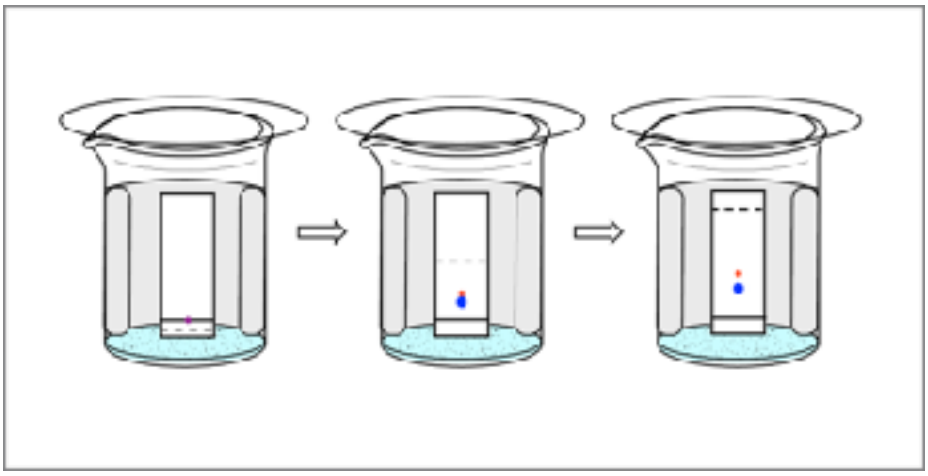
Thin Layer Chromatography

Determining the Composition of Unknown Compounds and Analyzing the Effect of Solvents on TLCs



Procedure:

As described in the Organic Chemistry Laboratory Manual on pages 17 to 19.

Data and Observations:

Part A: Identifying the components of an unknown mixture

Biphenyl: Transparent, colourless liquid with a mildly pleasant odour

Benzophenone: Transparent, colourless liquid with a faint odour

Unknown Sample (91): White, solid crystals

Dichloromethane: Transparent, colourless liquid with a faint odour

2:8 ethyl acetate and hexane (solvent): Transparent, colourless liquid with a mild odour

Part B: Effect of solvent on TLC

Ethyl acetate: Transparent, colourless liquid with an odour that ressembles nail polish remover

Hexane: Transparent, colourless liquid with a gas-like odour.

Part C: Ratio of compounds:

YY: Transparent, colourless liquid with a strong odour

9:1 Hexanes: Ethyl Acetates: Transparent, colourless liquid with a strong nail polish remover odour

(A) *ortho*-bromonitrobenzene: Transparent, colourless liquid

(B) *meta*-bromonitrobenzene: Transparent, colourless liquid with an unpleasant odour.

(C) *para*-bromonitrobenzene: transparent, yellow liquid with a faint odour

TLC:

Part A

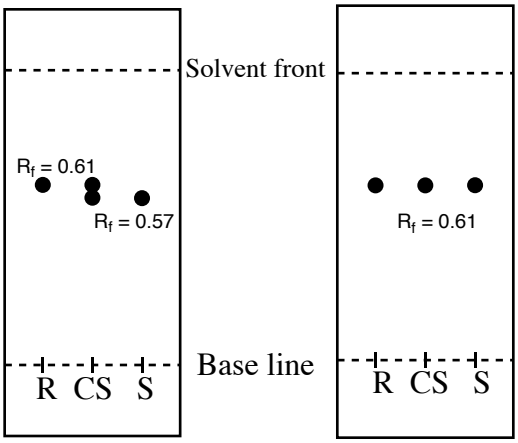


Figure 1:
Comparing 91 to biphenyl
R: reference - biphenyl
Co spot: reference + sample
Sample: unknown 91
Solvent System:
EtOAc : Hexanes 2:8

Figure 2:
Comparing 91 to benzophenone
R: reference - benzophenone
Co spot: reference + sample
Sample: unknown 91
Solvent System:
EtOAc : Hexanes 2:8

Table 1: R_f values for Part A

Spot number (left to right)	Figure 1	Figure 2
1	0.611	0.609
2	0.611	0.609
3	0.566	0.609
4	0.566	

