

FRACTIONAL AND SIMPLE DISTILLATION OF CYCLOHEXANE AND TOLUENE
FROM UNKNOWN SAMPLE Z

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Introduction: The purpose of this experiment is to separate a sample of cyclohexane and toluene of unknown proportions using fractional distillation. The two components of the mixture are able to be separated because toluene's boiling point is 30°C higher than cyclohexane's boiling point. Cyclohexane should boil and distil before toluene. Even though their boiling points are different, it is difficult to isolate each component entirely. The vapor above the solution that is formed during distillation is not pure. It is a mixture of cyclohexane and toluene vapors. The composition of that vapor mixture is dependent upon the solution's composition according to Raoult's law which states that the partial vapor pressure (P_X) of a component at a specific temperature is equal to the pure vapor pressure (P_X^o) of that component multiplied by the mole fraction (N_X) of that component in solution (Eq. 1).

$$P_X = P_X^o N_X \quad (1)$$

The purity of each component will increase as the solution is distilled multiple times. Fractional distillation is used because it can complete several little distillations, or theoretical plates, in one distillation. The purity of each fraction isolated during the distillation is measured using gas-liquid chromatography, GC. Since each component has a different boiling point and affinity for the liquid stationary phase, each component will have a different response time through the column. This will result in each component having its own peak. The area under each peak should be proportional to the amount of each component in the mixture.

A secondary goal of this experiment is to compare the effectiveness of fractional distillation with simple distillation. This is accomplished by comparing the two graphs of head temperature versus distillate volume. Since there are two components, the graphs should have two plateaus where relatively pure components with unique boiling points will be collected. The distillation technique that produces the graph with the two best plateaus will be most effective.

A minor goal of this experiment is to compare the integrating techniques used to find the area under the GC peaks. The GC apparatus automatically integrates the area under each curve. A second method uses the mass of the cut-out peaks to find the ratios of the components. A third method assumes each peak is an isosceles triangle. Multiplying the height of each peak by one-half of the base of each peak would yield relatively accurate areas for each peak.

Experimental Procedure: A fractional distillation apparatus was assembled as shown in Figure 1. The neck of the 50mL, round-bottom flask was insulated with several layers of aluminum foil. The fractionating column was packed with steel sponge and then insulated with several layers of aluminum foil. A 30mL sample of unknown Z was obtained and about 0.5mL was saved in a labeled Erlenmeyer flask for later GC inspection. The voltage to the Thermowell heater was adjusted so that one drop of distillate formed every one to two seconds. The first fraction was collected in a 25mL graduated cylinder. The head temperature was recorded with the first drop of distillate and every 2mL afterwards. The second fraction was collected in a 10mL graduated cylinder when the change in head temperature rose drastically in comparison to the previous measurements. The first two fractions were transferred to labeled Erlenmeyer flasks, and the dried 25mL graduated cylinder was used to collect the third fraction when the change in head temperature dropped drastically. After approximately 1mL of solution was left in the round-bottom flask, the heat source was removed and the fractional distillation apparatus was allowed to cool. The third fraction was transferred to a labeled Erlenmeyer flask.

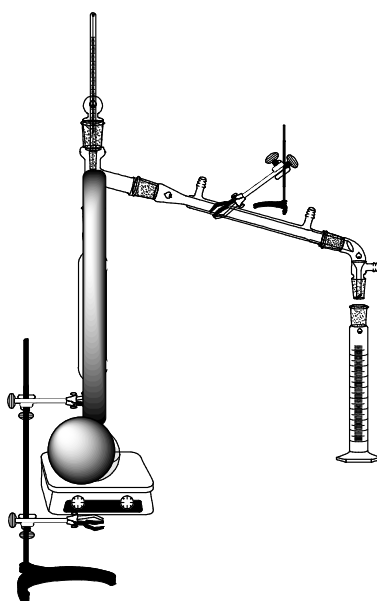


FIGURE 1 An insulated, fractional distillation apparatus.

GC traces were obtained for each of the four samples: unknown Z, fraction A, fraction B, and fraction C. A syringe was used to inject $2.5\mu\text{L}$ of sample into the injector. To ensure similar response times, the syringe was injected into the port in 3 seconds, the syringe's plunger was depressed in 2 seconds, the syringe was withdrawn, and then the injection button was pressed.

