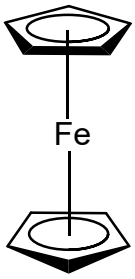
Column Chromatography: The Separation of an Unknown Mass Percentage Mixture of Ferrocene and Fluorenone and TLC Analysis

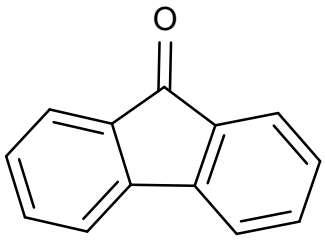
Experiment Modification: In this experiment, you will be separating the two compounds ferrocene and fluorenone. We will not be performing the experiment in the lab manual at all. However, you will still be responsible for the theory behind column chromatography that is in the lab manual (chapter 9, pp. 185 – 190), and the pre-lab exercise. *Your data table should revolve around this document, not the lab manual.*

Introduction: Ferrocene and fluorenone (figure 1) are aromatic compounds; the former has a relatively unique structure. Ferrocene is part of a class of compounds known as sandwich compounds. Organometallic (molecules that contain a carbon and a metal) compounds in which there are two aromatic groups (in this case, with two cyclopentadienes as the "bread") strongly bound by a transition metal (iron, in this example). These Lewis acid/base complexes are extremely stable; they can be stored in open atmosphere without noticeable decomposition. On the other hand, ferrocene is a fairly reactive aromatic species when exposed to highly reactive electrophiles, which you have not yet seen in lecture.

Figure 1. Structures of the sandwich compound ferrocene and the ketone fluorenone



Ferrocene



Fluorenone

Fluorenone is not nearly an interesting of a structure when compared to ferrocene; however, it has unique properties as well. Since aromatic stabilization has not yet been covered in lecture, we will not go into any further details about its reactivity or stabilization.

Prelab: You may either print out your prelab and bring it with you to lab, or bring your computer. Your TA will grade it on the spot before you begin the experiment. For the in lab observations, you may use scratch paper and record later in your ELN, or bring your computer and record directly in your ELN.

Postlab Report: Make sure to use the non-formal postlab report template on the course website!

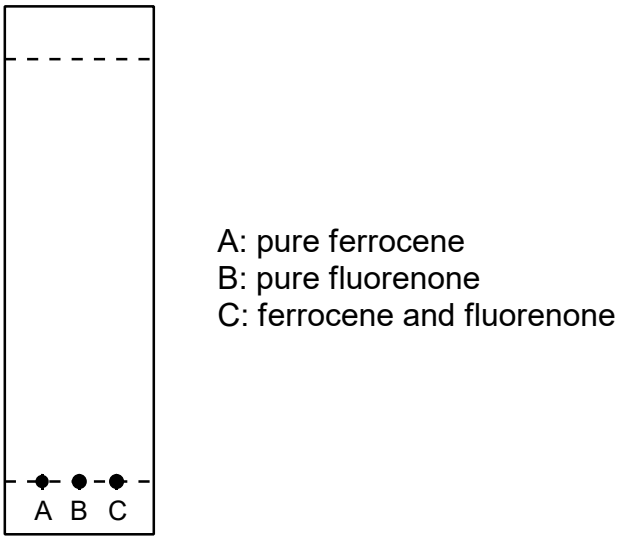
The Procedure: You must read **ALL** the sections in the lab manual, most importantly "Loading the Sample onto the Column" and "Running and Monitoring the Column."

Part 1. TLC Analysis of Pure Ferrocene and Fluorenone:

1. Obtain a small amount (~ 10 mg) of pure ferrocene and fluorenone.
2. Place each of your pure samples into two (2) test tubes.
3. You should now have two test tubes, each containing pure material.
4. Using your TLC technique skills, prepare a plate that will contain three lanes (figure 2).
5. In the first lane, spot pure ferrocene.
6. In the second lane, you should spot pure fluorenone.
7. The third lane is prepared as a co-spot (spots on top of each other).

