EXTRACTION OF CAFFEINE: A REVIEW

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Abstract: ***Caffeine is a bitter, white crystalline xanthine alkaloid and a stimulant drug. It is found in varying quantities in the seeds, leaves, and fruit of some plants, where it acts as a natural pesticide that paralyzes and kills certain insects feeding on the plants, as well as enhancing the reward memory of pollinators. Part of the reason caffeine is classified by the Food and Drug Administration as GRAS (Generally Recognized As Safe) is that toxic doses (over 10 grams for an average adult) are much higher than typically used doses (less than 500 milligrams).***

Index Terms – Caffeine, Liquid-Liquid Extraction and Iodometric back titration

I. INTRODUCTION

Caffeine and other purine alkaloids, including theobromine and theophylline, have played a major role in the long-standing popularity of non-alcoholic beverages and foods such as coffee, tea, cocoa, chocolate and a wide range of soft drinks (Asahihara 2008). Caffeine is a naturally occurring chemical stimulant found in the leaves, seeds and fruits of a numerous plant species of a group of compounds called trimethylxanthine. Its chemical formula is $C_8 H_{10} N_4 O_2$.

Properties of Caffeine:

- **Systematic name :**1,3,7-trimethyl-*1H*-purine- 2,6(*3H,7H*)-Dione
- **Other name :** 1,3,7-trimethylxanthine & 1,3,7-trimethyl-2,6-dioxopurine
- **Molecular formula :** $C_8H_{10}N_4O_2$
- **Molecular mass :** 194.19 g/mole
- **Melting point :** 238°C
- **Solubility in water :** slightly soluble

Effects of Caffeine:

- Caffeine increases blood pressure.
- Caffeine stimulates the central nervous system.
- Caffeine promotes urine formation.
- Caffeine stimulates the action of heart and lungs.

Advantages of Caffeine:

- Treats Migraine.
- Increases the potency of analgesics.
- Relieves Asthma Attack.
- Caffeine can reduce the developing risk of Parkinson's disease.

Structure of Caffeine:

Fig No.1- Structure of caffeine

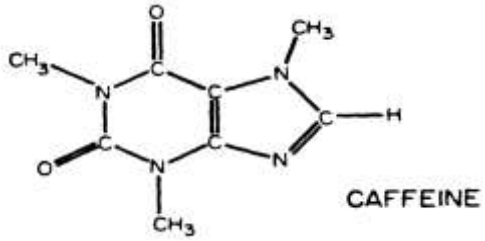

Table No-1: Caffeine Content of Common Food and Drugs

Espresso	120 mg per 2 Oz
Coffee, Regular, Brewed	103 mg per cup
Instant Coffee	57mg per cup
Coffee, Decaffeinated	2 to 4 mg per cup
Tea	30-75 mg per cup

Cocoa	5-40mg per cup
Milk Chocolate	6mg per Oz
Baking Chocolate	35mg per Oz
Coca-Cola Classis	46mg per 12 Oz
Jolt Cola	72mg per 12 Oz
Anacin Bromo Seltzer Midol	32mg per pill
Excedrin Extra Strength	65mg per pill
Dexatrim Dietac Vivarin	200mg per pill
Dristan	16mg per pill
No-Doz	100mg per pill

In table 1 the mentioned beverages and drugs are frequently used and it reveals that among them, Espresso contains the maximum amount of caffeine as compared to other beverages and drugs.

In its pure form, caffeine is a white crystalline powder that tastes very bitter. It is medically useful to stimulate the heart and also serves as increasing the rate of urine excretion. It is one of the most studied ingredients in the food supply. The most commonly known sources of caffeine are coffee and cocoa beans, guarana, and tea leaves. The amount of caffeine in food and beverage products varies depending on the serving size, the type of product and preparation method. Tea which we generally drink is made from the leaves of an Asian evergreen known as *Camellia sinensis*. The presence of caffeine in plants helps to prevent them from insects and other herbivores with the compound's bitter taste and stimulating qualities. The caffeine content of tea leaves depends on the variety and where they were grown; most tea has 3-5% by weight. The optical transition properties of caffeine were measured in different solvents (dichloromethane, water, chloroform and ethyl acetate). Caffeine has highest optical transitions in dichloromethane than the other solvents. Caffeine can be extracted more at the boiling temperature than at 30°C. Caffeine had been widely used in the food and pharma industry. The cost of extraction of caffeine from natural source is more. Research has been taken to extract it from natural source more economically.