After the fractional distillation apparatus was cool, it was disassembled and a simple distillation apparatus was assembled as shown in Figure 2. The individual fractions were combined in the round-bottom flask, and the simple distillation was started. A 25mL graduated cylinder was used to collect the distillate. The heat source was adjusted so that one drop of distillate formed every 1-2 seconds. The head temperature was recorded with the first drop of distillate and every 2mL afterwards. The heat source was removed when approximately 1mL of sample remained in the round-bottom flask.

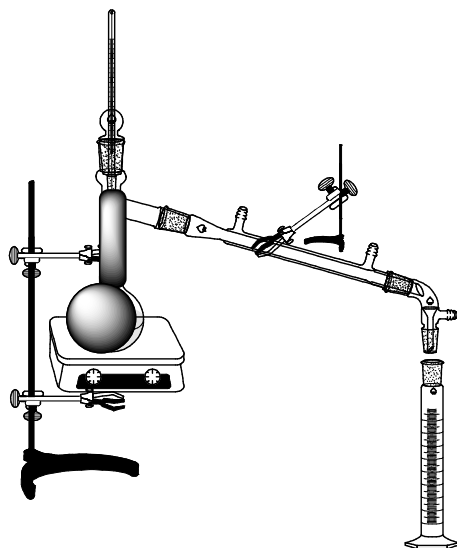


FIGURE 2 An insulated, simple distillation apparatus.

Compound	Mol. Wt. (amu)	B.P. (°C)	Density (g/mL)	Vap. Pres. (mmHg @ 20°C)	GC Response Factor
cyclohexane	84.1608	80.7	0.779	95	TCD $W_f = 1.11$
toluene	92.1402	110.6	0.867	22	TCD $W_f = 1.02$ $M_f = 0.86$

TABLE 1 Table of reagents.

Results and Observations: The voltage for the Thermowell heater was originally set at 45V, but after 50 minutes there was no temperature rise observed. The voltage was increased to 50V.

Three quarters of the fractionating column was warm after fifteen minutes, so the voltage was increased to 60V. Ten minutes later there was a steady drip of distillate every two seconds. The flow of distillate slowed to one drop every 5-6 seconds after 9.5mL of distillate was collected.

The temperature started to drop a little, so the voltage was increased to 64V. Fraction A was collected until 11.0mL of distillate formed. Fraction B was collected until 3.0mL of distillate formed. The head temperature drastically decreased from 104°C to 75°C at the beginning of fraction C. The voltage was increased to 80V and after 10 minutes, the temperature quickly rose to 104°C and began to distill again. Fraction C was collected until 8.0mL of distillate formed. A summary of distillation data is listed in Table 2 and graphically shown in Figures 3 and 4.

	Fractional Distillation		Simple Distillation	
	Distillate Volume (mL)	Head Temp. (°C)	Distillate Volume (mL)	Head Temp. (°C)
Fraction A	0.0	78.0	0.0	85.0
	2.0	81.6	2.0	87.0
	4.0	82.1	4.5	88.0
	6.0	83.2	6.0	89.0
	8.0	85.0	7.0	90.8
	10.0	84.9	8.5	92.8
	11.0	89.0	9.0	93.0
Fraction B	12.0	95.0	10.0	94.0
	13.0	101.5	12.0	96.0
	14.0	104.0	14.0	97.0
Fraction C	15.0	104.0	15.0	98.8
	16.0	104.5	16.5	100.0
	18.0	105.0	18.0	101.2
	20.0	105.5	19.0	102.5
	22.0	105.5	20.0	103.0
			22.0	105.0
		24.0	106.0	
		25.0	106.0	

TABLE 2 Fractional and simple distillation data.

