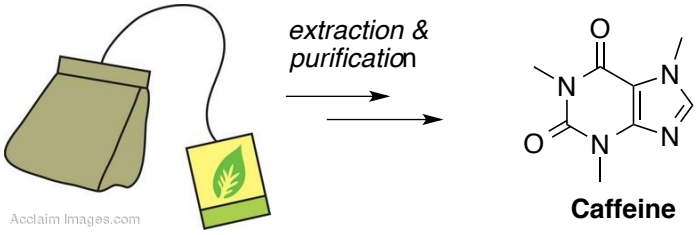
# Experiment 3 – Isolation and Sublimation of Caffeine from Tea Leaves

Reading Assignment
Chapter 9 (filtration), 10 (extraction), 11 (drying agents) & intro to Chapter 16 (sublimation)

**Extraction** is the physical process by which a compound (or mixture of compounds) is transferred from one phase to another. An extraction is taking place each time coffee or tea is made. Water-soluble components in the tealeaves or coffee beans are being transferred from a solid phase, the leaves or beans, into a liquid phase, the hot water. This is an example of **solid-liquid extraction.**

In this experiment, students will use an organic solvent to extract the organic components, namely caffeine, from tea. This process, known as **liquid-liquid extraction**, is a basic operation that should be mastered in the organic chemistry laboratory. This allows the isolation of single components from a mixture. The physical process that rules liquid-liquid extraction is known as **solvent-solvent partitioning**, or the distribution of solutes between a pair of solvents.




**Scheme 1.** Overview of caffeine extraction.

Organic solvents such as diethyl ether, toluene, and methylene chloride (dichloromethane, DCM) have a very limited solubility in water. These solvents are **immiscible** with water. For example, if toluene is mixed with water, a two-layer system is obtained. The upper layer contains the less-dense solvent, which in this case is toluene (d 0.867 g/mL) and the lower layer contains the denser solvent, being water in this case. The toluene layer along with its components is called the organic phase and the water layer along with its components is called the aqueous phase.

Suppose solute A is added to a mixture of water and toluene. The system is shaken and attains equilibrium. Solute A will be present in both layers, but larger amounts of it will be in the solvent for which it has a higher affinity. The distribution between both solvents is dictated by the **partition coefficient, K** of A between the two solvents. *The partition coefficient is the equilibrium constant for the distribution of a solute between two immiscible layers* (**eq. 1** and **2**). If A has a greater solubility in toluene, then $K_{T/W} > 1$. The higher the value of $K_{T/W}$, the greater yield there will be for the liquid-liquid extraction.

$$A_{water} \overset{K_{T/W}}{\rightleftharpoons} A_{toluene} \qquad \textbf{(1)}$$

$$K_{T/W} = \frac{\text{(Concentration A in toluene)}}{\text{(Concentration A in water)}} \qquad \textbf{(2)}$$

A partition coefficient can be *estimated* as the ratio of solubilities of the compound in both solvents. For example, suppose 1.1 g of caffeine is dissolved in 100 mL of water then 100 mL of chloroform (a water-immiscible solvent) is added. The solubility of caffeine in water is about 1.8 g/100 mL, while the solubility of chloroform is about 18.0 g/100 mL. Most of the

caffeine in the original water layer is transferred to the organic layer after mixing. The partition coefficient for caffeine between chloroform and water, $K_{C/W}$, can be *estimated* as follows (**eq. 3**).

$$K_{C/W} \approx \frac{\text{solubility in chloroform}}{\text{solubility in water}} = \frac{18.0 \text{ g/100 mL}}{1.8 \text{ g/100 mL}} = 10 \qquad \textbf{(3)}$$

In our example, since caffeine prefers chloroform 10 times over water, after equilibrium there will be 1.0 g in the organic layer and 0.1 g in the aqueous layer. Caffeine can be recovered from the organic phase by evaporation of the solvent. The evaporation will yield no more than 1.0 g of caffeine (assume for this case that 1.0 g is recovered). The crude recovery of caffeine from the organic phase before further purification is expressed as a percentage of the initial amount (**eq. 4**). It measures the efficiency of the extraction. Increasing the volume of organic solvent increases the percent recovery as more solute is extracted into the larger organic phase. Performing several consecutive extractions also results in a higher efficiency for the extraction process. It is standard to perform three organic extractions, where the bulk of the caffeine is extracted in the first extraction, nearly the rest of it in the second, and a third extraction is done for good measure!

