

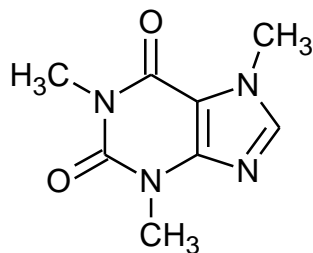
## Extraction of Caffeine from Tea Leaves

### Introduction

Extraction is a common technique used in organic chemistry to separate or isolate a desired compound from a mixture. The two major types of extractions used in the organic laboratory are solid-liquid extraction and liquid-liquid extraction. Solid-liquid extraction is often used to isolate a natural product from its biological source, such as the leaves or bark of a tree. For example, the anti-cancer drug paclitaxel (Taxol®) can be isolated from the bark of the Pacific yew tree by solid-liquid extraction with methanol. Liquid-liquid extraction is the most common extraction technique, and involves partitioning a solute between two immiscible liquid phases, usually an aqueous (water) phase and an organic solvent phase. The relative concentration of solute in each phase depends on the solubility of the solute in each phase and is given by the partition coefficient (K):

$$\text{Partition coefficient (K)} = \frac{[\text{g}/100 \text{ mL}] \text{ in organic phase}}{[\text{g}/100 \text{ mL}] \text{ in aqueous phase}}$$

Caffeine is an *alkaloid* (a class of naturally occurring compounds containing nitrogen and exhibiting the properties of an alkali, hence the term *alkaloid*) which is found in many sources, such as tea and coffee. In fact, the amount of caffeine in tea leaves can be as much as 5%.



**Caffeine**

In this experiment, you will first use an aqueous medium (sodium carbonate in water) to extract caffeine (along with tannins, gallic acid, flavinoid pigments, and some other compounds) from tea leaves by a solid-liquid extraction process, in other words, you will make tea (albeit tea that is basic). Caffeine, tannins, gallic acid, and the flavinoid pigments are soluble in this alkaline medium, but the main component of tea leaves – cellulose – is not. You will then perform a liquid-liquid extraction of the tea solution with an organic solvent, dichloromethane, to separate the caffeine from the basic tea solution and away from the tannins, gallic acid and the remainder of the tea components. Since caffeine is more soluble in the organic solvent dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) than in water, it partitions primarily into the dichloromethane. The tannins and gallic acid, being acidic compounds, are converted to water soluble salts by the sodium carbonate, and remain in the aqueous layer during the extraction. The other components of tea are not very soluble in dichloromethane. Therefore, the extraction of tea solution with dichloromethane removes virtually no other compound but caffeine. The solid caffeine can be then be isolated by evaporation of the low-boiling dichloromethane and identified by its melting point and mass spectrum.

## Required Reading:

*Padias:*

Extraction (pp. 128 – 137)

Drying the Organic Fraction (pp. 137 – 140)

Mass Spectrometry (pp. 106 – 114)

## Special Safety Notes:

- Dichloromethane is a somewhat toxic solvent, so handle it as much as possible in a hood, and avoid spilling it on yourself.

## Procedure:

### Preparation of Tea

Place about 30 mL of water into a 100 mL beaker (use the beaker markings to estimate the volume). Cover the beaker with a watch glass and heat the water to a gentle boil. Remove the watch glass and place a tea bag (the instructor will give you the weight of the tea in the bag) into the gently boiling water so that it is covered as completely as possible by the water. Note the approximate level of the liquid in the beaker at this point. Replace the watch glass and continue gently boiling the mixture for about 15 minutes. Water may evaporate during this step; you may add water to maintain the liquid level. Occasionally push down (GENTLY!) on the tea bag with the closed end of a test tube to maintain contact of the tea in the bag with the solution. After the 15 minute boiling period, remove the beaker from the hot plate and squeeze any excess liquid out of the tea bag into the beaker (use a stir rod or test tube to roll the tea bag against the side of the beaker – the tea bag will be HOT!), then add 1.1 g of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and stir the hot solution with a stir rod until the sodium carbonate is dissolved. Allow the tea solution in the beaker to cool to room temperature. While this initial tea solution is cooling, place the tea bag into a 50 mL beaker, add 5 mL of water, cover with a watch glass, and heat this to a gentle boil for about 2 minutes. Remove this beaker from the hotplate, squeeze the excess liquid out of the tea bag into beaker, then add the contents of this beaker to the tea solution in the original beaker. ***Be sure the tea solution has cooled to room temperature before you proceed to the next section!*** The tea bag from this step can be discarded.

