. The peak(s) on the left corresponds to the 5 protons attached to the aromatic ring of toluene. The peak in the center corresponds to the 3 protons in the methyl group for the toluene. (The 2 toluene peaks provide similar calculation results, so we will be using the one(s) on the left only.)
2. To calculate the percent composition of cyclohexane from your data:

   Area of the peak (value below the peak) ÷ number of protons = moles

   moles x molar mass = grams

   Mass % = [mass A / (mass A + mass B)] x 100

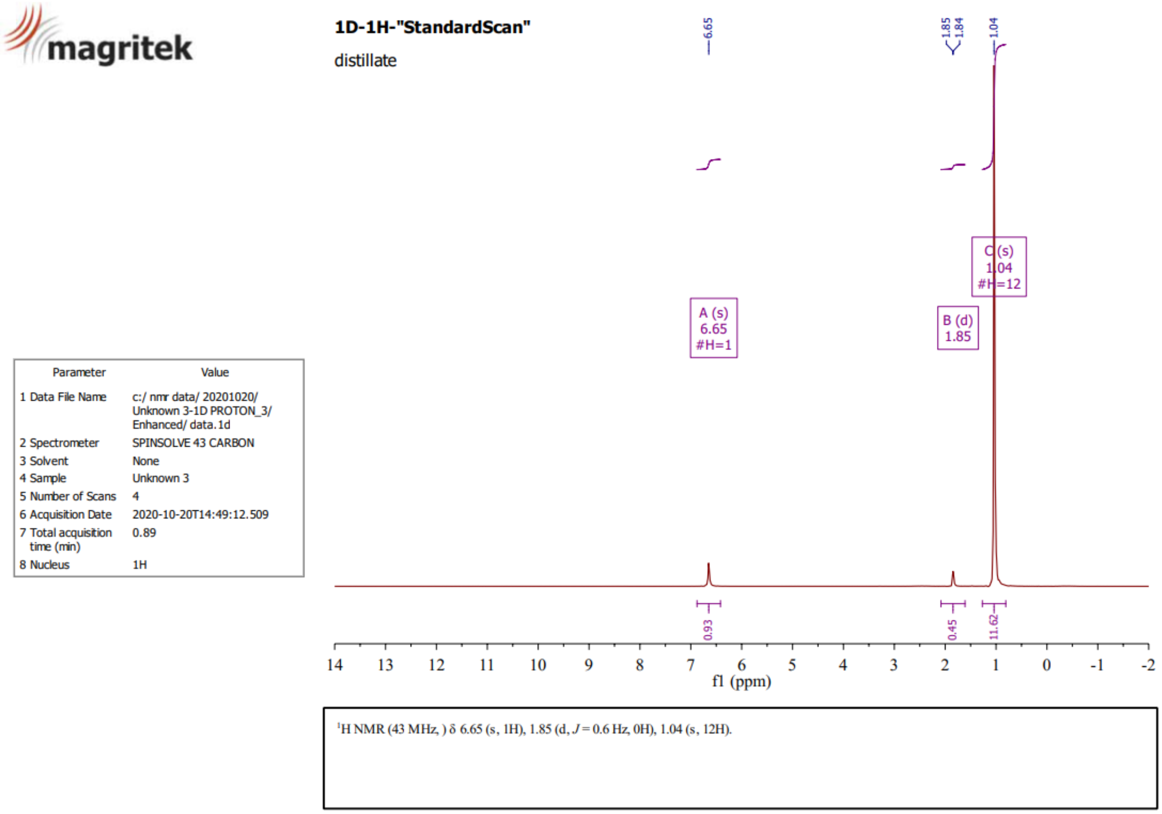
Example below:

Cyclohexane: 11.62 / 12 = 0.9683 moles
0.9683 moles x (84.16 g/mole) = 81.49 g

Toluene: 0.93 / 5 = 0.186 moles
0.186 moles x (92.14 g/mole) = 17.14 g

Mass % Cyclohexane: [81.49 / (17.14 + 81.49)] x 100 = **82.47%**

3. Substitute the NMR % Composition for the NMR % Composition in the % Error of Composition Equation. (*i.e., Refractive Index % Composition = theoretical value and NMR % Composition = observed value.*)



Parameter	Value
1 Data File Name	c:/ nmr data/ 20201020/ Unknown 3-1D PROTON_3/ Enhanced/ data.1d
2 Spectrometer	SPINSOLVE 43 CARBON
3 Solvent	None
4 Sample	Unknown 3
5 Number of Scans	4
6 Acquisition Date	2020-10-20T14:49:12.509
7 Total acquisition time (min)	0.89
8 Nucleus	1H

^{1}H NMR (43 MHz,) δ 6.65 (s, 1H), 1.85 (d, *J* = 0.6 Hz, 0H), 1.04 (s, 12H).