$$\textbf{\% Recovery of Extraction} = \frac{\text{mass of organic extract}}{\text{original amount}} \times 100 = \frac{1.0 \text{ g}}{1.1 \text{ g}} = 91\% \qquad \textbf{(4)}$$

In this experiment, % recovery (in-lab #1) will be determined using **eq. 4** - the mass of organic extract (after solvent evaporation in the round-bottom flask) and the original mass of tea leaves used in the experiment (contents of six tea bags). *Student's calculated recovery will be very low due to the small amount of caffeine in tea – nowhere near 100%!* Students also calculate theoretical recovery for comparison using **eq. 4** - compare the amount of caffeine in Lipton tea to the mass of tea leaves used in the experiment. You can either use the amounts for six tea bags or one; the ratio is the same.

The crude organic extract will contain impurities that were not removed in the aqueous layer. After concentration of the organic phase using a rota-vap (rotary evaporator), there will be "brown gunk" in the bottom of the flask that will require further purification. The percent recovery from the sublimation process itself should be calculated as shown in **equation 5** below.

$$\textbf{\% Recovery of Sublimation} = \frac{\text{mass of pure caffeine}}{\text{mass of crude extract}} \times 100\% \qquad \textbf{(5)}$$

The calculated results require context to determine whether results are as expected. For comparison, students once again use the theoretical amount of caffeine in Lipton tea (x6) and compare this to the experimentally recovered caffeine after sublimation (**eq. 6**, in-lab #3).

$$\textbf{\% Recovery of Caffeine} = \frac{\text{mass after sublimation}}{\text{theoretical mass}} \times 100\% \qquad \textbf{(6)}$$

Notice that the different % Recovery calculations for different parts of the experiment all stem from the same idea. Simply stated, *percent recovery reflects the amount recovered from the initial amount used in a particular process.*

