



## CH 2270/2290

**Extraction: A Separation and Isolation Technique** (Adapted from *Laboratory Manual* to Accompany *Organic Chemistry: A Short Course*, H. Hart, L. E. Craine, D. J. Hart, and T.K. Vinod 12th ed. Houghton-Mifflin, Boston, 2007.)

### Materials

From the Chemicals Hood:		From the Stockroom (Blue Bin)
<b>Week 1:</b> Unknowns A – F Diethyl ether Calcium chloride 10% hydrochloric acid aqueous solution (3 M) 10% sodium hydroxide aqueous solution Concentrated hydrochloric acid Brine Sodium bicarbonate aqueous solution (squirt bottle)	<b>Week 2:</b> <i>m</i> -nitroaniline <i>p</i> -toluidine <i>p</i> -chloroaniline benzoic acid 2-naphthol <i>trans</i> -cinnamic acid naphthalene biphenyl <i>p</i> -dichlorobenzene	<b>Week 1:</b> Separatory funnel with stopcock  Glass stopper 

An excellent video to review before lab is found on the Massachusetts Institute of Technology's "OpenCourseWare":

<http://ocw.mit.edu/resources/res-5-0001-digital-lab-techniques-manual-spring-2007/videos/reaction-work-up-i/>  
or <https://www.youtube.com/watch?v=DmvaOb1xb1o>

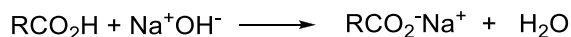
In synthesis, the desired product must be separated from the by-products, excess reactants, impurities, and other substances that may be present in the reaction mixture. Similarly, substances in nature are always mixed with other substances. **Extraction** is the most common technique used to separate a desired organic product from a reaction mixture or to isolate an organic substance from its natural source.

### General Principles

An extraction solvent must readily dissolve the substance to be extracted, yet it must be only sparingly soluble in the solvent from which the desired substance is to be extracted. Also, it should extract only the desired substance or as small an amount as possible of any other substance present; it should not react chemically with the solute in an undesirable way, and it should be easily separated from the desired solute after extraction. This last requirement can be met if the solvent is low-boiling and easily removed by distillation.

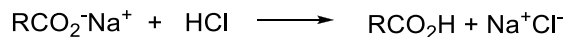
Common organic solvents that fulfill these requirements include many hydrocarbons and their chloro derivatives. Diethyl ether is another common extraction solvent, but care is necessary. Diethyl ether (usually referred to simply as ether) is highly flammable. Furthermore, ether is slightly water-soluble (about 7g/100 mL). Nevertheless, because most organic compounds are highly soluble in it and because of its low boiling point (35°C), ether is frequently used despite its drawbacks.

Sometimes we can use desirable, easily reversed chemical reactions such as acid-base reactions to effect separations by extraction. For example, dilute sodium hydroxide (an inorganic base) converts organic acids to their sodium salts:



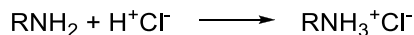
Although a particular acid may not be soluble in water, its more polar sodium salt usually is. When a mixture of a neutral compound and an acidic, water-insoluble compound in an organic solvent is shaken

with dilute aqueous sodium hydroxide, the acid is converted to its sodium salt, which dissolves in the aqueous layer, and the neutral compound remains in the organic layer. After the layers are separated, the acid is recovered by acidifying the aqueous layer with a strong acid.

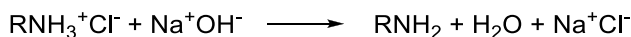


Thus acids can easily be separated from neutral (or basic) contaminants by extraction with aqueous alkali (base).

Dilute aqueous acid can be used to extract basic compounds, particularly amines, from neutral or acidic substances by converting them to water-soluble alkylammonium salts:



After separating the organic and aqueous layers, we can recover the amine from the aqueous layer by making the solution alkaline with a strong base.



In this experiment we will apply these ideas in order to separate a three-component mixture of organic compounds by extraction.

## Use of the Separatory Funnel

Extractions are usually performed with a separatory funnel. Improperly handled, this moderately expensive piece of glassware is easily broken. Always follow proper handling technique.

Support the funnel in an iron ring. Be sure the ring is small enough to support your funnel. Close the stopcock, and add the liquids to be separated. Maybe *use a funnel*. Insert the stopper and invert the funnel, *being sure to hold the stopper in one hand and the stopcock in with the other*. Then with the barrel pointed up and away from you and from anyone else in the vicinity, slowly open the stopcock. This will relieve any pressure that may have built up inside the funnel. Pressure buildup is quite common when volatile solvents such as ether are used because the vapor pressure of the solvent adds to the atmospheric pressure already present. This situation is further aggravated when the funnel is warmed by the heat of your hands or when a gas is generated during the extraction, as happens when an ether solution of an acid is extracted with sodium bicarbonate.

After the pressure is released, close the stopcock, shake the funnel gently two or three times, and again invert the funnel and release the pressure by opening the stopcock. Repeat this process until the pressure buildup is slight. Then shake the contents vigorously to complete the extraction.

Replace the funnel in the iron ring and *remove the stopper immediately*. Place the stopper on a clean watch glass on the bench top. Allow the funnel to stand until the layers separate cleanly. Then slowly draw off the lower layer through the stopcock into a flask or beaker of appropriate size. As the boundary between the two layers approaches the stopcock, slow the flow. Close the stopcock just as the upper layer enters the stopcock bore. If the upper layer is to be transferred to another vessel, pour it out *through the top of the funnel*. *Do not run the upper layer through the stopcock*.