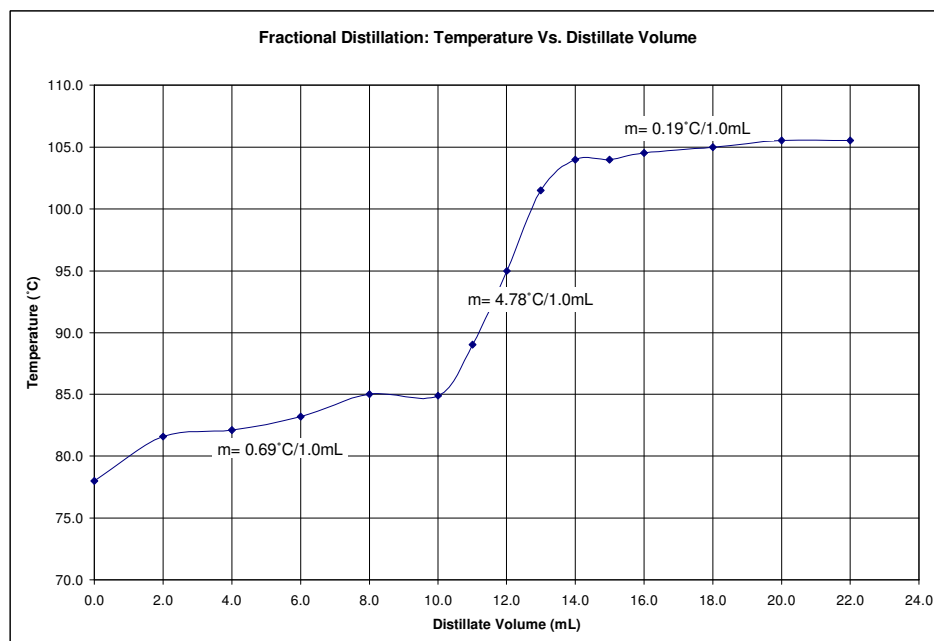


FIGURE 3 Graph of head temperature versus distillate volume for fractional distillation.

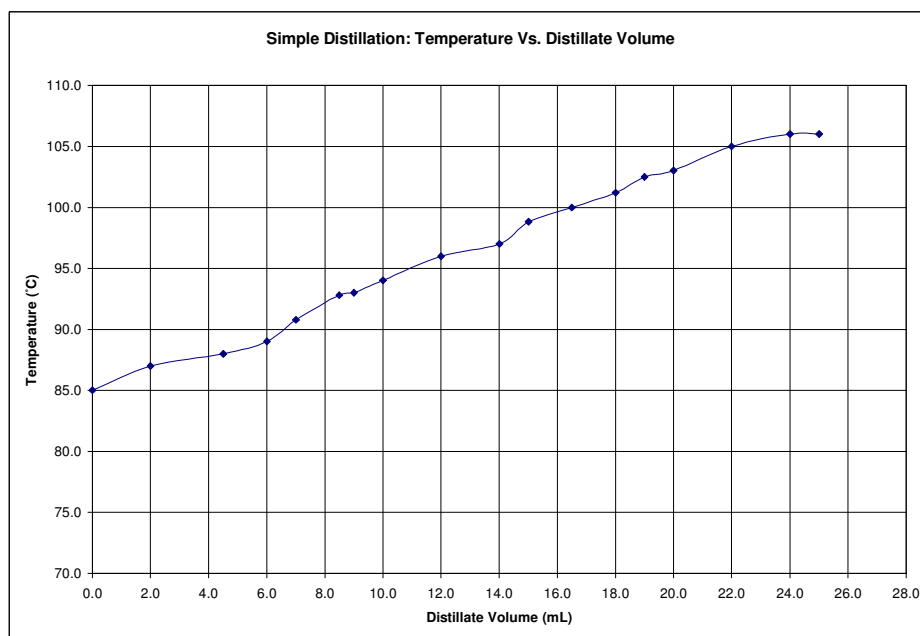
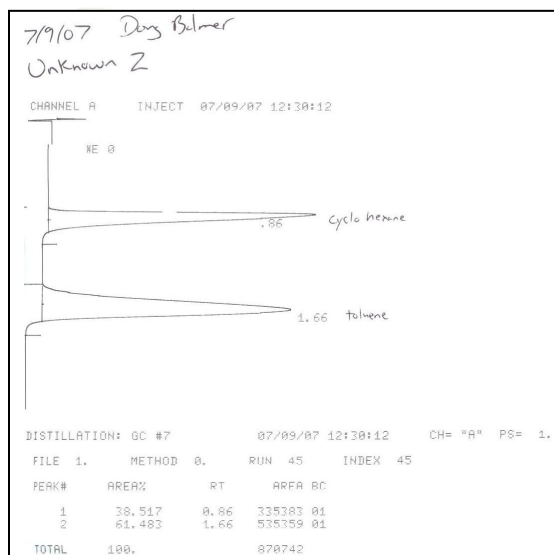
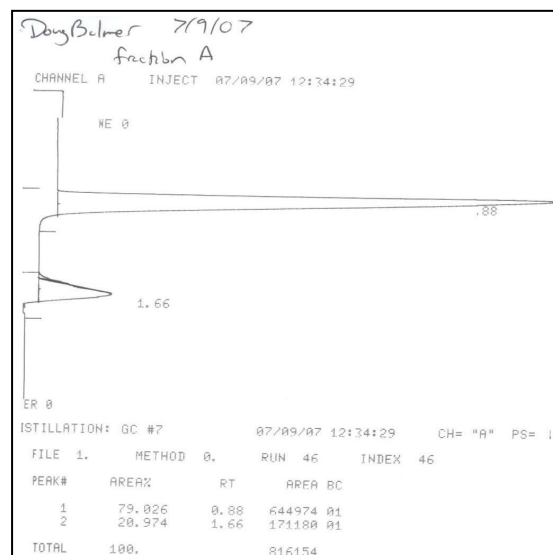


