

Fractional Distillation

Distillation is the most common separation method used when purifying liquid organic samples. It is widely used in both industrial and research applications. Distillation separates components of a mixture based on the differences in boiling points of the pure components. The closer the boiling points are to each other, the more difficult the separation. This experiment will begin with a mixture of two liquid esters and via distillation these will be separated into two different fractions. The boiling point ranges of each component will be obtained. The better the separation, the closer these boiling point ranges will be to the literature value of the pure material. The separate fractions will be analyzed by either gas chromatography (GC) or index of refraction (RI) to determine the composition and assess the quality of the separation.

Pre-Experiment Assignment

Study this chapter of the manual and the notes on the Chemistry Department web site. Do the first 7 parts of your notebook write-up.

A student who has prepared for the Fractional Distillation experiment should be able to:

1. Perform all of the tasks listed under the Boiling Point and Index of Refraction experiment.
2. Understand basic theory of chromatographic separation including partitioning between mobile and stationary phases.
3. Define, and explain the difference between, simple and fractional distillation.
4. Define, recognize, and explain: reflux, theoretical plates, azeotrope.
5. Give a drawing of, and identify the components from a drawing of, the apparatus used for simple and fractional distillation. Give the function of the components, and predict the consequences of improper assembly and use (including thermometer bulb placement, distilling to dryness, use of boiling stones and closed systems).
6. Draw the structure given the name, or give the name from the structure, of the compounds used in the day's experiment, and give the role of each (reactant, solvent, catalyst, etc.).
7. Identify and explain safety considerations for this experiment.
8. Perform the day's experiment safely and successfully.

Quizzes given after the experiment has been performed may also include:

9. Predict results of experiments using simple, fractional, and vacuum distillation, and decide which of the three is best for a given sample from the necessary data about the sample.

10. Draw and interpret distillation curves; for example, determine boiling points and distinguish between simple and fractional distillation from these curves.
11. Understand composition of sample based on index of refraction or GC data.

Safety considerations for this experiment:

A sand bath, especially the top portion, can get very hot during the experiment, and you won't be able to tell by looking. Handle the sand bath with care. Also, a sand bath is an electrical apparatus; notify your instructor if its wires are frayed or exposed, and don't splash water on it.

You'll be using a thermometer. These are fragile--handle them carefully, especially when you're installing them in the top of the distillation apparatus.

Ethyl Acetate and Butyl Acetate are both highly flammable. Our lab equipment and safety regulations are selected to avoid flames. Also, avoid direct contact with these compounds. Work in the hood if sufficient space is available. This will reduce any inhalation hazards and isolate any fires which may occur.

When distilling an organic liquid it is important not to boil all of the liquid out of this flask. This is called distilling to dryness. When a distillation flask is allowed to boil dry, peroxides may form, concentrate and detonate.

Use a boiling stone whenever heating a liquid. The boiling stone provides a nucleation site onto which vapors can start to form bubbles. Boiling stones allow smooth boiling to occur. If a boiling stone is not present, the vapors can coalesce all at once and shoot out of the flask. This is called bumping. It often sprays boiling hot reagents out of the vessel spraying equipment, bench and exposed body parts. Always have a boiling stone or other nucleation center present when heating liquids.

The experiment

You will work in partners for this experiment. Turn your sand bath on and set it to about 30 or 40. Later you will have to adjust this setting. While waiting for the sand bath to heat up, assemble the apparatus as shown on the on-line notes. The apparatus should be set up above the sand bath and lowered into place when you are ready to start heating. The flask is the 5 mL long-necked round bottom flask from your kit. Place a boiling chip and approximately 4 mL of sample mixture into the flask. Place a small amount of copper sponge down into the neck of the round bottom flask. Be sure not to pack the copper too tightly or have any copper caught between the top of the flask and the rubber adaptor. Attach rubber adaptor with metal rod and the still head. Connect rod to clamp, attach clamp to ring stand.

Be careful when setting up and taking apart the apparatus. Be firm but gentle, especially with the thermometer. The placement of the thermometer is

critically important. A good rule of thumb is that the top of the thermometer bulb should be even with the bottom of the side arm of the distillation apparatus. It should not be too high or too low. The end of the distilling head should fit well into the receiver. The receiver should sit on an insulating tile on edge of sand bath. An alternative method is to put receiver in a 50 mL beaker filled with ice and clamped to the ring stand. This alternative method needs proper clamp placement to ensure apparatus remains aligned.