The relative positions of the aqueous and organic layers in the separatory funnel depend on their densities. *The more dense solvent forms the lower layer*. Hydrocarbons and ether are less dense than water, whereas chlorinated hydrocarbons are *more* dense than water. If you have any doubt about which is

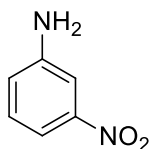
the organic layer and which is the aqueous (water) layer, withdraw a few drops of the lower layer into 0.5-1.0 mL of water in a test tube. If the lower layer liquid dissolves in water, it is the aqueous layer. If the lower layer doesn't dissolve, it is not the aqueous layer. The layer may sink to the bottom, float on top, do both, or even turn the water cloudy. It will not, however, dissolve.

Sometimes, especially with alkaline solution, it is difficult to obtain a sharp separation of layers because an emulsion has formed. Gentle swirling of the funnel in a near-upright position, gentle stirring with a glass rod, and addition of salt to the aqueous layer may overcome this difficulty. If you add salt to a separatory funnel, don't add so much that it clogs up the stopcock!

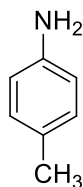
### Separation of a Three-Component Mixture by Extraction

A mixture of a base, an acid, and a neutral substance will be separated into its components by extraction.

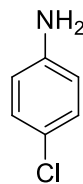
#### **BASE**



*meta*-nitroaniline  
mp 111-114 °C

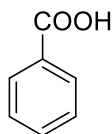


*para*-toluidine  
mp 41-46 °C

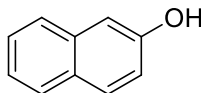


*para*-chloroaniline  
mp 69-73 °C

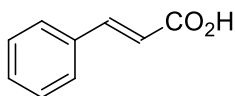
#### **ACID**



benzoic acid  
mp 121-122 °C

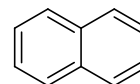


2-naphthol  
mp 121-123 °C

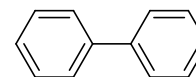


*trans*-cinnamic acid  
mp 131-136 °C

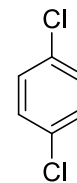
#### **NEUTRAL**



naphthalene  
mp 79-82 °C



biphenyl  
mp 69-72 °C



*para*-dichlorobenzene  
mp 52-56 °C

Your mixture will contain one of the acids, one of the bases, and one of the neutral compounds. You will identify the components by their melting points.

**Caution** Ether is highly flammable: no hot plates are allowed to be used in the laboratory when this experiment is being performed. If any solutions are to be heated, use a steam bath.

## Procedure

Obtain a 1.5 g sample of the three-component mixture (in the balance room) and dissolve it in 20 mL of ether (in the hood) in a beaker. Make sure the stopcock for the separatory funnel (from the stockroom) is closed, then pour the solution through your long-stem funnel into the separatory funnel. To extract the basic component from the mixture, add a solution of 14 mL of 10% hydrochloric acid (3 M HCl) (in the hood) and shake thoroughly using proper technique (see above). Draw off the lower (aqueous) layer into a 125 mL Erlenmeyer flask and repeat the extraction two more times, each time with 14 mL of 10% HCl. Do NOT add more of the solid mixture or diethyl ether! Just add more acid to the separatory funnel. Finally, extract with 5 mL of water to remove excess hydrochloric acid that may be dissolved in the ether layer. Combine the three acid extracts with the water extract and set them aside. (It is likely that some of the ether would have evaporated off, due to its low boiling point, during the extractions and may require replenishment).

To separate the acidic component from the mixture, extract the remaining ether solution three times with 14 mL of 10% aqueous sodium hydroxide and once with 5 mL of water. Combine the alkaline and water layers and set them aside. (It is likely that some of the ether would have evaporated off during the extractions and may require replenishment).

Pour out the remaining ether solution (which should contain only the neutral component) through the top of the separatory funnel into a small Erlenmeyer flask. Add enough anhydrous magnesium sulfate (from the hood) to cover the bottom of the small Erlenmeyer flask, and swirl the mixture occasionally for 5 min. Then decant the ether into a small Erlenmeyer flask of known weight (**YOU** have to weigh it!). Rinse the flask contents with a small amount (~3 ml) of ether, and add the rinsing to the Erlenmeyer flask. Then place the flask on a steam bath in the hood. Use a wooden stick to facilitate boiling. Once boiling is complete (you no longer see bubbles from evaporation), cover the Erlenmeyer flask with Parafilm and allow the product to air-dry until next period, then weigh it and determine its melting point.

Place the combined acidic extracts in an ice bath and neutralize by cautiously adding 10% aqueous sodium hydroxide 10 mL at a time until a precipitate forms and the solution is alkaline to pH paper (side shelf) (the proper way to test with litmus paper is to dip a clean glass rod into the solution and then touch it to the pH paper. This method prevents sample contamination. Rinse the glass rod with water between tests). Vacuum filter the solid and save it for melting point analysis next period.

Place the combined alkaline extracts in an ice bath and neutralize by adding concentrated hydrochloric acid one pipetful at a time (with a plastic pipet from the hood) until a precipitate forms and the solution is acidic to pH paper. Recover the precipitated acidic component by vacuum filtration using a Buchner funnel. Allow the product to air-dry until next period, then weigh it, and determine its melting point.

Calculate the percent yield for each component you recovered, assuming your 1.5 g mixture was an even distribution of 0.5 g of each component.

Identify each component you isolated from the mixture. Each compound extracted should be a pure product with a sharp melting point. If you are unsure of the identity of any of your components, there will be “authentic” samples of all nine compounds available for comparison; perform a mixed melting point analysis to confirm your identity and check with your TA.

## Waste Disposal

Pour the basic and acidic aqueous filtrates, respectively, into “basic waste” and “acidic waste” bottles in the hood.