FIGURE 4 Graph of head temperature versus distillate volume for simple distillation.

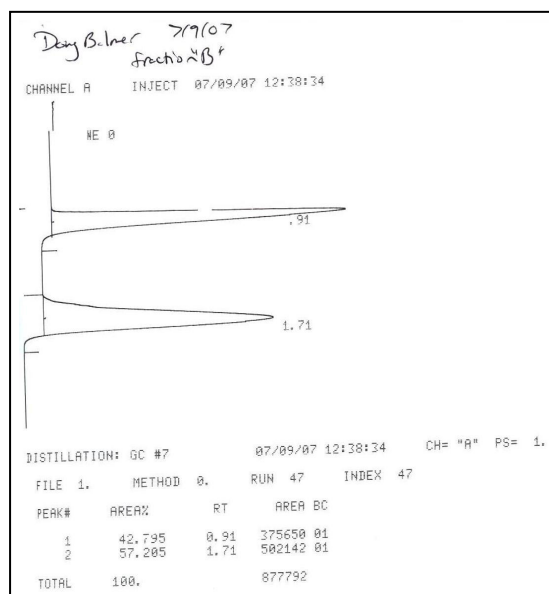
The GC traces (Fig. 5) were obtained from CG #7. The column, detector, and injector temperatures were pre-set to 103°C, 105°C, and 125°C, respectively. The current was pre-set to 100mA and the polarity was negative. The areas under the peaks and their respective proportions were calculated by the integrator, the cut-and-weigh method, and the isosceles triangle method (Tbl. 3). Unknown Z contained 38.517% cyclohexane and 61.483% toluene. Fraction A contained 79.026% cyclohexane and 20.974% toluene. Fraction B contained 42.795% cyclohexane and 57.205% toluene. Fraction C contained 4.687% cyclohexane and 95.313% toluene.



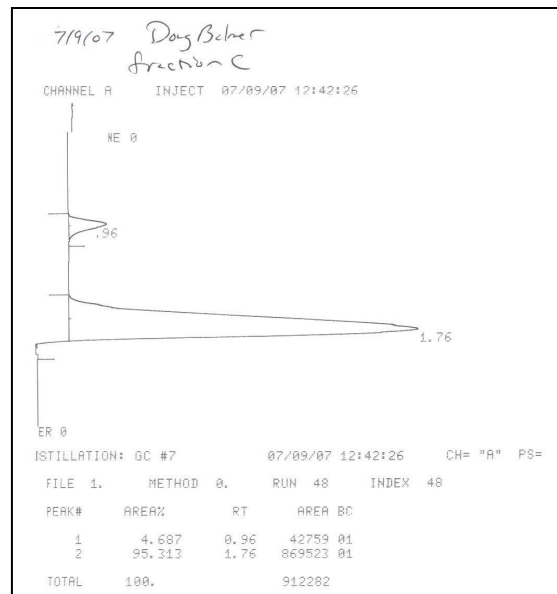
A) Unknown Z



B) Fraction A



C) Fraction B



D) Fraction C

FIGURE 5 GC traces for unknown Z, fraction A, fraction B, and fraction C. Peak 1 corresponds to cyclohexane and peak 2 corresponds to toluene.

