

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 tealeaves; 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, tealeaves, 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.

Beverage	Caffeine (mg)/cup
Coffee	80 – 125
Coffee, decaffeinated	2 - 4
Tea	30 – 75
Chocolate milk/cocoa	3 – 30
Soft drink	20 – 50

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 (CHCl_3), and more recently methylene chloride (CH_2Cl_2), 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 CO₂. The green coffee beans are steam softened with water and then supercritical CO₂ 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 CO₂ returns to the gas phase. Then the CO₂ 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

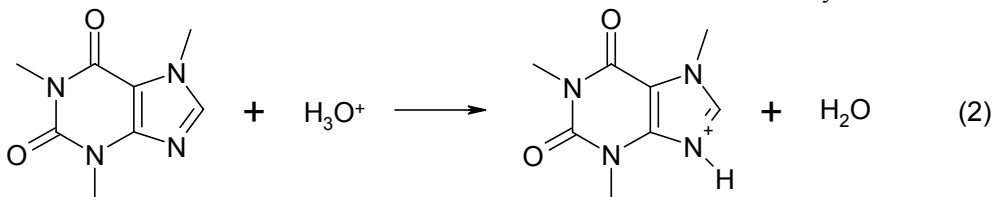
Caffeine (C₈H₁₀N₄O₂) is an alkaloid with the structure given below.



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.

In order to successfully extract any substance from one solvent into another, we must maximize differences in solubility. By choosing a green process we have traded some efficiency for human and environmental health. While 1-propanol is a less efficient extractor than CHCl₃ and CH₂Cl₂, we can maximize our efficiency by using a few simple techniques. Adding NaCl to the water to increase the polarity of the water and Ca(OH)₂ which makes the solution basic.

Caffeine is now in its least polar form and more readily solvated in 1-propanol than water.

The extraction is analyzed by determining the partition coefficient (K_p)

$$K_p = \frac{\text{solubility in extractant}}{\text{solubility in source solution}} \quad (3)$$

where solubility is usually given in g/mL. Partition functions with larger values result in more efficient extractions. Our process has a K_p of approximately 4, which makes for an effective extraction. Extractions are most effective when repeated several times with small volumes of solvent rather than once with a large volume.

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 1-propanol. Making the solution basic with $\text{Ca}(\text{OH})_2$ forms insoluble tannin salts which removes them from the solution before the caffeine is extracted into 1-propanol. The 1-propanol extract will primarily contain caffeine with small amounts of impurities. This solution is washed with 10% NaOH to remove impurities. Caffeine is also water soluble, but by keeping the washing solution basic it minimizes the caffeine lost, while maximizing the removal of impurities.

Procedure

Heat 20 mL of distilled water in a beaker to boiling. Turn off the heat and prepare your tea solution by adding 2 pre-weighed tea bags*. Let the solution steep for 10 minutes. Decant the tea solution and press out as much of the water in the tea bags as possible to maximize solvent recovery. Set the extracted solution aside, allowing it to cool. Repeat this procedure twice with 4 mL of hot distilled water each, let stand for five minutes, decant and press out as much water as possible. Combine the washings with the initially extracted solution.

Add sodium chloride (2.6g per 10 mL extracted tea) and about 0.1 gram of calcium hydroxide to the combined extracts, the latter to precipitate tannins. Heat and stir the solution for 15 minutes (near boiling). This process will dissolve the salt and digest the precipitate that forms. Decant the solution using gravity filtration (flute the filter paper) and recover the remaining extract.

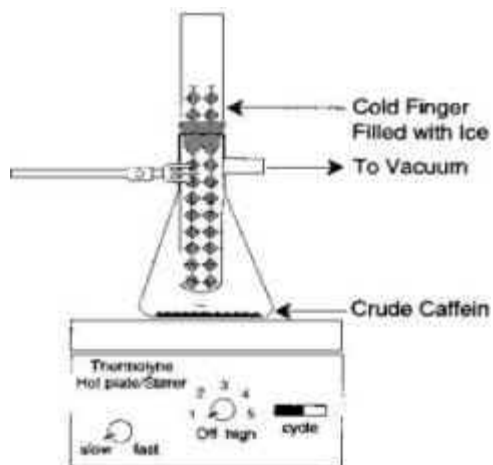
Transfer the combined extracts into a separatory funnel and extract with four successive 2.5 mL portions of 1-propanol. Remember to mix the solutions gently to minimize emulsion formation and vent the separatory funnel frequently, especially initially. Make sure the emulsion layer has mostly disappeared before separating. Combine the 1-propanol extracts in a separatory funnel and wash once with 2.5 mL of 10% aqueous NaOH solution. Dry the 1-propanol solution by adding anhydrous magnesium sulfate until it no longer clumps and filter. Transfer the 1-propanol solution into a round bottom flask and add a few boiling chips.

Prepare a simple distillation apparatus. Distill the 1-propanol from the caffeine extract. Carefully monitor the sample so as not to overheat the caffeine product as the 1-propanol distills away. The crude caffeine should be a light tan and only turns dark brown when degraded due to high heat. Stop the distillation (remove the heating mantle) just before the flask is dry. Take your distilled 1-propanol product, and add it to the recycled 1-propanol collection container located in the hood. It will be used next year for this experiment.

Rinse the residue in the flask with two successive 1-mL portions of acetone to extract the crude caffeine. Filter the acetone extract and carefully boil off the acetone. Take your crude caffeine product and determine its mass.

* Alternatively, add 10 – 12 grams of ground coffee to the 200 mL of boiling water. The final washing of the coffee grounds may need to be filtered to recover all the extracts.

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. Use the FT-IR to identify your product as caffeine.



Questions

1. Explain why salt is added to the water before the caffeine is extracted with 1-propanol.
2. What two things does the addition of $\text{Ca}(\text{OH})_2$ do to aid the extraction of caffeine.

References

- Murray, D.S.; Hansen, P.J., *J. Chem. Educ.*, **1995** (72) 851.
Hampp, A., *J. Chem. Educ.*, **1996** (73) 1172.

Notes

The partition coefficient of caffeine between the 1-propanol and aqueous phases was determined to be approximately 3.7. This is probably lower than the corresponding values for the CH_2Cl_2 /water systems, which is about 8.

The experimental conditions using 1-propanol produce about 80% crude caffeine. Using a larger quantity of 1-propanol or smaller quantity of water would obviously increase the percentage of caffeine extracted.

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!!!