International Journal of Advanced Research in Chemical Science (IJARCS)
Volume 6, Issue 9, 2019, PP 11-19
ISSN No. (Online) 2349-0403
DOI: http://dx.doi.org/10.20431/2349-0403.0609002
www.arcjournals.org

Extraction of Caffeine

Aniket Chaugule, Hitesh Patil, Shreyans Pagariya, Pradnya Ingle*

Associate Professor Department of Chemical Engineering, Shivajirao S Jondhale College of Engineering, Dombivli (E), 421201, University of Mumbai, India

Corresponding Author:** ***Pradnya Ingle, *Associate Professor Department of Chemical Engineering, Shivajirao S Jondhale College of Engineering, Dombivli (E), 421201, University of Mumbai, India*

Abstract: Caffeine is a chemical found in coffee, tea, cola, guarana, mate, and other products.Caffeine is one of the most commonly used stimulants among athletes. Taking caffeine, within limits, is allowed by the National Collegiate Athletic Association (NCAA). Urine concentrations over 15 mg/mL are prohibited. It takes most people about 8 cups of coffee providing 100 mg/cup to reach this urine concentration. The aim of this study is to determine the concentration of caffeine in reputed tea types and coffee. The Technique used here is Liquid-Liquid Extraction to extract caffeine. The Study also focused whether we can extract a significant amount of caffeine using different extracting solvents and different bases.

Keywords: *Caffeine, Liquid-Liquid Extraction and Iodometric back titration*

1. INTRODUCTION

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. Caffeine is most commonly used to improve mental alertness, but it has many other uses. Caffeine is used by mouth or rectally in combination with painkillers (such as aspirin and acetaminophen) and a chemical called ergotamine for treating migraine headaches. It is also used with painkillers for simple headaches and preventing and treating headaches after epidural anesthesia.

1.1. 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

1.2. Health Benefits of Caffeine

- Research indicates that caffeine may help protect human brain cells, which lowers the risk of developing some diseases, such as Parkinson's.
- Regular cups of coffee may stimulate the gallbladder and reduce the risk of gallstones.
- Caffeine causes the blood vessels to constrict, which may help relieve some headache pain.
- Coffee reduces inflammation and may help prevent certain heart related illnesses.
- Treats Migraine.
- Relieves Asthma Attack
- Increases the potency of analgesics.
- Caffeine is also used for weight loss and type 2 diabetes.

- Very high doses are used, often in combination with ephedrine, as an alternative to illegal stimulants.
- Caffeine creams are applied to the skin to reduce redness and itching in dermatitis.

1.3. Adverse Effects of Caffeine

- There is a significant association between drinking caffeinated coffee and the decrease of bone mineral density, which leads to osteoporosis.
- The daily consumption of caffeinated drinks can increase blood sugar levels and cause problems for people with diabetes.
- Caffeine is a diuretic and can cause dehydration.
- Caffeine can prevent some from falling asleep and interferes with deep sleep, which can lead to fatigue during the day.

The level of caffeine can vary depending on what is consumed. A piece of chocolate may have as little as five milligrams while energy drinks contain as much as 160 milligrams. Make sure to read the labels of pain medications and diet pills as products can have levels of caffeine as high as 200 milligrams. Michigan State University Extension recommends moderate doses of caffeine, 200 to 300 milligrams per day, which is equivalent to two to four cups of brewed coffee and is considered safe for most adults. If you are consuming more than 500 to 600 milligrams of caffeine per day, which equals four to seven cups of coffee, you may be prone to health problems including insomnia, nervousness, nausea or gastrointestinal problems, elevated heartbeat, headaches, etc. If you are experiencing unusual side-effects associated with the consumption of foods with caffeine, you should consult your physician.

1.4. How Does Caffeine Works?

Caffeine works by stimulating the central nervous system (CNS), heart, muscles, and the centers that control blood pressure. Caffeine can raise blood pressure, but might not have this effect in people who use it all the time. Caffeine can also act like a "water pill" that increases urine flow. But again, it may not have this effect in people who use caffeine regularly. Also, drinking caffeine during moderate exercise is not likely to cause dehydration.

