Extraction of Caffeine from Tea Leaves

Introduction
The active ingredient that makes tea and coffee valuable to humans is caffeine. Caffeine is an alkaloid, a class of naturally occurring compounds containing nitrogen and having the properties of an organic amine base. Caffeine is a naturally occurring alkaloid found in over 60 plant species. Caffeine belongs to a family of naturally occurring compounds known as xanthines. The xanthines, which come from plants, are possibly the oldest known stimulants. Caffeine is the most powerful xanthine in its ability to increase alertness, put off sleep and to increase ones capacity for thinking. Caffeine is a vasodilator (relaxes the blood vessels) as well as a diuretic (increases urination). Caffeine does not exist alone in tea leaves; the leaves are mainly cellulose, pigments and chlorophylls, and tannins. Tannins are phenolic compounds of high molecular weight that have certain properties in common.

Some of the better-known plant sources are coffee and cocoa beans, tea leaves, and kola nuts. While coffee and tea are both popular products containing caffeine, the amounts vary widely in a single serving. To further confuse the matter, coffee beans contain less caffeine than tea leaves when measured dry. However, a serving of coffee contains roughly twice the caffeine of tea. Much of the flavor of coffee and tea comes from tannins and other flavoring agents. Caffeine has a slightly bitter flavor. As a result, decaffeinating coffee beans and tea leaves will leave the flavor slightly changed even if no other compounds are lost.

<table>
<thead>
<tr>
<th>Beverage</th>
<th>Caffeine (mg)/cup</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coffee</td>
<td>80 – 125</td>
</tr>
<tr>
<td>Coffee, decaffeinated</td>
<td>2 - 4</td>
</tr>
<tr>
<td>Tea</td>
<td>30 – 75</td>
</tr>
<tr>
<td>Chocolate milk/cocoa</td>
<td>3 – 30</td>
</tr>
<tr>
<td>Soft drink</td>
<td>20 – 50</td>
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</tbody>
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Several health concerns have been raised over the consumption of caffeine. The Food and Drug Administration (FDA) has extensively studied the consumption of caffeine and its health effects. In 1987 the FDA concluded that normal caffeine consumption does not increase risk to health. These studies included cancer risk, coronary heart disease, osteoporosis, reproductive function, birth defects, and behavior of children. Many consumers prefer to avoid caffeine partially or altogether due to its stimulant effects and others still have health concerns. This makes decaffeinating coffee and tea an important industrial process. Decaffeination is also significant for the world’s economy; approximately eight billion pounds of coffee are grown a year making it second only to oil as an international commodity. It should be noted that decaffeinated coffee and tea are not caffeine free. These products can be labeled decaffeinated as long as 97% of the caffeine has been removed.

Greening the Chemistry
The industrial decaffeination process has evolved over the years. Initially direct contact methods used chloroform (CHCl₃), and more recently methylene chloride (CH₂Cl₂), as the solvent to repeatedly rinse the green (unroasted) coffee beans that had been softened by steam. Once sufficient caffeine had been removed, the beans would be roasted. Since these organic solvents have a high vapor pressure and low boiling point, any solvent remaining in the beans is removed during roasting. This method has several brown characteristics. Both of these solvents are carcinogenic and have several human health concerns with methylene chloride having the lesser overall hazard. Chlorinated hydrocarbon waste has significant environmental impacts and is costly to dispose. Roasting also does not guarantee full removal of the solvent, although solvent levels are rarely detectable. So why were these solvents used in the first place? Their advantages are that they are not water-soluble, have a low boiling point, and remove caffeine.
without removing significant amounts of other compounds, leaving the majority of the flavor unaltered.

Recently the direct contact process has been greened significantly using supercritical CO\textsubscript{2}. The green coffee beans are steam softened with water and then supercritical CO\textsubscript{2} is used to extract the caffeine. Once the system is returned to room temperature and pressure the coffee beans and separated caffeine are now solvent free as CO\textsubscript{2} returns to the gas phase. Then the CO\textsubscript{2} can be captured and reused. This method has all the advantages of the above technique without the environmental and human health risks.

Indirect contact methods have also been developed to decaffeinate coffee. The green coffee beans are soaked (steeped) in almost boiling water until the caffeine is removed from the bean. The coffee solution is then treated with ethyl acetate (a natural ester), which has moderate human health hazards but is not carcinogenic. Ethyl acetate solvates caffeine more effectively than water and extracts the caffeine. The remaining ethyl acetate is removed from the coffee solution by steaming. The coffee solution is then combined with the beans, which reabsorb the coffee oils as they are dried.

**Theory**

Caffeine (C\textsubscript{8}H\textsubscript{10}N\textsubscript{4}O\textsubscript{2}) is an alkaloid with the structure given below.

\[ \text{(1)} \]

Alkaloids are bitter tasting, natural nitrogen-containing compounds found in plants. The basic property of alkaloids comes from the lone pair of electrons found on at least one nitrogen. Alkaloids are often found to have potent physiological activity. Some better-known examples are morphine, heroin, lysergic acid (LSD), cocaine, quinine, strychnine, and nicotine. The basic N in caffeine can be used to increase or decrease its water solubility. Acidic conditions will form the conjugate acid salt giving caffeine increased water solubility as a cation. On the other hand if caffeine is in a basic environment it takes the neutral form and is only somewhat polar. Tea leaves contain tannins, which are acidic, as well as a number of colored compounds and a small amount of undecomposed chlorophyll (soluble in dichloromethane). To ensure that the acidic substance remains water soluble and that the caffeine will be present as the free base, sodium carbonate is added to the extraction medium. In order to successfully extract any substance from one solvent into another, we must maximize differences in solubility. Adding base to the solution has a second important effect. The water solution contains much more than just caffeine, and some of these compounds are also soluble in dichloromethane. Making the solution basic forms insoluble tannin salts which removes them from the solution before the caffeine is extracted. The dichloromethane extract will primarily contain caffeine with small amounts of impurities. Caffeine is also water soluble, but by keeping the washing solution basic it minimizes the caffeine lost, while maximizing the removal of impurities.