Fraction _{Peak}	Integrator Area	Integrator %	Cut-Weigh Mass (g)	Cut-Weigh %	Triangle Area (cm ²)	Triangle %
Unknown Z ₁	335383	38.517%	0.030	41%	3.3	39%
Unknown Z ₂	535359	61.483%	0.044	59%	5.14	61%
A ₁	644974	79.026%	0.052	79%	6.1	85%
A ₂	171180	20.974%	0.014	21%	1.1	15%
B ₁	375650	42.795%	0.030	43%	3.5	43%
B ₂	502142	57.205%	0.039	57%	4.66	57%
C ₁	42759	4.687%	0.007	10.%	0.49	4%
C ₂	869523	95.313%	0.066	90.%	10.8	96%

TABLE 3 GC peak areas and percentages. Peak 1 refers to cyclohexane and peak 2 refers to toluene.

Conclusions: The experimental data showed that Unknown Z contained 38.5% cyclohexane and 61.5% toluene. The data showed that fractional distillation was able to roughly separate the mixture. Fraction A still consisted of 21.0% toluene. The switch between fraction A and fraction B was made at 11.0mL of distillate. Figure 3 shows a considerable temperature increase starting at 10.0mL of distillate. The switch from fraction A to B should have taken place at 10.0mL. Assuming the eleventh milliliter had the consistency of fraction B and not A, the percentage of toluene in fraction A rose with the addition of the last milliliter. A few simple calculations show that fraction A would have contained 82.6% cyclohexane and 17.4% toluene had the switch from A to B taken place at 10.0mL. Overall it did not make that much of an impact. As predicted, fraction A was still not 100% cyclohexane. A taller fractionating column and possible multiple fractional distillations would have been needed to obtain a more complete separation.

A comparison of the head temperature versus distillate volume graphs in Figures 3 and 4 shows that fractional distillation is much more effective at isolating volatile organic liquids.

Figure 3 shows two plateaus where semi-pure cyclohexane and toluene were collected. Figure 4

shows several tiny plateaus, but no big plateaus. This indicates simple distillation did not isolate the two components with their unique boiling points but rather an infinite number of cyclohexane and toluene mixtures with an increasing percentage of toluene. This steadily increased the boiling point of the mixture and therefore the head temperature also rose steadily.

Finally, a comparison of the integrating techniques showed that the cut-and-weigh and isosceles triangle methods yielded relatively similar results as the GC's integrator. The cut-and-weigh method was least accurate when finding the mass of a small peak like peak 1 in fraction C. The cut-and-weigh method had a 5.6% error in fraction C and the triangle method had a 7.6% error in fraction A. When a rough proportion of components is needed, either the cut-and-weigh method or the isosceles triangle method would be equally suitable.

Answers to Assigned Questions: Page 128 (11)

11) At 50°C, the vapor pressures for methanol and ethanol are 406 and 222 Torr, respectively. Given a mixture at 50°C that contains 0.1mol methanol and 0.2mol of ethanol, compute the partial pressures of each liquid and the total pressure.

$$\text{Raoult's law} \\ P_{X\text{vapor}} = P_X^{\circ} N_{X\text{solution}}$$

$$P_{\text{methanol}}^{\circ} @ 50^{\circ}\text{C} = 406 \text{ Torr}$$

$$P_{\text{ethanol}}^{\circ} @ 50^{\circ}\text{C} = 222 \text{ Torr}$$

$$N_{\text{methanol}} = 0.1\text{mol methanol} / (0.1\text{mol methanol} + 0.2\text{mol ethanol}) = 0.33$$

$$N_{\text{ethanol}} = 0.2\text{mol ethanol} / (0.1\text{mol methanol} + 0.2\text{mol ethanol}) = 0.67$$

$$P_{\text{methanol}} = 406\text{Torr} \times 0.33 = 135\text{Torr}$$

$$P_{\text{ethanol}} = 222\text{Torr} \times 0.67 = 149\text{Torr}$$

$$P_{\text{total}} = 135\text{Torr} + 149\text{Torr} = 284\text{Torr}$$