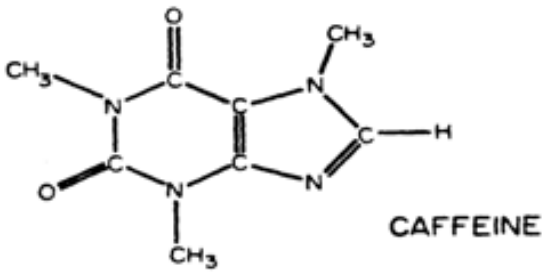

Fig1. *Structure of caffeine*

Table1. *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
DexatrimDietacVivarin	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.

Table2. *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

2. MATERIALS AND METHODS

Liquid–liquid extraction (LLE) is a method to separate compounds or metal complexes, based on their relative solubilities in two different immiscible liquids, usually water (polar) and an organic solvent (non-polar). There is a net transfer of one or more species from one liquid into another liquid phase, generally from aqueous to organic. The transfer is driven by chemical potential, i.e. once the transfer is complete, the overall system of protons and electrons that make up the solutes and the solvents are in a more stable configuration (lower free energy). The solvent that is enriched in solute(s) is called extract. The feed solution that is depleted in solute(s) is called the raffinate. LLE is a basic technique in chemical laboratories, where it is performed using a variety of apparatus, from separatory funnels to countercurrent distribution equipment called as mixer settlers. This type of process is commonly performed after a chemical reaction as part of the work-up, often including an acidic work-up.

Extraction is a method used for the separation of organic compound from a mixture of compound. This technique selectively dissolves one or more compounds into an appropriate solvent. The solution of these dissolved compounds is referred to as the extract. In the case of Caffeine extraction from tea powder, the solubility of caffeine in water is 22mg/ml at 25°C, 180mg/ml at 80°C, and 670mg/ml at 100°C. Here the organic solvent Dichloromethane is used to extract caffeine from aqueous extract of tea powder because caffeine is more soluble in dichloromethane (140mg/ml) than it is in water (22mg/ml).The dichloromethane - caffeine mixture can then be separated on the basis of the different densities of dichloromethane and water because dichloromethane is much denser than water and insoluble in it. Residual water is separated from dichloromethane by drain out the dichloromethane through separating funnel, thus dichloromethane passed through the funnel while polar solvents such as water is still remaining in the funnel.

In the first phase of experimentation screening was carried out in order to determine the maximum content of caffeine among black tea, green tea and coffee. The procedure was as follows: 10gm of tea, green tea and coffee sample was taken and boiled for 15 minutes along with the addition of 6gm of sodium carbonate which acts like a base which reacts with tannins to form sodium salts of tannins.

Next step is to filter the solution using vacuum filtration technique. The filtrate obtained is then used for liquid-liquid extraction to extract the caffeine into a organic solvent. Dichloromethane is used as solvent in liquid-liquid extraction because caffeine has higher solubility in Dichloromethane as compared to other solvents. After separation of organic layer from the separating funnel it is then kept for evaporationso as to evaporate the dichloromethane present in it. Now raw crude yellowish caffeine is further sent to recrystallisation in order to obtain pure white caffeine. Ethanol is used for recrystallisation as solvent.

Now after carrying out the above experiment and comparing the quantities of the caffeine obtained, we came to the results that caffeine content is higher in coffee as compared to green tea and black tea.