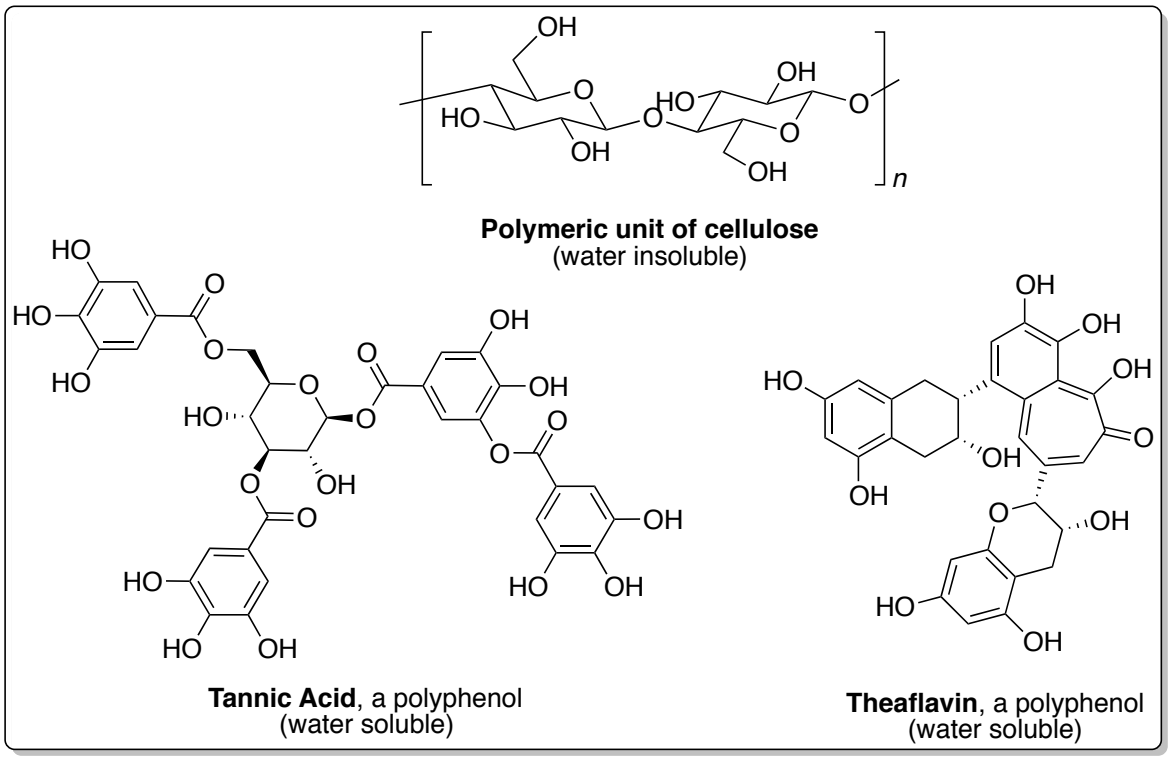
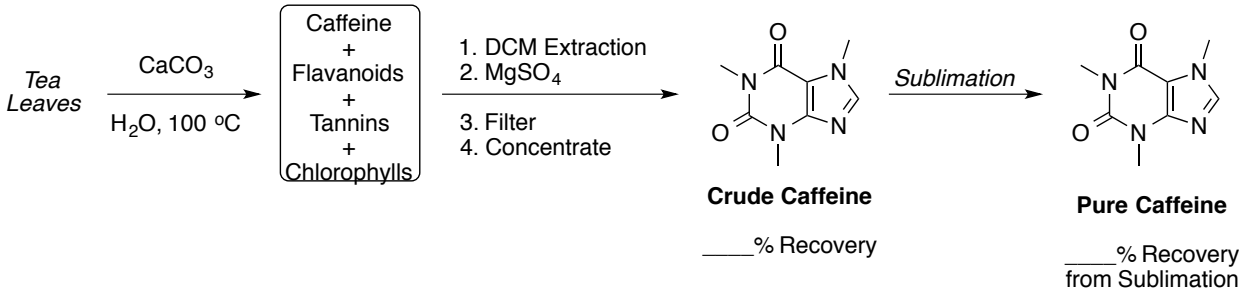



**Figure 1.** Examples of Tea Components.

There are many more organic components aside from caffeine in tea leaves (**Figure 1**). The other components include cellulose and classes of compounds called tannins and flavins. Cellulose is a major structural component of all plant cells and is virtually insoluble in water. The remaining compounds are water-soluble and are found in brewed tea. They serve as pigments and are responsible for flavors, including bitterness. Caffeine has a higher affinity for certain organic solvents than water at room temperature and can therefore be isolated from tannins and flavins using a simple liquid-liquid extraction.

The overall steps in the extraction and purification of caffeine from Lipton tea are outlined in **Scheme 2** below. The tea is made under basic conditions to ionize mildly acidic flavinoids and tannins, causing them to be more water-soluble. In the liquid-liquid (DCM-water) extraction, caffeine will be separated from the water-soluble pigments. After removing trace amounts of water, the low-boiling solvent is evaporated to yield the crude organic extracts. Further purification by sublimation results in white crystals of caffeine.




**Scheme 2.** Isolation of caffeine from tea leaves.*

* Use this as the scheme for the purpose of the experiment. Take any liberties to draw a pretty tea leaf.

**Notebook Preparation**

- *Purpose*: one-sentence description plus **Scheme 2**.
- *Reagent Table*: water, calcium carbonate, tea leaves, sodium chloride, dichloromethane (DCM), and caffeine. Indicate the amounts to be used (mmol, mg or mL), fill in columns with properties (MW, BP/MP, density, one-word hazard), and leave space to record actual amounts used. Do not report mmoles or properties for the tea leaves! Include a list of materials (chemicals, glassware, equipment, etc.) underneath the table.
- *Procedure*: Hand-written, step-wise procedure in your own words. Include **Figure 2** for sublimation. Additional pictures and flow chart encouraged. Keep this section as brief as possible while still maintaining clarity and ease of use.
- *Safety & Clean-up* – Copy the table at the end of the procedure into your notebook.