When everything is assembled and ready to go, scoop an indentation in the hot sand using your spatula or scoopula. Lower the apparatus so that the bottom of the distilling pot (the 5 mL flask) is just touching the surface of the sand in the indentation. You can control the heating rate by piling sand around the pot or scraping it away with your spatula. Don't expect the temperature on the thermometer to begin rising immediately. The thermometer temperature will not start to register an increase until the vapor from the boiling liquid reaches the thermometer bulb. This will take several minutes.

After the sand bath has been on for approximately 5 minutes carefully touch the bottom of the sand bath, gradually move your fingers toward the sand, and ensure the sand is getting hot. Do not simply stick your fingers directly into sand. Hot sand looks exactly like cold sand.

A vapor ring or visible boiling should be present after 10 minutes of heating. If not, turn transformer up slightly.

The distillation process should be relatively slow. Adjust the rate of heating by manipulating the sand in the sand bath as described above so that the rate that drops enter the receiver is no faster than two or three drops per minute. The slower the distillation is the better the separation will be. Record the thermometer reading each time a drop enters the receiver. (This means that you should end up with a table that tells you that drop 1 appeared at a certain temperature, drop 2 appeared at a certain temperature, and so on. It does NOT mean that you should end up with a table that tells you that so many drops appeared at one temperature, so many drops appeared at another temperature, and so on.)

After at least 15 drops have been collected, pay close attention to the temperature. When the temperature rises substantially, switch to the second receiver. Ensure receivers have been switched by the time 100° have been reached. Do not stop the distillation to do this and keep recording the temperatures as before. All of these data go into the same table--do not start a new table when you switch receivers. Continue distilling until only about 0.5 mL of liquid remains in the flask. To help you estimate that amount, remember that it's about one tenth of the starting volume. This volume should just cover a medium sized boiling stone.

If you stop too early, you will not have enough data for a good distillation graph. The temperature at the end of your experiment should be at least 115°C and preferably more, unless your pot is about to distil to dryness before this happens. *You must stop while there is still liquid in the pot.* Distilling to complete dryness is dangerous because many organic liquids contain trace amounts of peroxides that can explode when heated (see Williamson, chapter 2).

Measure the purity of the first fraction, the second fraction and the pot residue using either the index of refraction or gas chromatography.

Analysis

If analyzing fractions using index of refraction refer to procedure used previously in this course.

If analyzing fractions using gas chromatography, your instructor will demonstrate the proper procedure. Pay close attention. Be very careful when handling syringe. Do not bend syringe needle or plunger. Each syringe costs approximately \$100 to replace.

Gow-Mac Gas Chromatography

Record all machine conditions in lab notebook including machine number, carrier gas type, flow rate, injector temperature, detector temperature, column temperature, column type and injection size. Rinse syringe three times with sample. Be very careful not to bend syringe needle or plunger. Pull up desired sample size (typically 5 μ L) into syringe. Holding syringe perpendicular to machine front, not at angle, insert needle into injection port. Insert needle until base of barrel touches port. If significant resistance is met, do not force. Instead remove syringe and try again. Once syringe is inserted, quickly depress plunger (note end of plunger stops before reaching barrel). Quickly remove syringe and hit "start" on integrator. Ensure integrator responds or hit "start" again.

Once peaks for both compounds have emerged on integrator, hit "stop". Write name and sample id on chromatogram. Inject next sample and repeat.

All chromatograms will be ejected from integrator, cut up and distributed at end of class.

Vernier mini GC™

Detailed instructions on how to use Vernier Mini GC will be distributed separately.

Clean-up

Unplug heating equipment. Excess distillation mixtures and products go in the non-halogenated liquid waste container in the hood. Used Pasteur pipettes go in the broken glass box.

Rinse scintillation receiving vials with a bit of acetone. Return upside down to box at front of classroom.

Clean and replace all glassware in drawers.

Post-experiment Assignment

Make a graph of number of drops (x-axis) versus temperature. Remember what you learned in CHEM 1011L about proper graphing techniques. Use the majority of the space available on your graph paper. (Remember that you are plotting the temperature at which each drop appeared, **not** how many drops

appeared at each temperature.) Draw the best fitting smooth curve that fits the data--do not "connect the dots." From your curve, predict the boiling points of the fractions. This may be done by choosing the best two flat plateaus and reading their temperature from the y-axis.

Complete the provided data sheet. Attach graph to data sheet. Turn in at end of class or at other time specified by your instructor.

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