

The position of the resulting colored spot on the paper can be measured and the  $R_f$  value of the phenol calculated. Also, since different phenols form different colored dyes, the color of the spot also aids in identifying the phenol. A disadvantage of this procedure, however, is that the original phenol is destroyed (changed to an azo compound) and cannot be recovered.

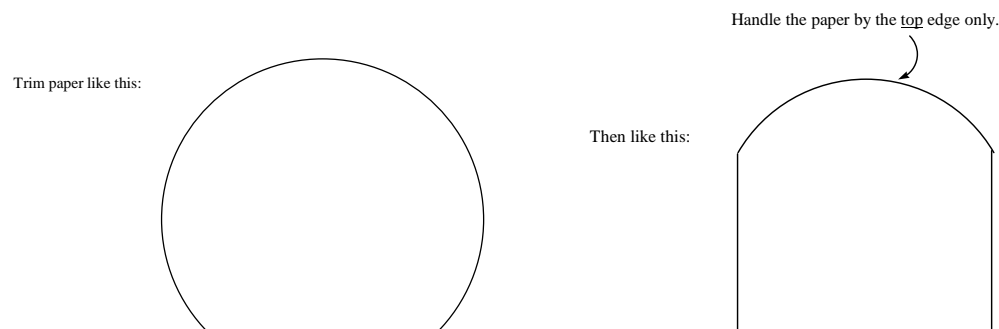
### Safety

• Observe the general safety precautions outlined in the section titled **SAFETY in the ORGANIC LAB**. In addition to the general safety precautions the special safety precautions for this specific experiment are as follows:

- Chloroform is toxic and can enter the body by inhalation of the vapor or by absorption through intact skin. Work in a well-ventilated area. Wash up any spills on the bench or on yourself with soap and water.
- Acetic acid is corrosive and its vapor is very irritating to the eyes and nose. Work in a well-ventilated area. Wash up any spills on the bench or on yourself with soap and water.
- *p*-nitroaniline is a very toxic material. It can enter the body by inhalation of the finely divided solid or by absorption through intact skin. Work in a well-ventilated area. Any material spilled on the bench or on yourself should be washed away with soap and water.
- Concentrated sulfuric acid is a strong acid and is a very corrosive material. It causes very severe burns when it comes into contact with the body. Any material spilled on the bench should be neutralized with aqueous  $\text{NaHCO}_3$  and wiped up. Any material spilled on yourself should be immediately washed away with a large quantity of cold water at the sink or under the safety shower.
- Sodium nitrite is toxic. Its solutions should be handled with care.
- Ethanol and ethyl acetate are flammable. There should be **absolutely no flames** in the laboratory while ethanol and or ethyl acetate is/are being used.

### Procedure

1. Mix 40 mL of chloroform, 40 mL of acetic acid and 20 mL of water in a separatory funnel. Shake the mixture well then let the layers separate. Draw off the organic layer into a 250-mL Erlenmeyer flask and keep the flask under your personal hood. Discard the aqueous layer.
2. Secure an 18 ½ cm circle of Whatman #1 filter paper and trim it as shown below:



3. Draw a line parallel to, and about  $\frac{1}{2}$  inch from, the bottom of the paper. Equally space seven x-marks on the line and write below the x-marks their identifying numbers/letter as follows: 1, 2, 3, 4, 5, 6, M. Make sure to note your unknown number in your lab notebook. *[As always, when using paper chromatography, the marks must be made lightly, with a pencil.]*
4. Spot each phenol (as a 1% solution in ether) on its numbered spot and your unknown mixture on the spot marked "M" using capillary tubes.
5. Roll the paper into a cylinder and use two staples (close to top and bottom) to hold the two edges about one-eighth of an inch apart. Make sure that the edges do not overlap or touch each other.
6. Pour some of the organic layer from step 1 into a clean, dry, 1000-mL beaker so that the liquid level will be below the starting line of the chromatography paper you prepared in step 3 above.
7. After the spots have dried, carefully place the paper cylinder in the beaker with the solvent and cover the beaker as tightly as possible with a sheet of paper. Keep the beaker under your personal hood area.
8. Allow the chromatography to proceed undisturbed for at least 50 minutes. During this time prepare the *p*-nitrobenzenediazonium salt solution described below.
9. *Steps 9-15 are to be carried out in pairs.* In a small beaker weigh out 0.03 mole of *p*-nitroaniline.
10. In a 125-mL Erlenmeyer flask mix 25 mL of water with 6 mL of concentrated sulfuric acid. Add the *p*-nitroaniline from step 9 to this acid solution.
11. Set the hot plate heater knob to about 5-6 and heat the mixture to effect solution for about 15 minutes.
12. Then place reaction flask in an ice-water bath to cool the content to below 10°C.
13. Slowly add 25 mL of aqueous 1.5 M sodium nitrite solution (0.0375 moles) to the mixture, a small aliquot at a time, keeping the solution temperature below 10°C.
14. Using a stir bar stir the cooled solution for 5 minutes and then filter it into another cold Erlenmeyer flask to remove any remaining solid.
15. Divide the filtrate, *p*-nitrobenzenediazonium hydrogen sulfate solution, into three equal parts and keep each third in a large test tube in an ice-water bath until needed.
16. After 50 minutes have elapsed, quickly mark the position of the solvent front then remove the chromatography paper cylinder from the beaker. Carefully remove the staples and lay the chromatogram on a three-fold paper towel keeping it under your personal hood. Allow the paper to dry for 5-10 minutes.
17. Your instructor will collect one third of the diazonium salt solution that you prepared above and will use it to spray your paper chromatogram thus developing your chromatogram. Take your chromatogram to the spraying area and let your instructor spray your chromatography paper.
18. Keep your chromatogram on a paper towel under your personal hood. Describe the colored spots as best you can. Determine the  $R_f$  value for each of the phenols listed above and present them in a tabular form. Report the phenol(s) present in your unknown mixture by their common name(s).