**PROCEDURE** - *The phrases below in quotations represent an abbreviated version of the procedure, as an experienced chemist would understand it. These phrases would be used in writing the experimental methods section. Pay attention to the writing style for future work.*

**Part A – Isolation of Caffeine**

*"To a 500-mL Erlenmeyer flask was added $CaCO_3$ (5 g), 6 Lipton tea bags, and water (180 mL) and the mixture brought to a boil for 20 minutes. The mixture was vacuum filtered…"*

**Brew the tea, but don't drink it!** One person in the room will open a tea bag (Lipton), weigh its contents, then report that mass on the board for the class to share (record this mass in your notebook). This information will be used to calculate the percentage yield of the extraction. Dispose of the tea leaves in the waste container once you are done with them (do not discard them in the sink; they will clog the drain). Place 6 tea bags, 5 g of calcium carbonate powder, and 180 mL of water in a 500-mL Erlenmeyer flask. Keep the strings and tags attached to the tea bags, provided the strings are long enough for the bag to reach the water. Bring the mixture to a gentle boil on a heating plate. Use a glass rod to stir the mixture and prevent bumping (be careful not to puncture the bags). Boil the mixture for 20 minutes (set up the separatory funnel on a ring stand in the meantime). Remove the tea bags, gently squeezing them against the flask with the glass rod. Let the solids settle and vacuum-filter the system while still hot using coarse filter paper (Whatman 4) and a 500-mL filter flask.

*"…and NaCl (5 g) was added to the filtrate. The filtrate was extracted with DCM (3 x 25 mL)…"*

**Extraction with Methylene Chloride** – *perform this part of the experiment in one of the fume hoods.* Allow the filtrate to cool down by placing the flask in an ice-water bath. When the filtrate has reached ambient temperature, add approximiately 5 g of sodium chloride and extract the solution with a 25-mL portion of methylene chloride (dichloromethane, DCM) using a 250-mL separatory funnel; the addition of sodium chloride decreases the miscibility of the aqueous and organic layers and helps in avoiding the formation of unwanted emulsions (mixture of water and organic solvent). The presence of saponins in the extract favors the formation of stubborn emulsions that make the separation of layers difficult. To minimize this problem *do not shake the separatory funnel vigorously* (as is customary in "liquid-liquid extraction). Instead, just invert and rotate the separatory funnel gently several times for a period of about five minutes. **Vent the funnel after every two inversions by slowly opening the stopcock to release any pressure buildup. *Venting early and often* is pivotal in preventing harmful chemical exposure.** When releasing the pressure, point the stem of the separatory funnel into the fume hood, away from your face and others.

Separate both layers as follows: support the separatory funnel on a ring, remove the stopper and carefully open the stopcock, collect the lower layer in a 125-mL Erlenmeyer flask ("Organic extracts"), cap with a cork or rubber stopper. Some emulsion may be present in the organic phase. Repeat this extraction two more times with two portions of DCM, combining all the organic extracts in one flask. The remaining aqueous portion should be collected in a flask labeled "aqueous extracts" and discarded at the end of the experiment in the aqueous waste.

*"…dried ($MgSO_4$),…"*

**Dry the organic extract.** The organic layer is treated with a drying agent with the dual purpose of removing water and breaking any emulsions. Add a generous scoop of anhydrous magnesium sulfate ($MgSO_4$) to the organic phase and swirl. Immediately clean up the $MgSO_4$ snowstorm that is undoubtedly on the bench top. It may be necessary to add more, depending on how much water is in the sample. Large amounts of water that have been soaked up by $MgSO_4$ can be seen in a white clump (or clumps) at the bottom of the flask. When enough $MgSO_4$ has been added, flakes of white solid can be seen swirling around in the flask like a snow globe. Cover the flask with a cork stopper and set it aside for 10 minutes with occasional swirling. While waiting, obtain a small piece of cotton to prepare for gravity filtration.