Part B

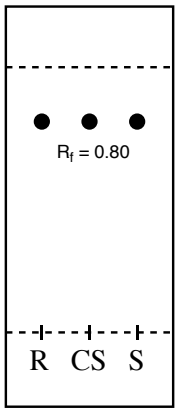


Figure 3:
biphenyl & a polar solvent
R: reference - biphenyl
Co spot: reference + sample
Sample: unknown 91
Solvent System:
EtOAc

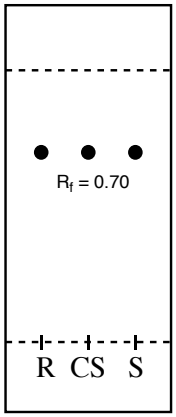


Figure 4:
benzophenone & a polar solvent
R: reference - benzophenone
Co spot: reference + sample
Sample: unknown 91
Solvent System:
EtOAc

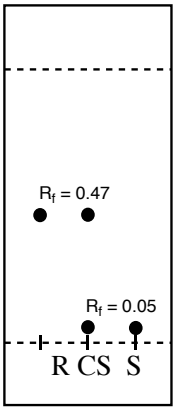


Figure 5:
$C_{12}H_{10}$ & a non polar solvent
R: reference - biphenyl
Co spot: reference + sample
Sample: unknown 91
Solvent System:
Hexanes

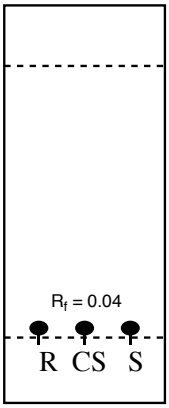


Figure 6:
$C_{13}H_{10}O$ & a non polar solvent
R: reference - benzophenone
Co spot: reference + sample
Sample: unknown 91
Solvent System:
Hexanes

Table 2: R_f values for Part B

Spot number (left to right)	Figure 3	Figure 4	Figure 5	Figure 6
1	0.795	0.698	0.467	0.035
2	0.795	0.698	0.467	0.035
3	0.795	0.698	0.054	0.035
4	–	–	0.051	–

Table 3: R_f values for Part C

Spot number (left to right & top to bottom)	Figure 7	Figure 8	Figure 9
1	0.641	0.847	0.722
2	0.844	0.777	0.722
3	0.641	0.653	0.569
4	0.844	0.347	0.722
5	0.641	0.777	0.569
6	–	0.653	–

Part C

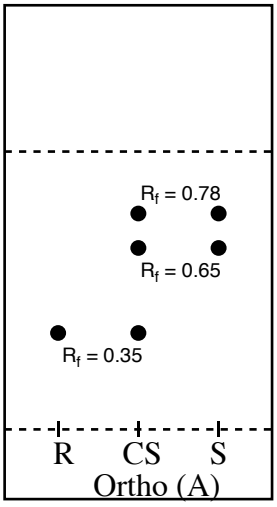


Figure 7:
Comparing YY to ortho
R: reference - *ortho*-bromonitrobenze
Co spot: reference + sample
Sample: unknown YY

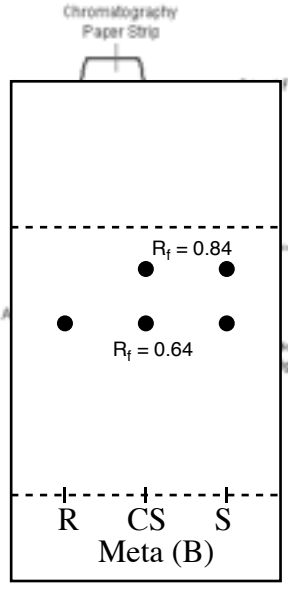


Figure 8:
Comparing YY to meta
R: reference - *meta*-bromonitrobenze
Co spot: reference + sample
Sample: unknown YY

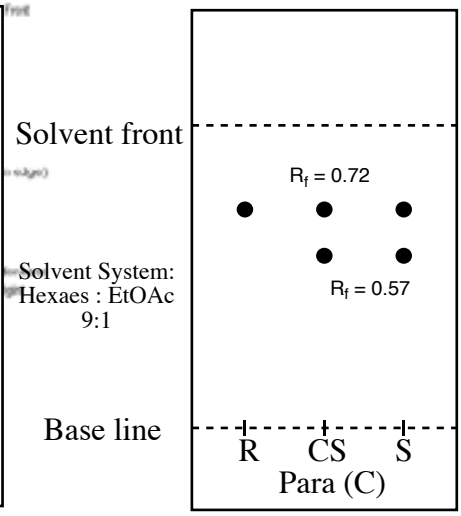


Figure 9:
Comparing YY to para
R: reference - *para*-bromonitrobenze
Co spot: reference + sample
Sample: unknown YY

