“Extraction of caffeine using Natural sources”

Submitted in partial fulfilment of the requirements

For the award of the degree of

Master of Science

IN

INDUSTRIAL CHEMISTRY

Submitted By

MR. BALDHA DIXIT R.	[ENROLLMENT NO. 210722005]
MR. BHALODIA RUSHI P.	[ENROLLMENT NO. 210722006]
MR. BHETARIYA DEVASHISH J.	[ENROLLMENT NO. 210722007]
MR. BHUNDIYA VIRAJ R.	[ENROLLMENT NO. 210722008]

Under the guidance of

(DR.)VIRAL H. KARIYA
Assistant Professor
Department of Industrial Chemistry
Faculty of Science
Atmiya University
Rajkot - 360005

DEPARTMENT OF INDUSTRIAL CHEMISTRY
FACULTY OF SCIENCE (FoS)
ATMIYA UNIVERSITY
RAJKOT-360 005, GUJARAT, INDIA.

A.Y. - 2022-2023

Dedicated to

My Beloved Family

Without their love, support, and constant encouragement,
this would not have been possible

ACKNOWLEGMENT

First and foremost, from the bottom of heart, body, mind and soul, praises and thanks to our parents, the god, an almighty, for his showers of blessings throughout this research work. We must pray in the lotus feet of **H.D.H. P.P. Hariprasad Swamiji Maharaj** for their divine blessings. We convey our heartfelt thanks to the **Department of Industrial Chemistry, Faculty of Science, Atmiya University, Rajkot,** for providing laboratory facilities for the course of this work.

We warmly thank our research supervisor **(Dr.) Viral H. Kariya,** Assistant Professor, Department of Industrial Chemistry, Faculty of Science, Atmiya University, Rajkot for his splendid guidance, authentic supervision, moral support, constant encouragement and giving us an opportunity to work under him with compilation of magnificent experience.

We warmly thank **P.P. Tyagvallabh Swamiji**, President, Atmiya University, **Dr. Shivkumar Tripathi (**Vice-chancellor) Atmiya University, **Dr. Jayesh V Deshkar** (Pro Vice-chancellor) Atmiya University **Dr. Sheela Ramchandran** (Pro-chancellor) Atmiya University, **Dr. D. D. Vyas** (Registrar) Atmiya University, **Dr. Ashish M. Kothari** (Director -Research, Innovation and Translation) Atmiya University and **(Dr.) Ravi S. Tank**, (Head) Department of Industrial Chemistry, Atmiya University, Rajkot for providing us all the required facilities to carry out our research work.

We thank our Dissertation Review-I & II committee members, **(Dr.) Ravi S. Tank, Er. Dhaval A. Tank, Dr. Mehul L. Savaliya** and **Dr. Goving V. Vagadiya** from Department of Industrial Chemistry for their insightful comments, suggestions, and unconditional help in our research work.

We are very much delightful to **NFDD Centre**, **Saurashtra University, Rajkot, Gujarat, INDIA** for analytical assistance in spectral characterization of the synthesized samples.

At last, but not the least, we are very much thankful to all teaching & non-teaching staff members, **Mr. Sagar Patel, Mr. Jigneshbhai Gohel, Mr. Sunilbhai Parmar**and co-researchers of Department of Industrial Chemistry for their helping hands.

DECLARATION

We undersigned, hereby declare that the work assimilated in the dissertation thesis entitled "**Extraction of caffeine using Natural sources**" has been carried out by us at the Department of Industrial Chemistry, Faculty of Science, Atmiya University, Rajkot, Gujarat, India. under the supervision and Guidance of (**Dr.) Viral H. Kariya, Assistant Professor, Department of Industrial Chemistry, Faculty of Science, Atmiya University, Rajkot, Gujarat, India.**

To the best of our knowledge and belief, the work included in this thesis is quite original and has not submitted to any other Institution or University for the award of any degree either in this or any other form.

BALDHA DIXIT R.