The next attempt of experimentation is to extract caffeine using different solvents and different bases. Using coffee for further extraction procedure because caffeine content is more in coffee as compared to green tea, black tea and coffee. First of all, keeping the base as constant i.e. sodium carbonate and varying solvents we are going to extract caffeine from coffee. 10 gm of coffee was boiled for 15-20 mins with sodium carbonate as base. This step is called as Solid-Liquid Extraction. Now the next step is filtration which is carried using vacuum filtration instead of gravity filtration so as to minimize the time required for filtration. Filtrate obtained is used for liquid-liquid extraction using different solvents such as dichloromethane, acetone and ethanol. These solvents are not used simultaneously. For each solvent, different liquid liquid extraction is carried out and then the product obtained which is present in the organic layer is kept for evaporation. Then the quantity of caffeine from each of the solvent used is compared in the results.

The final step of the experimentation is to determine what happens to the quantity and quality of caffeine when we change the base used during solid-liquid Extraction. For this again 10 gm of coffee is used and boiled along with the addition of sodium hydroxide as base instead of sodium carbonate. Then again vacuum filtration is carried out in order to separate the particles of coffee beans present. Then liquid-liquid extraction is used to separate caffeine in organic layer. Then organic layer obtained is kept for evaporation and the product obtained is compared.

The procedure along with some snapshots are depicted as follows:

In order to extract caffeine from tea, several techniques are accompanied. 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 boiling tea leaves with the addition of sodium carbonate as a base. Further to separate the tannins vacuum filtration is used.

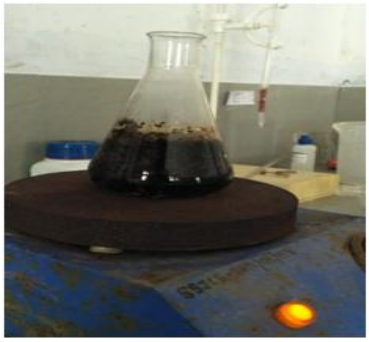

Fig2. *Solid-Liquid Extraction*

Fig3. *Vacuum Filtration*

After Vacuum Filtration, Liquid-Liquid extraction is used to separate caffeine in organic layer.

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).

Fig4. *Liquid-Liquid Extraction*

Now the next step is to keep the organic layer for evaporation of solvent which is dichloromethane. After evaporation of solvent the left product is raw crude caffeine which is further sent to analysis.

Fig5. *Crude Caffeine*

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.

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

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

$$\%\text{Recovery} = \frac{Grams\ of\ caffeine\ \ Recovered}{Grams\ of\ tea\ leaves}$$

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.

2.1. Analysis Techniques for Caffeine

- **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

$$\text{Rf}= \frac{Grams\ of\ caffeine\ \ RecoveredDistance\ \ travelled\ by\ the\ component\ \ substance\ \ from\ the\ baseline}{Distance\ \ travelled\ \ by\ the\ sovent\ \ from\ \ the\ baseline}$$

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.

- **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:

$$C_8H_{10}N_4O_2 + 2\ I_2 + KI + H_2SO_4 \rightarrow C_8H_{10}N_4O_2.HI\ .I_4 + KHSO_4$$

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

The Analysis Technique used here is iodometric back titration. The procedure is as follows:

Caffeine solution was prepared using sulphuric acid as an acidic medium. Iodine was added to it and then the solution was titrated against sodium thiosulphate till the solution becomes pale brown in color. Then starch was added as indicator after the solution becomes pale brown. Again, the solution is titrated against sodium thiosulphate and the endpoint of the reaction is dark blue to colorless solution.

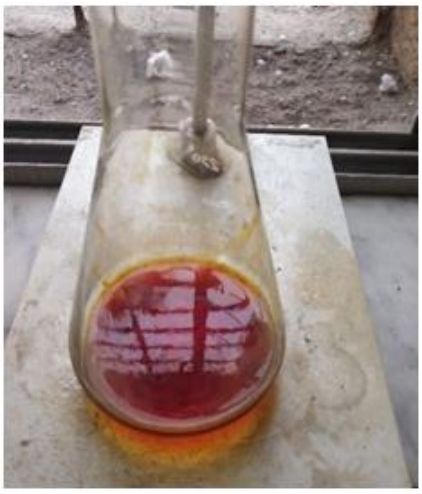

Fig6. *Before addition of starch*

Before the addition of starch the color of the solution is pale brown but after the addition of starch indicator the color of the solution changes to dark blue which then after titration with sodium thiosulphate the color of the solution turns colorless