Calculations:

Part A & B:

$R_f = [(a + b) / 2] \div d$

$R_f = [(3 + 2.5) / 2] \div 4.5$

$R_f = [(5.5) / 2] \div 4.5$

$R_f = [2.75] \div 4.5$

$R_f = 0.611$

Part C:

Absorbance (Meta) = 6464.037

Absorbance (Para) = 5523.128

% Absorbance (meta) = [(absorbance meta) ÷ (absorbance meta + absorbance para)] x 100

= [6464.037 ÷ (6464.037 + 5523.128)] x 100

= 53.9%

% Absorbance (para) = 100 - [% Absorbance (meta)]

= 100 - 53.9

= 46.1%

<u>Calculating the mole %</u>

y = 0.976x + 0.804

53.9 = 0.976x + 0.804

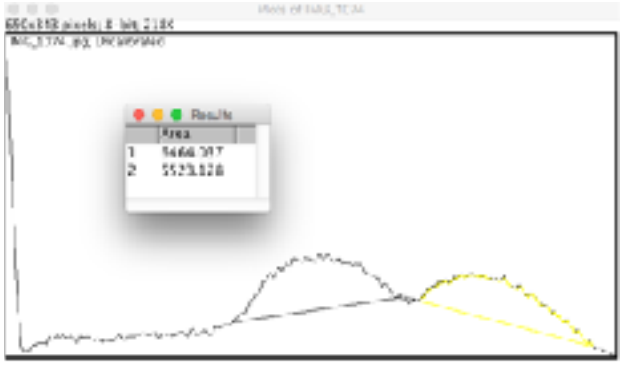
53.9 - 0.804 = 0.976x

53.096 ÷ 0.976 = x

54.4% = x (mole% meta)

100 - x = mole% para

100 - 54.4 = 45.6%



Discussion:

Part A—

The goal of this section was to identify the components of our unknown substance, #91. 10mg of the unknown sample 91 was mixed with 2mL of dichloromethane so that the sample would be in liquid form. Dichloromethane is widely used as a solvent in organic chemistry. Benzophenone was placed on the reference and co-spot of one TLC and biphenyl was placed on the reference and co-spot of the other TLC. The solution on the co-spot had to be placed last because we did not want to contaminate the capillary with the sample that was placed previously in the same spot. We had to include the reference spot so that we could compare the components of our sample to compounds we already knew. We placed the TLCs into a developing jar so that the mobile phase could draw the sample up towards the solvent front/the top of the TLC. The

polarity of the compounds is what causes them to stop at different phases on the silica gel. We had to mark the solvent front immediately upon removal because that line is important in determining the R_f value; if too much time passed, the line would disappear. We concluded that the unknown sample 91 was benzophenone because the R_f value was 0.609 for both the reference and the sample spot, and the spots formed a horizontal line across the TLC plate. The fact that the co-spot column showed only 1 dot means that the same compound, with the same polarity, was used for the reference and the sample. Consequently, the unknown sample 91 did not contain biphenyl because the sample had a R_f value of 0.566 and biphenyl had a R_f value of 0.611, which means the spot did not line up due to their difference in polarity.

Part B—

The objective of Part B was to identify how the polarity of a solvent can alter the R_f of the TLC. Ethyl acetate is a polar solvent so it was expected to interfere with the intermolecular forces between the silica gel and the sample, causing the spots to move closer to the top of the TLC plate. Hexanes is a less polar solvent so decreasing the polarity will decrease the distance that the compound will move on the silica gel. When the solvent was the polar ethyl acetate, the R_f values were larger: 0.795 for biphenyl and 0.698 for benzophenone and the spots were located close to the solvent front. With Hexanes, which is a non polar solvent, the R_f values were very small: 0.035 for benzophenone and when biphenyl was used the reference spot had a R_f value of 0.467 but the sample had a R_f value of 0.054 because the sample spot did not move at all. This means that benzophenone bonded to the silica gel instead, so there is no need for it to travel up the gel. Overall, the polarity of the solvent will have a large impact on the R_f.