*"…filtered,…"*

**Filter the organic phase** using a small piece of cotton *loosely* packed in the neck of a glass funnel. With a glass rod apply gentle pressure to secure the cotton plug to the neck of the funnel while doing the filtration. Collect the filtrate in a pre-weighed, dry 100-mL round-bottom flask. Rinse the magnesium sulfate with 2 mL of fresh methylene chloride. The filtrate should be clear without traces of water or magnesium sulfate. If water is still present, transfer the liquid back to the Erlenmeyer flask and repeat the drying with additional anhydrous magnesium sulfate. If solid passes through the cotton plug, re-filter the solution using a larger piece of cotton.

*"…and concentrated in vacuo to afford crude caffeine as an off-while solid (xx g, xx% recovery)."*

**Concentrate.** Remove the solvent using a rotatory evaporator (rota-vap) equipped with a lukewarm water bath and connected to a cold trap. Your TA will set this up for you. Weigh the product ("crude organic extract" – this is not just caffeine). Calculate the percent recovery based on the amount of tea originally used.

**Part B – Purification of Caffeine by Sublimation**

*"The crude extract was purified via sublimation to yield caffeine as (description) (xx g, xx% recovery)."*

Scrape as much of the crude extract as possible out of the round-bottom flask into the bottom of a clean, dry Petri dish. Place the Petri dish on a hot plate and cover the dish with a stack of three disks of Whatman 1 filter paper (draw **Figure 2** in the notebook). Cover the disks with a 250-mL beaker or a 250-mL Erlenmeyer flask about $^1/_3$ full with water and a few small ice cubes. The beaker or Erlenmeyer flask helps keep the filter paper in place and provides cooling but if the water is too cold, condensation forms and ruins the experiment. Turn on the heat to a low setting. After a few minutes you will observe, when looking from the side, the white vapors of caffeine inside the Petri dish. Let the sublimation continue for an additional 5 minutes then turn off the heat. Make "oooh" and "aaahh" sounds when the solid sublimes as observed by white gas formation. Let the *closed* system cool down at room temperature. Taking the beaker off the setup pre-maturely will cause the caffeine vapors to escape.

**DO NOT REMOVE THE HOT APPARATUS FROM THE HOTPLATE!!! After the system has reached room temperature,** carefully pour out the water from the beaker or Erlenmeyer flask in the sink and scrape the purified caffeine from the filter paper onto a piece of pre-weighed weighing paper. Weigh the purified caffeine and determine the recovery of the sublimation process. Note the color and shape of crude and sublimed caffeine crystals. Dispose of caffeine in the solid waste container.

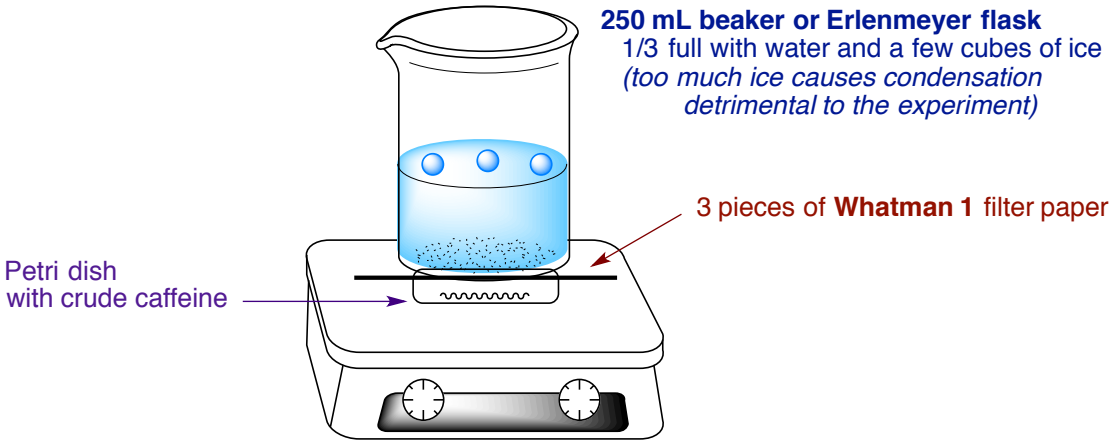



**Figure 2.** Components of sublimation apparatus; *copy into your notebook.*

| Clean-up and Waste | Safety |
|---|---|
| **Aqueous waste*: aqueous layers from extractions<br>**Solid Waste*: tea bags and leaves, caffeine crystals, $CaCO_3$, filter paper, $MgSO_4$, and cotton plug from filtration<br>*DCM from rota-vap trap into labeled *recycled solvent bottle* | * DCM is a possible carcinogen. Handle in fume hoods.<br>* When releasing pressure during extractions, point the separatory funnel stem away from face (into fume hood).<br>* The salts in this lab ($MgSO_4$, $CaCO_3$, NaCl) are relatively harmless, but you should still minimize exposure.<br>* Caffeine is a stimulant and is NOT to be ingested or taken home. |