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To Calculate Percent Composition based on the NMR Data Using Sample from the Still Pot:

Note: *An example of how to do the calculation is provided on pp 52-53 of the 8-2219 Gas Chromatography PowerPoint.*

1. Using the NMR data (example shown below) for the distillate calculate the percent composition of cyclohexane to toluene. The peak on the far right of the spectrum corresponds to the 12 protons of cyclohexane. The peak(s) on the left corresponds to the 5 protons attached to the aromatic ring of toluene. The peak in the center corresponds to the 3 protons in the methyl group for the toluene. (The 2 toluene peaks provide similar calculation results, so we will be using the one(s) on the left only.)
2. To calculate the percent composition of cyclohexane from your data:

   Area of the peak (value below the peak) ÷ number of protons = moles

   moles x molar mass = grams

   Mass % = [mass A / (mass A + mass B)] x 100

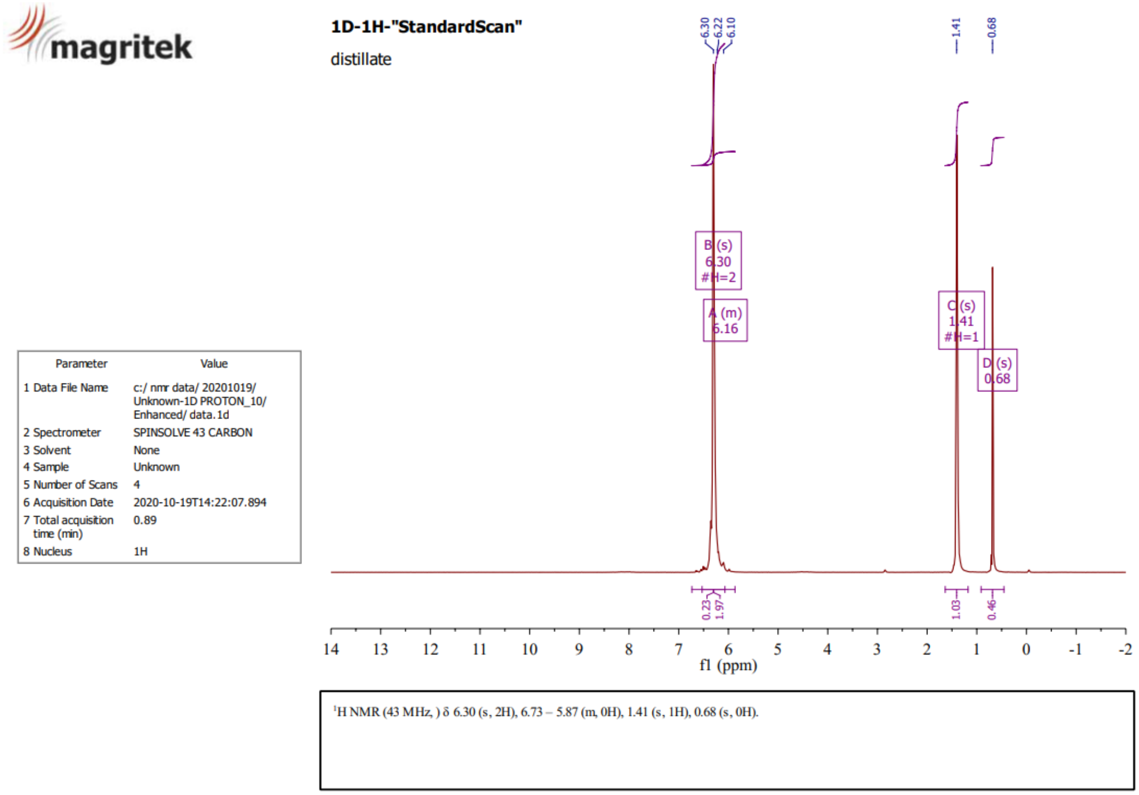
Example below:

Cyclohexane: 0.46 / 12 = 0.0383 moles
0.0383 moles x (84.16 g/mole) = 3.23 g

Toluene: (1.97 + 0.23) / 5 = 0.44 moles
0.44 moles x (92.14 g/mole) = 40.54 g

Mass % Toluene: [40.54 / (3.23 + 40.54)] x 100 = **92.62%**

3. Substitute the NMR % Composition for the GC % Composition in the % Error of Composition Equation. (*i.e., Refractive Index % Composition = theoretical value and NMR % Composition = observed value*.)



Parameter	Value
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2 Spectrometer	SPINSOLVE 43 CARBON
3 Solvent	None
4 Sample	Unknown
5 Number of Scans	4
6 Acquisition Date	2020-10-19T14:22:07.894
7 Total acquisition time (min)	0.89
8 Nucleus	1H

^{1}H NMR (43 MHz,) δ 6.30 (s, 2H), 6.73 – 5.87 (m, 0H), 1.41 (s, 1H), 0.68 (s, 0H).