Part C—

The purpose was to determine the components of another unknown sample: YY. This time 9:1 Hexanes: ethyl acetate was used because it had an optimal polarity for this solvent system. 3 different TLC plates were used because each one contained a different reference compound. After completing the experiment, it was determined that the unknown YY contained *meta*-bromonitrobenze and *para*-bromonitrobenze. We know this because the sample and reference spots lined up in both these cases and had the same R_f (table 3). On the *ortho*-bromonitrobenze TLC there was no dot in the sample column that corresponded to the reference dot. The polarity of each reference from least polar to most polar was *para*-bromonitrobenze, *meta*-bromonitrobenze, *ortho*-bromonitrobenze respectively. This can be identified by determining which solution moved further than the others on the TLC plate. The mole percentage ratio was required thus ImageJ was used to analyze the area under the curve (which was the distance each spot travelled with respect to the solvent front). With that information, we could calculate the %mole of *meta*-bromonitrobenze (54.4%) and *para*-bromonitrobenze (45.6%) in the unknown substance.

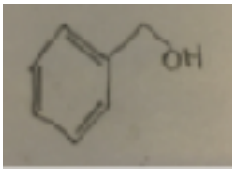
Sources of Error—

In this experiment, there were many chances for an error to occur, which would result in incorrect data. For instance, if too much solution was placed onto the TLC then the dots would smudge together and could not be recognized under the UV light. Also, if you pressed too hard on the silica or touched it with your fingers, it would cause the powder to move and/or fall off. When placing the solution onto the co-spot, it had do be done last because if not, the capillary

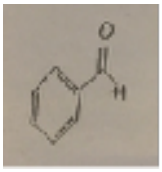
would touch the other liquid and contaminate the reference spot. It was easy to mix up the sample, biphenyl, and benzophenone solutions because they all had similar characteristics, so it was important to label everything. Finally, not drawing the solvent front immediately upon removal from the jar would alter you calculations for the R_f. To ease the process of this lab in the future, I will label all required the TLC plates in the beginning and do all the calculations at the very end.

Questions:

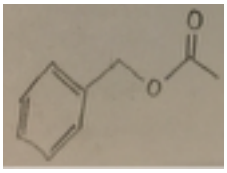
1. Increasing the polarity of the solvent system causes the results to be skewed. In a non polar solvent system, polar molecules will be near the baseline (e.g. figure 6) and non polar molecules will slowly move away from the baseline (e.g. figure 5). When the solvent system is very polar, both polar and non polar compounds will be significantly high on the TLC plate, closer to the solvent front; however, when you compare the R_f values, the non polar compound will have a larger value and thus be higher. The results depend on the polarity of the compound you are testing because polar compounds are strongly attracted to the silica, so they will move extremely slowly, if at all.
2. a) Benzyl alcohol would have the smallest R_f because it is the most polar of all the compounds listed, and can form the most hydrogen bonds.



Benzyl alcohol

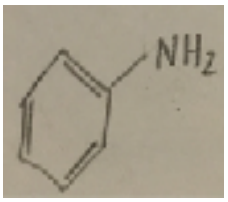


Benzaldehyde

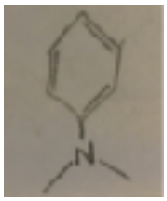


Benzyl acetate

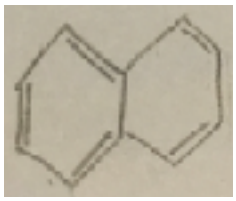
b) Aniline would have the smallest R_f because the NH_2 functional group can form more hydrogen bonds than N, N-dimethylaniline or naphthalene can, making it polar.



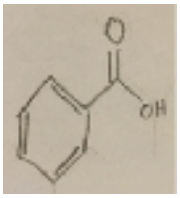
Aniline



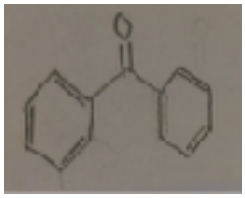
N, N-dimethylaniline


naphthalene

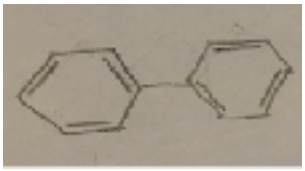
c) Benzoic acid would have the smallest R_f because it is the most polar. It would be attracted to the silica and therefore not move as far on the TLC plate.



Benzoic acid



Benzophenone


Biphenyl

Raw Data