### ***B) Synthesis via diazonium salt***

1. In a 600-mL beaker, dissolve 0.030 mole of potassium iodide in 50 mL of water.
2. Stir the solution at room temperature while adding, over a period of ten minutes, one of the one-third portions of the diazonium salt solution you made earlier.
3. Allow the reaction mixture to stand with occasional stirring for ten minutes then add 100 mL of water. Separate the crude product using suction filtration and wash the crude product twice with cold water. Recrystallize from ethyl acetate/ethanol solvent mixture.
4. Place the recrystallized product in a pre-weighed plastic boat and allow your product to dry in your drawer until the next lab session.
5. Properly label your product and determine the actual yield, % yield, etc. Characterize your product by its melting point and by spectrometric methods as requested by your instructor. Turn in the product as instructed.

### ***Disposal/Cleanup***

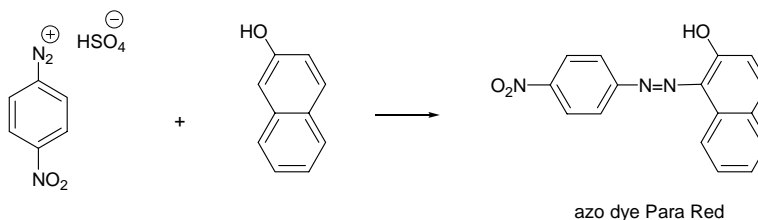
- *Dispose of the chromatography and reaction solutions and aqueous washes in the sink.*
- *Wash all glassware thoroughly with water, soap water and rinse them with plenty of water.*

### ***Questions***

#### ***Before lab (BL)***

***BL #1:*** Draw the structures of azo dyes that might form when THC, CBN, and CBD react with *p*-nitrobenzenediazonium chloride.

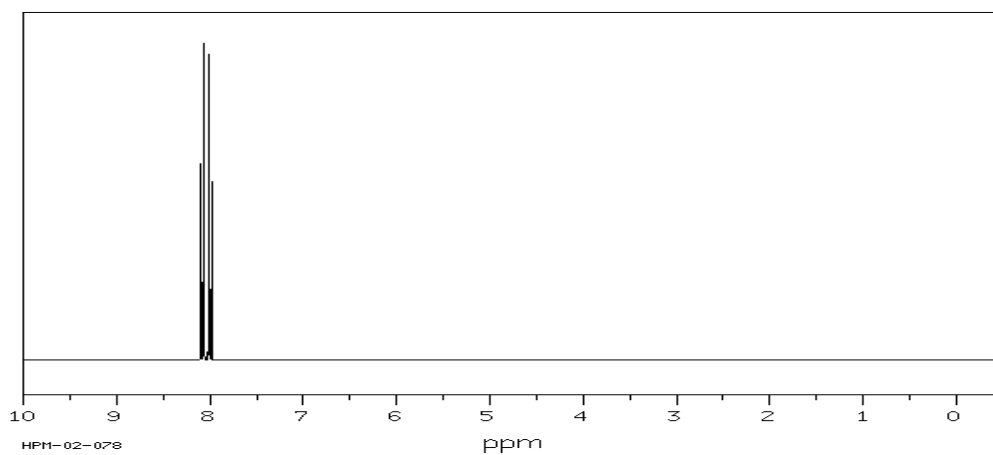
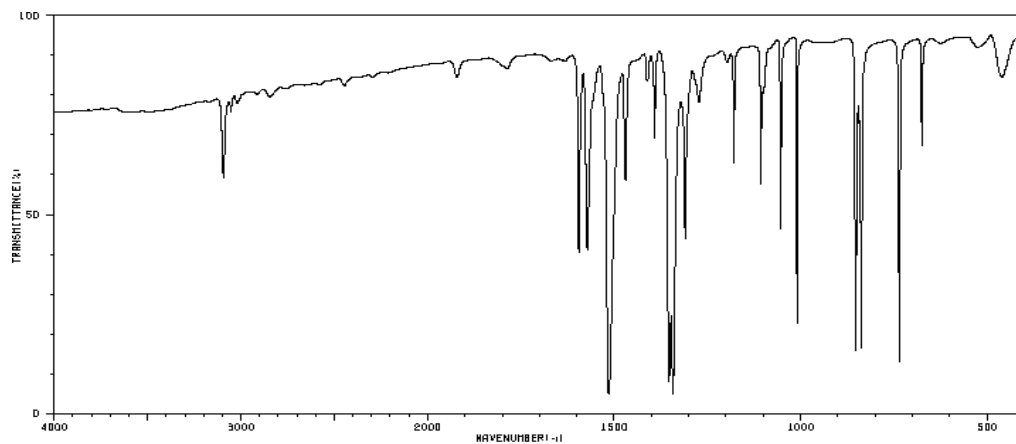
***BL #2:*** The coupling reaction between *p*-nitrobenzenediazonium hydrogen sulfate and 2-naphthol is shown below:



Write the corresponding diazo coupling reaction for the five remaining hydroxybenzenes listed above.

#### ***After lab (AL)***

***AL #1:*** Below are the IR and NMR spectra for the compound prepared in this experiment. Analyze each spectrum by noting beside as many peaks as you can the molecular feature which gives rise to that peak.



**AL #2:** Compare the spectrum (spectra) of your product to the reference spectra shown above.