The solubility of caffeine in water in 2.2 mg/mL at 25 °C, 180 mg/mL at 80 °C, and 670 mg/mL at 100 °C. It is quite soluble in dichloromethane, the solvent used in this experiment to extract the caffeine from water. Caffeine can be extracted easily from tea bags. The procedure one would use to make a cup of tea - simply “steeping” the tea with very hot water for about 7 min - extracts most of the caffeine. There is no advantage to boiling the tea leaves with water for 20 min. Since caffeine is a white, slightly bitter, odorless, crystalline solid, it is obvious that water extracts more than just caffeine. When the brown aqueous solution is subsequently extracted with dichloromethane, primarily caffeine dissolves in the organic solvent. Evaporation of the solvent leaves crude caffeine, which on sublimation yields a relatively pure product. When the concentrated tea solution is extracted with dichloromethane, emulsions can form very easily. There are substances in tea that cause small droplets of the
organic layer to remain suspended in the aqueous layer. Prevention is the best cure for emulsions. This means shaking the solution to be extracted very gently until you see that the two layers will separate readily. If a bit of emulsion forms it may break simply on standing for a sufficient length of time. Making the aqueous layer highly ionic will help. Add as much sodium chloride as will dissolve, and shake the mixture gently. Centrifugation works very well for breaking emulsions. This is especially easy on a small scale.

Microscale Procedure

In a 30-mL beaker place 15 mL of water, 2 g of sodium carbonate, and a wooden boiling stick. Bring the water to a boil on a sand bath, remove the boiling stick, and brew a very concentrated tea solution by immersing a tea bag (2.4 g tea) in the very hot water for 5 min. Squeeze as much water form the bag as possible after it cools enough to handle, be careful not to break the bag. Add water if necessary to keep the volume at about 10 mL. Again bring the water to a boil, and add a new tea bag to the hot solution. After 5 min, remove the tea bag, and squeeze out as much water as possible. Rinse the bag with a few milliliters of very hot water, but be sure the total volume of aqueous extract does not exceed 12 mL. Pour the extract into a 15-mL centrifuge tube, and cool the solution in ice to below 40 °C (the boiling point of dichloromethane).

Using three separate 2-mL portions of dichloromethane, extract the caffeine from the tea. Cork the tube, and use a gentle rocking motion to carry out the extraction. Vigorous shaking will produce an intractable emulsion, while extremely gentle mixing will fail to extract the caffeine. If you have ready access to a centrifuge, the shaking can be very vigorous because any emulsions formed can be broken fairly well by centrifugation for about 90 sec. After each extraction, remove the lower organic layer into a reaction tube, leaving any emulsion layer behind. Dry the combined organic extracts over anhydrous calcium chloride pellets for 5 or 10 min in an Erlenmeyer flask. Add the drying agent in portions with shaking until it no longer clumps together. Transfer the dry solution to a tared 25-mL filter flask. Wash the anhydrous calcium chloride drying agent twice with 2-mL portions of dichloromethane and add the washings to the filter flask. Evaporate the dichloromethane solution in the filter flask to dryness in the hood. The residue will be crude caffeine. Determine its weight and purify the caffeine by sublimation.

Fit the filter flask with a Pluro stopper or no. 2 neoprene adapter through which is thrust a 15-mL centrifuge tube. Clamp the flask with a large three-prong clamp, fill the centrifuge tube with ice and water, and heat the flask on a hot sand bath. (See figure below) Caffeine is reported to sublime at about 170 °C. Tilt the filter flask, and rotate it in the hot sand bath to drive more caffeine onto the centrifuge tube. When sublimation ceases, remove the ice water, and allow the flask to cool somewhat before removing the centrifuge tube. Scrape the caffeine onto a tared weighing paper, weigh, and using the plastic funnel, transfer it to a small vial or a plastic bag. Determine the melting point of your caffeine. Using the centrifugation technique to separate the extracts, about 30 mg of crude caffeine can be obtained. This will give you 10 to 15 mg of sublimed material, depending on the caffeine content of the particular tea being used. Save your extracted caffeine for the next experiment: the preparation of caffeine salicylate.

Cleaning Up
Discard the tea bags in the nonhazardous solid waste container. Allow the solvent to evaporate from the drying agent, and discard in the same container. Place any unused and unrecovered dichloromethane in the chlorinated organic compounds container. The apparatus can be cleaned with soap and hot water.
Purify your caffeine by sublimation, carefully monitoring the heat so as to minimize the decomposition of your caffeine. Determine the mass of the pure product and the melting point.

References

Helpful websites:
http://swampfox.fmarion.edu/web/chem/aclabo/caffeine.PDF
http://www.sinc.sunysb.edu/Class/orgolab/newcaffeineexperiment.PDF

Go to
http://wwwchem.uwimona.edu.jm:1104/lectures/coffee.html or
http://www.sinc.sunysb.edu/Class/orgolab/Caffeine_New.PDF
to find some interesting facts about coffee!!!