   This is done because compounds sometimes run differently when they are together! To do this, spot ferrocene in lane 3, then spot fluorenone directly on top of the ferrocene spot in lane 3.

Figure 2. A TLC plate spotted with 3 lanes: Pure ferrocene, pure fluorenone and a mixture



8. Run the TLC plate in 100% hexanes and note how each spot moves. Record the R_f value of each spot in your lab notebook. Take a picture of this TLC plate to include in your final report.
9. Run another TLC plate (spotted identically) in 50% hexanes:diethyl ether and note how each spot moves. Record the R_f value of each spot in your lab notebook. Take a picture of this TLC plate to include in your final report.

Using your TLC plate, answer the following questions: (1) Which compound is more polar? (2) Which compound will elute first from a column?

Part 2. Packing the Column:

WARNING: NEVER LET THE COLUMN RUN DRY AFTER PACKING!

WARINING: THE SILICA GEL NEEDS TO BE LEVEL AFTER PACKING!

1. Due to the different polarities of the two compounds, we will switch the polarity of the solvents after the first compound has eluted (come off the column).
2. Obtain a vial of the unknown (by mass) of ferrocene and fluorenone from your instructor.

   Record the unknown number in your lab notebook.

3. First, check to make sure that your column stopcock does not leak. To do this, close the stopcock and put some hexanes into the column and observe the stopcock. If it leaks, take apart the pieces, clean, and reassemble.
4. Using a very small amount of cotton, push down into the neck using a capillary packing tube (do not pack the cotton, only push into the neck lightly).
5. Add sand to about 0.5 cm high.
6. Fill the column 2/3 full of pure hexanes.
7. Next, ***slowly*** add silica gel through the plastic funnel while tapping on the column with a rubber stopper. Let the silica gel settle and repeat until a height of ~ 10-12 cm is obtained.

   Note: *It is extremely important that this process is done slowly. If done too fast, you'll get air bubbles, which leads to poor separation of your compounds.*

   Note: *You can drain some solvent if it gets too high while you are adding silica; however, do not let the column run dry (always keep silica gel below solvent level).*

   Note: *The silica gel needs to be as level as possible. If it is not, tap the column with a rubber stopper to level it.*

Part 3. Loading the Column:

1. Weigh out approximately 200 mg of your unknown. Add to a test tube and lightly crush with a spatula, being careful not to puncture through the bottom of the tube.
2. To your weighed out unknown, add dichloromethane (DCM) drop by drop until it dissolves. You will use about 0.5 mL or so.

   You must use a minimum amount of DCM, otherwise you will get poor separation!

3. Drain your column just until the top of the level of the silica gel and immediately proceed to the next step! **Do NOT close the stopcock!**
4. With the stopcock open, slowly add your sample onto the column (loading) using a disposable pipet.

Keep the pipet vertical to avoid your sample squirting out of the pipet.

Drain the level of your now loaded sample solution to the level of the silica.

5. Add a small amount of pure hexanes (8-10 drops) to the top of the column, as close as you can get to the silica gel without actually touching it. Repeat this process 2 more times.

   If crystals form when you add hexanes, add a drop of dichloromethane.

6. Again, **add enough solvent** with your pipet as close as you can get to the silica gel without actually touching it **to a level of about 1 cm**.

7. Next, slowly add sand and let it settle to a level of 4-5 mm.

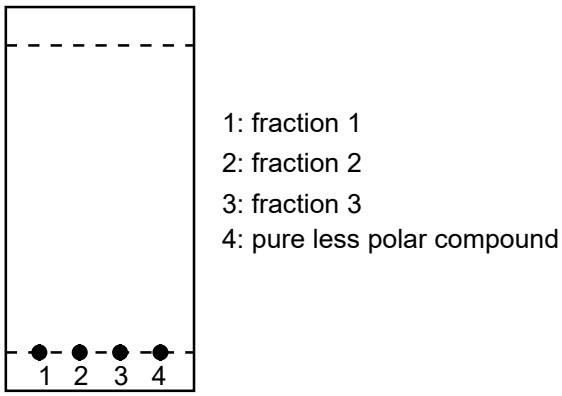
   The sand does not have to be level; it is merely there to protect the silica gel from becoming unlevel.