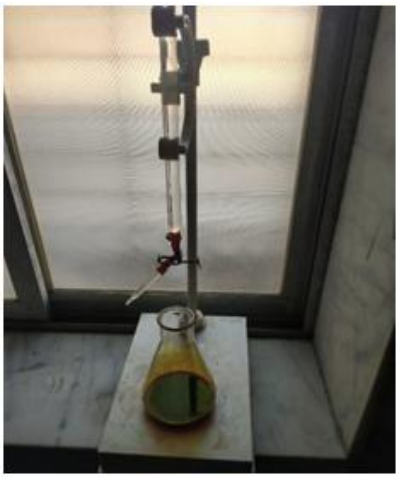

Fig7. *After addition of starch*

The solution is colorless that means the end point is reached and now calculating the amount of unreacted iodine with caffeine we can easily calculate the amount of reacted iodine with caffeine and hence by stoichiometry the amount of caffeine or the concentration of caffeine is determined.

Fig8. *Endpoint blue to colorless*

3. RESULTS

Table3. *Screening Results: To determine the maximum content of caffeine in different types of beverages.*

Type of Beverage	Amount of SampleTaken (gm)	Extracted Raw Crude Caffeine(mg)
Green tea	10	1.6
Black Tea	10	2
Coffee	10	40

Here Solvent used was Dichloromethane and base used was sodium Carbonate for extracting caffeinefrom above types of tea and coffee.

S. Parvathy ,Adlet Luiz and Jaya T. Vakrey in 2014 carried out the same analysis and they extracted more amount of caffeine from black tea as compared to our experiment because they used acidified water during solid-liquid extraction.

Amber Nawab, Quratulam Waseem, Javeria Asif, Fatima Ahmed in 2016 extracted caffeine from black tea and they got 3% caffeine in the sample.

Muthanna J.Mohammed,Firas A. Al-Bayati in 2008 also extracted caffeine from tea and they also got 3% caffeine as the result.

The variations in the caffeine content of the coffee and tea is because of using different techniques during extraction of caffeine.

Now for further experimentation coffee was used with different solvents and bases, as the caffeine content of coffee is much higher as compared to other types of tea and coffee.

Table4. *For carrying out each analysis using iodometric back titration as an analysis method, 10mgs of crude caffeine extracted from coffee was used and results were obtained as follows:*

Parameters Studied	Solvents Used	Base Used	Yield (mgs)(Pure Caffeine)	% Yield (Pure to Raw)
Solvents	Dichloromethane	Sodium Carbonate	6	60
	Acetone		3.0623	30.623
	Ethanol		4.2857	42.857
Base	Dichloromethane	Sodium Carbonate	6	60
		Sodium Hydroxide	4.42	44.2

R.R Shinde, N.H Shinde in 2017 extracted caffeine using acetone as solvent and the results were quite satisfying i.e. they obtained 11.27% of caffeine using acetone as solvent. We got more amount of caffeine as compared to them because we have used sodium carbonate as base during Solid-Liquid Extraction.

4. CONCLUSION

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%.

The Series of experiments that have been conducted, we can conclude that the caffeine content of coffee is relatively high as compared to other beverages and therefore we can also state that the caffeine is highly soluble in Dichloromethane as compared to other solvents and also the Tannins are more soluble in sodium carbonate as compared to other bases.

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 the project guide and the college for the immense help they have provided during experimentation.

REFERENCES

[1] Aniket Chaugule, Hitesh Patil, Shreyans Pagariya, Pradnya Ingle (2018). Extraction of caffeine: A review. Journal of emerging technology and innovative research, ISSN-2349-5162, Volume 5 Issue 9.