Table No-2: Caffeine Content in Tea/Coffee Sample (Extraction with water)

TEA/COFFEE SAMPLES	AMOUNT OF CAFFEINE (gm)
Brook Bond Red Label	0.01
AVT	0.03
Eastern Eastea	0.02
Palat	0.04
3 Roses	0.02
Kannan Devan	0.01
Bru gold Coffee	0.68
AVT Coffee	0.62

These are some of the popular Tea and coffee brands among which Bru Gold Coffee contains the maximum amount of caffeine, whereas Kannan Devan contains the least as mentioned in Table 2

II. ADOPTED TECHNIQUES FOR EXTRACTION OF CAFFEINE

In order to extract caffeine from tea, several techniques are used. First, a solid/liquid extraction must take place in order to get the solid natural product into the liquid solvent. This can be done by using an extractor, or by simply brewing a cup of tea. In order to isolate the desired reaction compounds from the natural product, liquid/liquid extractions are used.

Here Steeping process is used. Specifically Solid – liquid and Liquid – Liquid Extraction is carried out in order to extract Caffeine from tea leaves.

Solvent used for solid liquid extraction is sodium carbonate whereas solvent used for liquid-liquid extraction is Dichloromethane (CH_2Cl_2) (Note- Dichloromethane can irritate your skin so do not handle Dichloromethane bare handedly).

Note: The sodium carbonate acts as a base - you could use sodium hydroxide instead. When you boil tea leaves tannins dissolve in the water as well as the caffeine. If you do not use a base the tannins will also be extracted into the solvent (i.e. methylene chloride) used in the subsequent extraction. The base converts the tannins into their sodium salts - being ionic these salts are not soluble in solvents like methylene chloride so remain in the aqueous layer during extraction. This allows purer caffeine to be extracted.

Table No-3: Different Methods Adopted for Extraction of Caffeine

NAME	DIFFERENT METHODS ADOPTED
Gonul Serdar, Ezgi demir, Serhat Bayrak, Munevver Sokmen, 2017	Microwave Assisted extraction
Muthanna J. Mohammed, Firas A. Al-Bayati, 2008	1) Liquid-Liquid Extraction 2)Solid-Liquid Extraction
Gonul Serdar, Ezgi demir, Munevver Sokmen, 2015	1) Citric Acid Water Extraction 2) Ethanol Extraction 3)Two step Water Extraction 4)High Temperature pre-treatment Water extraction 5) Water Extraction 6) Solid-Liquid Extraction
Satarupa Banerjee, Jyotirmoy Chatterjee, 2015	1)Microwave Assisted Extraction 2)High pressure processing 3)Supercritical Fluid Extraction 4)Subcritical Water Extraction
Khalida Khan, M Naeem, M Arshad and M Asif, 2012	Column Extraction

The yield of caffeine extraction depends upon the technique adopted and the parameters studied. Table 3 shows the techniques that are adopted for the extraction of caffeine.

After carrying out repeated extractions and using gravity filtration we get crude greenish white crystalline caffeine as a product. Getting pure form of crystalline caffeine from crude caffeine, we need to carry out sublimation. Sublimation is a fast and easy way to purify the caffeine.

The Success Of extraction involving a natural product is often expressed as percentage recovery,

%Recovery= (Grams of caffeine Recovered) / (Grams of tea leaves)

The percentage recovery is called the purified percent recovery or crude percent recovery. The extraction with the highest percent recovery is considered the most successful extraction.

Table No-4: Liquid –Liquid Extraction Adopted for Extraction of Caffeine and Its Details

