

This experiment is not spelled out in as much detail as previous experiments. It requires careful preparation and careful lab technique. The notes below are basically changes and suggestions, NOT a detailed procedure. Specifics will be found in the lab text. You will prepare your detailed prelab will be prepared based on this handout and on the lab text.

This experiment combines techniques learned in previous experiments (recrystallization, MP) with a new technique: extraction. The separation is based on the acid/base properties of the substances in the mixture. To understand the principles behind the separation, it is essential that you understand the acid/base chemistry involved and why each species is soluble or insoluble in each layer (see p. 143). To help you with this, write out a flow diagram such as the one found on p. 142 and include your diagram as part of your prelab outline. Also, as part of your prelab outline, calculate the amount of concentrated HCl needed to neutralize 1.15 mL of saturated sodium bicarbonate and the amount of concentrated HCl needed to neutralize 1.0 mL of 3 M NaOH (concentrated HCl = 12 M, sat'd NaHCO<sub>3</sub> = 1 M).

In this lab, you will separate a mixture of three unknown components (one from each class) by extraction, purify the separate components by recrystallization, and identify the unknowns by MP.

**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!**

**Table 1. Possible unknowns**

Compound Type	Name (MP in °C)	Name (MP in °C)	Name (MP in °C)	Name (MP in °C)
Carboxylic Acid	3-toluic acid (112)	benzoic acid (122)	2-chlorobenzoic acid (142)	salicylic acid (159)
Phenols	4-bromophenol (66)	4- <i>tert</i> -butylphenol (101)	2-naphthol (123)	
Neutral Compound	vanillin (81)	benzyl (96)	<i>trans</i> -stilbene (125)	benzoin (133)

You are given ample time (2 lab periods) in which to finish this experiment. Each of you will work at a different pace. Think carefully about each step and don't rush. Label the tubes carefully so as not to mix them up. Do not think of the tubes as tube 1 and tube 2 as in the book. Instead, think of what chemical species is in each tube, why it is soluble in that solvent, and what each operation accomplishes. This will help you to better understand what you are doing and why, and help to decrease the possibility of error. The quantity of each component is small (~60 mg) so you must use care in doing manipulations such as transferring solutions from one vessel to another, recrystallizing, and removing crystals from reaction tubes. During the first week, you should at least isolate the three separate crude products. Many of you will even be able to recrystallize one or more of the crude products. Anything recrystallized from water or a solvent mixture containing water must be left to dry overnight, after which weights and MPs can be determined and % recoveries calculated.

In separating layers in a micro scale extraction, always remove the lower layer from the upper layer with a pipet, and transfer the lower layer to another tube. Never try to separate the upper layer from the lower layer - it is very difficult to get a clean and complete separation in this way (backwashing is an exception). In an extraction such as this one, it is important to keep track of the different solutions from the different separations. Label all tubes carefully and know exactly what species is in each tube and which layer is which. What physical property of the solvents determines which layer will be on top? A careful chemist does not throw anything away until they are certain of its identity. In extractions, it is important to mix the two solvents well. On the micro scale, this can be accomplished by drawing a portion of the lower layer up into the pipet and expelling it forcefully but carefully, back into the upper layer repeatedly for about three minutes.

Measure about 0.18 g ( $\pm$  0.01 g), but weigh it exactly. The organic solvent will be *tert*-butyl methyl ether.

Near the top of p. 146: as the ether solution (sol'n) is drying over calcium chloride, start the process explained in the next paragraph. As long as the tube is well stoppered, the sol'n can dry for longer than 5-10 minutes. In neutralizing the aqueous layer with concentrated HCl, be sure to mix the sol'n well after each addition of acid by stirring it well with a stirring rod or mixing and stirring with a pipet. Allow a moment for the neutralization to occur and for the product to precipitate. Be sure to add enough HCl and to mix well. If precipitate does not form, add a little extra HCl and mix well to be sure that the sol'n is

acidic. A common problem is not adding enough HCl or not mixing well, in which case, the yield of product would be decreased. Repeat this neutralization procedure for the tube containing the phenol salt (next paragraph, "In exactly the same way ...").

Now back to the ether layer that has been drying over calcium chloride: after the ether solution has been separated from the drying agent and transferred to a clean dry reaction tube, rinse the calcium chloride with a small amount of fresh ether and transfer this to the main ether layer. This helps to ensure that no neutral compound has been left behind with the drying agent. This is standard practice when transferring from one vessel to another – call it a transfer rinse. To evaporate ether from the neutral substance, pass a GENTLE stream of air over the sol'n in the hood and warm the tube with your hand, not with a warm water bath as described in the book. Be careful not to blow the sol'n out of the tube.

The neutral compound is recrystallized from ligroin (= hexanes). As with any recrystallization of an unknown, the amount of solvent to use is the minimum that dissolves it at the boiling point. More solvent than needed results in a reduced yield.

Report the % recovery of each compound and identify each based on MP. It is not necessary to save the compounds in a plastic bag, but save them until your TA has checked them. If you have time run a TLC analysis on the original mixture.

**CAUTION:** remember that when using the vacuum, always use a trap and clamp the filter flask securely to prevent it from tipping over.

**WASTE DISPOSAL:** Combine all acidic and other aqueous layers, washes, and filtrates and put them into the container labeled "Acidic Aqueous Solutions" in the waste hood. Do not place any organic solvents, including acetone rinses, into the aqueous acidic waste container. Put all other liquid wastes into the Nonhalogenated Liquid Waste bottle in the waste hood. Put the calcium chloride drying agent into the labeled evaporating dish in the waste hood. When finished with the products, after your TA has inspected them, place them in the Solid Waste container in the hood.

**BEFORE YOU LEAVE THE LAB:** turn off your hot plate and all other utilities, put away your equipment, clean up your work areas, close the fume hood sash completely and ask your TA for their signature. In general, please try to keep the lab as good condition as you found it. If you see caps off of bottles, replace the caps. If you see spilled chemicals, clean them up or at least report it to your TA.

### Postlab Questions

- 1.) Highly explosive peroxides form when certain ethers react with oxygen. What difference in structure makes *tert*-butyl methyl ether less prone than diethyl ether to peroxide formation (see pp. 30-32)?
- 2.) Extraction is commonly used in the isolation of reaction products. Which would lead to a better yield: extraction with one 6 mL portion of solvent or three 2 mL portions?
- 3.) If the carboxylic acid in the mixture were benzoic acid, how many moles of benzoic acid are present (assume it is 1/3 of the mixture)? How many moles of sodium bicarbonate are contained in 1 mL of an 8% aqueous solution? (See the inside back cover of the text to obtain concentration information.) Is the amount of sodium bicarbonate sufficient to react with all of the benzoic acid?
- 4.) To isolate the benzoic acid from the bicarbonate solution, it is acidified with concentrated HCl in Experiment 1. What volume of acid is required to neutralize the bicarbonate? (See the inside back cover of the text to obtain concentration information.)
- 5.) What would result if the mixture had been extracted with NaOH before extracting with bicarbonate?