**Introduction: Pre-lab Questions**
*Turn in typed responses in the beginning of lab. Answer in complete sentences. Show your work in pen where applicable.*

1. Use what you know about the relative polarity of functional groups to determine the final destination of the following compounds that are extracted from tea: caffeine, cellulose, tannins, calcium carbonate. Do the majority of each of these compounds end up in the tea bag, filtered solid, aqueous layer, or organic layer?

2. What is the role of calcium carbonate in the extraction? Draw the balanced reaction of calcium carbonate with a phenol (PhOH).

3. Why is sodium chloride added before extraction of the aqueous layer with DCM? What is the role of magnesium sulfate?

4. One gram of caffeine dissolves in 55 mL of water, 7 mL of DCM, 530 mL of diethyl ether, and 100 mL of benzene. Estimate the partition coefficient of caffeine between DCM and water, diethyl ether and water, and benzene and water. Which is the optimal solvent to extract caffeine from an aqueous solution? Why?

5. What is sublimation? Why is it possible to sublime caffeine? List another compound that sublimes near ambient pressure.

**In-lab Questions**

*Copy the questions into your notebook before lab. Complete in the lab notebook before leaving lab then type responses for the report. Answer in complete sentences and show your work in pen. Re-read the introduction to the experiment and copy the appropriate equations along with the questions.*

1. Report the mass of the crude extract and the total mass of dry tea leaves used in the extraction. Calculate the percent recovery of the crude extraction of caffeine from dry tea leaves (**eq. 4**).

2. Report the theoretical amount of caffeine in one bag of Lipton tea. Calculate the theoretical recovery of extraction (**eq. 4**) using the amount of caffeine on the ingredients label (or look online) and the mass of dry leaves in one tea bag. Is the percent recovery (in-lab #1) comparable to the theoretical recovery?

3. Describe the appearance of the crude extract and the purified product. Calculate the percent recovery of the sublimation process (**eq. 5**).

4. Report the theoretical amount of caffeine that could be extracted from six Lipton tea bags (amount in one tea bag is listed on the box and online). Calculate the percent recovery based on the amount of pure caffeine obtained vs. the theoretical amount (**eq. 6**). Briefly comment on the success of the experiment.

Adapted from…Palleros, D. R. "Extraction and Isolation of Caffeine from Tea Leaves," Experimental Organic Chemistry, **2000**. Wiley: New York.

**Exp 3 Extraction & Isolation of Caffeine From Tea Leaves**, *Due Date in Syllabus*

Name _____

Section Day _____ Time _____ TA Name _____

CHEM 8L GRADING RUBRIC – Use as cover page for report

| SECTION | INSTRUCTOR COMMENTS | POINTS ASSIGNED |
|---|---|---|
| **IN-LAB QUIZ** | | **/ 5** |
| **LAB REPORT** | | |
| **INTRODUCTION** Each pre-lab question is addressed in its own paragraph using complete sentences. Structures and calculations are hand-written, where appropriate. | | / **25** |
| **RESULTS** The main results are stated, as outlined in the post-lab questions, using complete sentences. | | / **30** |
| **NOTEBOOK PAGES** Proper format: reaction scheme, chemical info table, procedure, waste and clean-up procedure. | | / **25** |
| **NEATNESS AND ORGANIZATION** Proper grammar, order, and format (per instructions in syllabus). | | / **10** |
| **LAB TECHNIQUE & CLEAN UP** Lab space left clean, proper technique, instructions followed, checked in with TA before leaving. | | / **5** |
| | **LAB REPORT TOTAL** | **/ 100** |