(210722005)

BHALODIA RUSHI P.

(210722006)

BHETARIYA DEVASHISH J.

(210722007)

BHUNDIYA VIRAJ R.

(210722008)

We wish to express our sincere gratitude and honour to our Research supervisor **(Dr.) Viral H. Kariya, Assistant Professor, Department of Industrial Chemistry, Faculty of Science, Atmiya University, Rajkot.,** for his inspiring, splendid and authentic guidance, moral support and constant encouragement throughout our research work. His passion and dedication towards research has stimulated, provoked and facilitated us to complete this endeavour. We could not have imagined having a better Research Supervisor and mentor for our M. Sc study. Their role will always remain fundamental in shaping our future.

BALDHA DIXIT R.

(210722005)

BHALODIA RUSHI P.

(210722006)

BHETARIYA DEVASHISH J.

(210722007)

BHUNDIYA VIRAJ R.

(210722008)

Index

ABSTRACT

The extraction of caffeine from natural sources is a common process used to isolate caffeine from plants such as tea, coffee, and Green Tea. This process typically involves using solvents such as water, dichloromethane, or ethyl acetate to extract the caffeine from the plant material, followed by separation and purification steps to obtain a pure product. The choice of solvent and extraction method can affect the yield and purity of the caffeine extract, as well as the environmental impact of the process. The resulting caffeine extract can be used for various applications, including in the food, beverage, and pharmaceutical industries.

INTRODUCTION

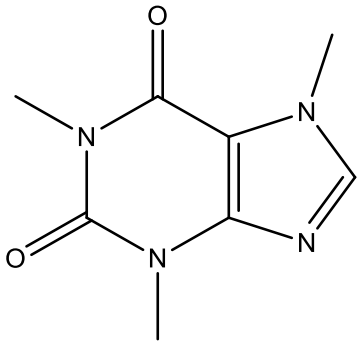
Caffeine is a natural alkaloid compound that belongs to a class of compounds known as methylxanthines. It is found in varying amounts in the seeds, leaves, and fruits of certain plants, such as coffee, tea, Green Tea, cocoa, yerba mate, and guarana. It is a central nervous system stimulant that is widely consumed around the world, primarily for its stimulating effects on the brain and body.

Caffeine is known to increase alertness, improve concentration, and reduce fatigue. It is also used in certain medicines as a pain reliever and in combination with other drugs to treat conditions such as migraines, asthma, and attention deficit hyperactivity disorder (ADHD).

Caffeine is used in combination with other drugs, such as aspirin and acetaminophen, to treat headaches and migraines. The combination of caffeine with other pain relievers can enhance their analgesic effects. Caffeine is used as a bronchodilator in the treatment of respiratory disorders such as asthma and chronic obstructive pulmonary disease (COPD). It helps to open the airways, making it easier to breathe.Caffeine is used in some weight loss medications and supplements due to its ability to boost metabolism and reduce appetite.

Caffeine has both positive and negative effects on human health, and its consumption should be monitored based on individual tolerance levels. Excessive consumption of caffeine can lead to side effects such as insomnia, anxiety, jitteriness, and increased heart rate. However, moderate consumption of caffeine has been associated with certain health benefits, such as a reduced risk of Parkinson's disease, liver disease, and certain types of cancer.

STRUCTURE OF CAFFEINE



CAFFEINE

Figure 1-Caffeine Structure

PHYSICAL PROPERTIES OF CAFFEINE

Caffeine has several physical properties, some of which are listed below:

I. Appearance: Caffeine is a white crystalline powder that is slightly bitter to taste.

Figure 2- Powder of Caffeine

II. Melting point: The melting point of caffeine is 237-238°C, which means that it can be easily melted and solidified at this temperature range.

III. Solubility: Caffeine is soluble in water, alcohol, and chloroform. It is sparingly soluble in ether and insoluble in benzene.