NAME	PARAMETERS STUDIED	READINGS	EXTRACTION PERIOD AND RESPECTIVE DATA	YIELD
Gonul Sardar,Ezgi Demir,Munevver Sokemen, 2016	Temperature	50°C 80°C 100°C	4 hrs 40 min 15 min	-------- Maximum --------
R.R Shinde, N.H Shinde, 2017	Constant Feed rate and varying in the time(Solvent-Acetone)	Feed Rate-20:300	30 min 60 min 90 min 120 min	11.27% 52.35% 56.10% 56.70
S. Parvathy ,Adlet Luiz and Jaya T. Vakrey, 2014	Caffeine Content in Different Brands of Tea/Coffee (50gm of Tea Leaves and Coffee as sample)	AVT Coffee 3 Roses	Extraction with water and acidified water	0.62&0.76g 0.02&0.54g
Amber Nawab,Quratulam Waseem,Javeria Asif, Fatima Ahmed, 2016	Caffeine Content in Different Brands of Black Tea	Boiling the tea bags for a period of time to extract maximum amount of caffeine.	7 min	Average of 3% of caffeine is present in Black Tea.
Muthanna J.Mohammed,Firas A. Al-Bayati, 2008	Extraction Based on Volume ratio of tea solution and Solvent	25:25ml of tea solution and dichloromethane	10 min	3%
L.Jeyanthi Rebecca,Candace Seshiah,Trisha Tishoppi, 2014	Number of usage of Green Tea	Initial Caffeine Content:- 75mg/100g of tea	Amount of caffeine after:- First use Second use Third use	. 80% 73% 51%

From Table 4 we can infer that Liquid-Liquid Extraction is widely used technique for extraction of caffeine and different parameters are studied such as temperature, pressure and initial caffeine content for optimum yield.

Analysis Techniques for Caffeine:

- Iodometric Back Titration :-

Iodometric Back Titration Caffeine reacts with excess accurately known amount of iodine in acidic environment, forming insoluble precipitate. Then the insoluble precipitate is removed by filtration. Using titration by a standard sodium thio-sulphate solution with starch solution as indicator, we can determine the amount of remaining iodine, and thus the amount of caffeine can be found. Here are the chemical equations:

$C_8H_{10}N_4O_2 + 2\ I_2 + KI + H2SO4 \rightarrow C_8H_{10}N_4O_2\ .HI\ .I_4 + KHSO_4$

$I_2 + 2\ Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$

- Thin Layer Chromatography (TLC) :-

There are different types of chromatographic methods such as paper chromatography, thin-layer chromatography, column chromatography, gas chromatography, etc. They have the same principle:

1. Different solutes have different solubility in a solvent /different solutes have different degrees of tendency to be dissolved in the same solvent.
2. As the solution (contains the solvent with the dissolved solutes) moves along a stationary solid surface (a solid surface), different solutes adsorbed onto the solid surface in different extent as they have different degree of adsorption characteristics (due to the different degrees of dissolve tendency)
3. The "less soluble" solute will be retained first, and the "more soluble" solutes will be retained afterwards. (Note: No two substances have the same solubility and adsorption characteristics.
4. Different solutes will then be separated on the different positions of the solid surface.
5. Retention Factor (RF) of each component is calculated as follow

Rf = (distance traveled by the component substance form the baseline)/(distance traveled by the solvent from the baseline). Pure caffeine and the extract are analyzed in the same TLC plate and compare any differences of their Rf.

- Spike Test :-

By adding known amount of standard caffeine in distilled water and raw coffee solution, then carry out solvent extraction. By comparing the extraction results, we can analyze the recovery percentage of the spiked caffeine and efficiency of solvent extraction.

III. CONCLUSIONS

Tea is very rich in antioxidants. It is the most widely used beverage all over the world. It also has medicinal properties. In this study teas will be decaffeinated using dichloromethane as a solvent. This study will be carried out to check the amount of caffeine in used tea leaves. It is acceptable that the amount of caffeine decreased with every use. Caffeine from tea is extracted by liquid-liquid extraction followed by recrystallization. Caffeine is the most commonly used psychoactive drug in the world. It is a pharmacological active substance and depending on the dose, can be a mild central nervous system stimulant. Approximately 80% of the world's Population Consumes Caffeine on daily basis. The purified caffeine is then analyzed by using high performance liquid chromatography or Iodometric back titration method. The serious concern about potential use of caffeine for pathogenic effects has made it one of the most broadly studied drugs.

In the present study Caffeine content of different tea and coffee samples were studied and it is found that the caffeine content varies from 1-5%.The values generally agree well with literature quoted values of 2-5%.

IV. ACKNOWLEDGEMENT

Authors acknowledge the immense help received from the scholars whose articles are cited and included in the references of the manuscript. Authors are also grateful to authors, editors, and publishers of all those articles, journals and books from where the literature for this article has been reviewed and discussed.

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