8. Start collecting fractions (3-4 mL) in your test tubes while running the column in pure hexanes.
9. Run TLC plates of each fraction. You can fit 3 fractions per TLC plate. As a reference, spot the compound (ferrocene or fluorenone) that you deemed less polar (figure 3).

   In an ideal world, you would see all of the non-polar compound completely elute.

   You must spot every fraction to make sure all the non-polar compound has eluted.

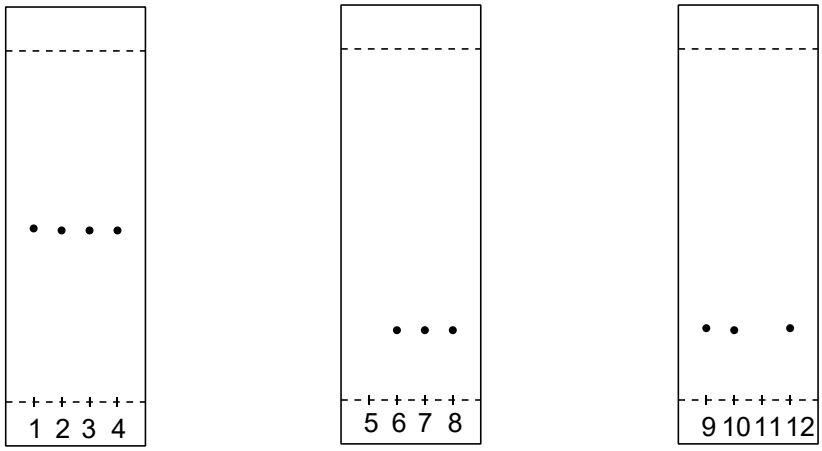
Figure 3. A TLC plate that monitors the columns progress



10. When all of the "top spot" has come off, change the solvent polarity to 50:50 hexanes:diethyl ether.
11. Collect fractions as before, and TLC these with the appropriate reference (more polar) known compound.

12. See figure 4 for a properly run column. Note that both fractions 5 and 11 do not show a spot! This is because we were patient and let all the non-polar compound elute, switched the solvent and let all of the more polar compound elute.

Figure 4. An ideal column separation. Note: The R_f values are NOT of ferrocene or fluorenone.



1: fraction 1
2: fraction 2
3: fraction 3
4: less polar pure

5: fraction 5
6: fraction 6
7: fraction 7
8: more polar pure

9: fraction 9
10 fraction 10
11: fraction 11
12: more polar pure

13. **Also note that this figure is a representative example of a column separation. The R_f values are not those of the compounds that you are separating, neither is the number of fractions shown.**
14. Once you have ascertained what compounds are in what fractions, combine the like fractions into **ONE VESSEL THAT YOU HAVE MASSED** and recorded in your notebook and leave in your drawer for the next lab period.

Do not speed up the evaporation by heating. Ferrocene sublimes.

Stop here for this week!

15. The solvent should be evaporated at this point.
16. Obtain the mass of each of your flasks.
17. Obtain the mass of each of your recovered pure ferrocene and fluorenone.
18. Determine the weight percent of ferrocene of your original unknown mixture using equation 1. Determine the percent of fluorenone in your original mixture, as well.

$$\%\ ferrocene\ = \left(\frac{mass\ of\ recovered\ ferrocene}{total\ mass\ of\ recovered\ solids}\right) * 100\% \qquad (\mathbf{1})$$

Post-lab Report Requirements:

1. Your TLC plates (a picture) from part 1 and 2 must ALL be included and submitted with your report.

Answer the post-lab questions below:

2. Explain how each of the following would affect the column separation:
    a. Starting the column in 100% diethyl ether.
    b. Collecting fractions which are too large a volume.
    c. You turn around just for a minute and your column has run dry.
3. How was TLC used in this experiment? What did it help us determine?
4. What is meant by an eluant or mobile phase? A stationary phase?