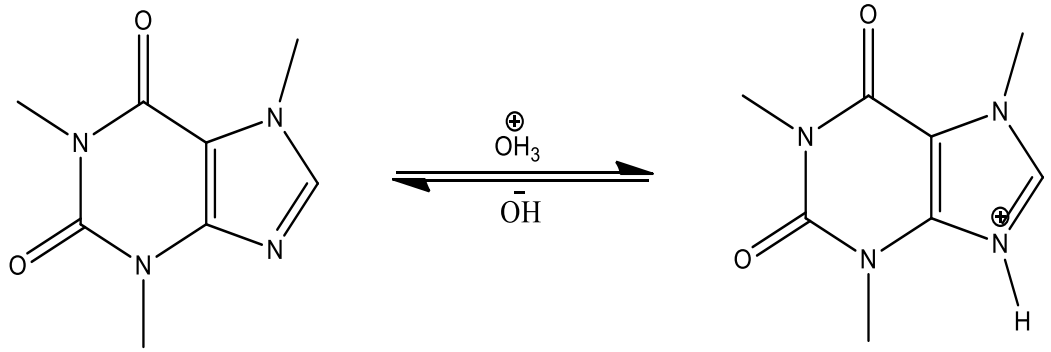
IV. Boiling point: The boiling point of caffeine is 178°Cat atmospheric pressure.

V. Density: The density of caffeine is 1.23 g/cm3.

VI. Molecular weight: The molecular weight of caffeine is 194.19 g/mol.

VII. pH: The pH of caffeine in water is approximately 6.9, which means that it is slightly acidic.

VIII. Optical activity: Caffeine is optically active and rotates the plane of polarized light to the right.



Natural form of caffeine
more soluble in a less polar solvent

Salt form of caffeine under acidic condition
more soluble in highly polar solvent

Reaction1- Reaction of Salt form of Caffeine

These physical properties are important for the purification and analysis of caffeine, as well as for understanding its behaviour in different environments and formulations.

PART – 1

EXTRACTION OF CAFFEINE FROM TEA LEAVE'S

MANUFACTURING PROCESS OF CAFFEINE FROM TEA LEAVE'S

- Weight Accurately 15gm of given Tea Leave's sample and crush it and then put it in a 250ml Conical flask.

- Add 5gms of Calcium Carbonate ($CaCO_3$) & 100ml Distilled water to the flask.

- Boil the Contain for 30 min., 60 min., 90min. With constantly Staring.

Figure3-Heating Processing of Tea leaves Mixtures

- Cool the mixture at room temperature and filter the content.

- Add filtrate in a separating funnel and add 25ml of Solvent like Di-chloromethane, Ethyl Acetate, Acetone, Hexane, etc.

- Separate Two Layers by shaking for 2 minutes. Allow the layers to separate. Collect to the Solvent layer in a small beaker. Repeat the procedure 3 Times.

Figure 4-Separating Column for Extraction of Caffeine by Tea Liquid Mixture

- Add a pinch of Anhydrous Sodium Sulphate (Na_2SO_4) to this beaker and filter it.

- Collect the filtrate in a clean beaker. Evaporate solvent in water bath and collect the crude caffeine as greenish residue.

- Weight crude caffeine & Calculate amount of caffeine in the given sample.

- Then compared, which solvent is Economically and Environmentally good and provided highest yield in Extraction Process.