[2] S. Venkatesh, M.M Swamy, Y.S.R Reddy, B. Suresh and M.Sethuraman (1994). A simple method for determination of caffeine content in tea samples. Journal Ancient Science of Life,14(1-2),35-38.

[3] G. Serdar, E. DEMIR and M. Sokmen (2016). Recycling of tea waste: Simple and effective separation of caffeine and catechins by Microwave Assisted Extraction (MAE). International Journal of Secondary Metabolite. INT. J. Sec. Metabolite,4(2),78-89.

[4] A. Chaudhary, S. Sarkar, A. Chaudhary, S. Bardhan, P. Mandal and M. Chaudhary (2016). Tea waste management: A case study from West Bengal, India. Indian Journal of Science and Technology, 9(42), 89790.

[5] CHEM 333L (2010). Organic chemistry laboratory. Revision1.3.Isolation of caffeine from tea.

[6] A. Postu and S. Wilson (2013). Isolation of caffeine from tea leaves via Acid-Base liquid-liquid extraction. Asian Journal of Science and Technology,12(2), 2157

[7] M. Debartolo, Fall (2002).Org Chem 1 Extraction of caffeine from tea Part 1.

[8] A. Amoozegaran and M. Javaherian (2014).Comparative Evaluation of caffeine extraction in waste tea as a potential low cost source relative to dry tea in different solvents. Natural products-An indian journal, 10(1), 27-29.

[9] L. jeyanthi Rebecca, C. Seshiah and T. Tissopi (2014). Extraction of caffeine from tea leaves. Journal The annals of "Valahia University" of Targoviste.

[10] C. Biological supply Company. Caffeine Extraction from tea. University of pittsburg at Bradford. Science in motion. Chemistry lab 023.

[11] I. Ahmed, T. Parveen, A. Yusuf Belel and H. Sikder. (2013).Extraction of caffeine from tea and development of caffeinated fruit juice. Journal of Food Chemistry and Nutritio, 2308-7943.

[12] D. Komes, D. Horzic, A. Belscak, K. Kovacevic Ganicc and A. Baljak. Determination of caffeine content in tea and mate tea by using different methods (2009). Journal Czech J. food sci, 27.

[13] P. Setyopratomo (2014). Extraction of phenolic compounds from green tea using Ethanol. Journal ARPN Journal of science and engineering and applied sciences, 9(09).

[14] G. Serdar, E. Demir, M. Sokmen (2016). New approaches for effective microwave assisted extraction of caffeine and catechins from green tea. Journal International Journal of Secondary Metabolite, 3,3-13.

[15] S. Anbuselvi, S. Sarvanthi and M. A. Nikhil Kumar (2017). Extraction of caffeine from different variety of tea samples. Journal International Journal of pharmacy and Technology. Coden-IJPTFI.

[16] G. Serdar, E. DEMIR and M. Sokmen (2015). Comparison of some extraction methods for isolation of catechins and caffeine from Turkish green tea. Journal international journal of secondary metabolite, 2, 16-25.

[17] S. Parvathy, A. luiz and J. Varkey (2014). Chemical analysis of caffeine content in tea and coffee samples. Asian journal of science and applied technology,3(1),1-4.

[18] Amber Nawab, Quratulam Waseem, Javeria Asif, Fatima Ahmed (2016). Determination of caffeine in beverages. American journal of engineering research, 3(8), 24-137.

[19] Muthanna J.Mohammed,Firas A. Al-Bayati (2008). Caffeine content of Brewed Teas. Journal of analytical Toxicology, 32.

[20] R.R Shinde, N.H Shinde (2017).).Extraction of caffeine from coffee and preparation of anacin drugs. International journal of engineering Research and Technology, 10(1), 236-239.

Citation: *Pradnya Ingle, et.al, "Extraction of Caffeine", International Journal of Advanced Research in Chemical Science, vol. 6, no. 9, p. 11-19, 2019. DOI: http://dx.doi.org/10.20431/2349-0403.0609002*