### Extraction of Caffeine from the Tea Solution

Pour the tea solution into a 60 mL separatory funnel (*be sure that the stopcock is closed before you add the tea solution to the separatory funnel!*). Extract the tea solution with 6 mL of dichloromethane ( $\text{CH}_2\text{Cl}_2$ , also called dichloromethane or DCM). Mix the two layers by inverting the funnel gently several times (do not shake the funnel too hard or an emulsion will form which is very difficult to separate). Vent the funnel frequently to avoid any pressure buildup. Place the funnel in a ring and allow the layers to separate. Drain the dichloromethane extract (the lower layer) into a **dry** 25 mL Erlenmeyer flask. Avoid draining any of the aqueous layer or any emulsion (a green-brown layer between the top aqueous layer and the lower dichloromethane layer) into the flask. Perform a second extraction in the same manner with another 6 mL of dichloromethane. Combine this dichloromethane extract with the first one by draining it into the same 25 mL Erlenmeyer flask. If there are any visible water drops in the dichloromethane solution, pour the extract back into the separatory funnel, allow the layers to separate, then drain the dichloromethane layer into a **dry** 25 mL Erlenmeyer flask. Dry the dichloromethane solution by adding a small amount of granular anhydrous sodium sulfate. Allow the dichloromethane solution to remain over the drying agent for about 10 minutes.

### Isolation of the Caffeine

Decant the dried dichloromethane solution into a **dry, pre-weighed** 30 mL beaker. Avoid transferring any of the sodium sulfate drying agent to the beaker (a Pasteur pipet works well for the transfer). Place the beaker on a hot plate (*UNDER THE HOOD!*) and evaporate the dichloromethane over a low. As soon as you see solid forming in the beaker, remove it from the heat (leave it in the hood). The residual heat should be enough to complete the evaporation of the dichloromethane. Do not heat the beaker after the solvent has evaporated, otherwise you may sublime the caffeine. Determine the weight and melting point of your caffeine.

### Obtaining the Mass Spectrum

Place 1–2 mg of your isolated caffeine in an autosampler vial. Fill the vial to the shoulder with methanol, cap the vial and shake to dissolve. Obtain the mass spectrum of your product (in Room 308).

### **References:**

- Pavia, D. L.; Lampman, G. M.; Kriz, G. S.; Engel, R. G. *Introduction to Organic Laboratory Techniques, A Microscale Approach*; 3<sup>rd</sup> ed.; Brooks/Cole: Pacific Grove, CA, 1999; pp. 125 – 127.
- Mayo, D. W.; Pike, R. M.; Butcher, S. S. *Microscale Organic Laboratory*; John Wiley & Sons: New York, 1986; pp. 124 – 125.
- Hill, R.; Barbaro, J. *Experiments in Organic Chemistry*; 3<sup>rd</sup> ed.; Contemporary Publishing Company: Raleigh, NC, 2005; pp. E4-1 – E4-4.

## Lab Report Guidance

### Title and Introduction

- Provide a short title that clearly describes exactly what the experiment involves.
- What is the scientific purpose of this experiment?
- Provide a short summary of the experimental approach you will use.
- For each of the newly introduced methods used in this experiment (extraction, drying of organic solvents), describe (1) the principles or theory behind it and (2) its practical use.
- Include figures of any newly introduced equipment and apparatus used in this experiment.

### Results and Discussion

Provide and discuss the following:

#### Recovery Data

- Mass of Tea Leaves
- Mass of Caffeine Recovered
- Percentage Recovery of Caffeine from Tea (Show % recovery calculation)
- How does your answer in Question 3 compare to the amount of caffeine normally found in tea, and why might it be different?

#### Melting Point Data

- Melting point of your product
- Literature melting point of product
- If the melting point of your caffeine is different from the literature value, why might it be different?

#### Mass Spectrometry Data

- Molecular ion: \_\_\_\_\_
- Best match (from NIST search): \_\_\_\_\_
- Provide a detailed explanation of how you identified your product as caffeine.

### Conclusion

- Provide short paragraph (1 – 3 sentences) that summarizes what happened in the experiment, and whether or not your purpose was achieved.

### Questions

1. Many organic solvents are used for extraction of organic materials from aqueous solutions. Some of the more common solvents (other than dichloromethane) are (a) chloroform, (b) toluene, (c) ethyl acetate, and (d) diethyl ether. For each of these solvents, draw the structure and indicate, for an extraction from aqueous medium, whether the solvent will be the top layer or the bottom layer. Explain your answer.
  
2. In drug discovery, the value “log P” (the log of the octanol-water partition coefficient) is often used as an estimate of the lipophilicity of a potential new drug.

$$\log P = \log([\text{solute}]_{\text{octanol}}/[\text{solute}]_{\text{water}})$$

The log P value for nicotine is 1.09. If 20 mL of 0.10 g/mL nicotine solution in water is extracted with 20 mL of octanol, how much nicotine is removed from the water layer into the octanol layer? If the same water solution is extracted with (2 x 10 mL) of octanol, how much nicotine is removed from the water layer? Both methods employ a total of 20 mL octanol for the extraction, but are they equally effective for removing nicotine from a water solution? Which method is more effective?

3. Outline a separation scheme for a mixture of benzoic acid, aniline, and ethylbenzene. Use a flowchart similar to that shown in Figure 3-8 in *Padías*. Explain the principle behind each of the steps in the separation scheme.