CONFIRMATIVE TEST FOR CAFFEINE DETECTION

❖ **Murexide test can be carried out for caffeine detection as follows:**

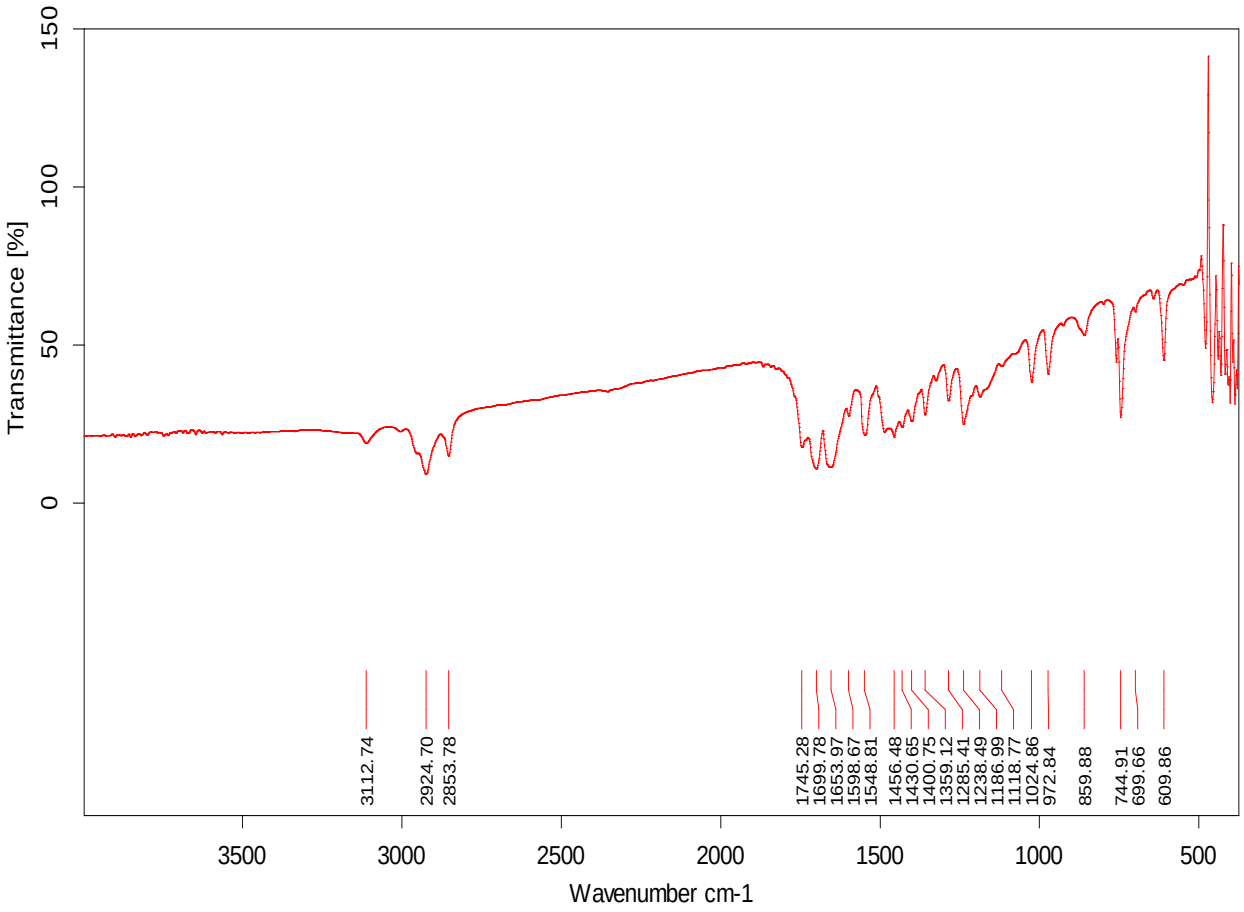
- In a watch glass, small amount of a sample with 2-3 drops of concentrated hydrochloric acid is mixing.
- Then we add a few small crystals of potassium chlorate and mix well.

Figure 5-Evaporate in Water Bath

- Heat the watch glass over a boiling water bath until the sample is dry.
- Allow to cool.
- Moisten with a drop of 'bench' (2 mol dm^{-3}) ammonia solution. The sample should turn purple.

Figure 6- Color Change

ANALYSIS GRAPHS (IR SPECTROSCOPY)



Graph.1- IR Graph of Caffeine Extracted by Tea Leave's

Table.1- Reading of IR spectroscopy

Sr.No.	Bond	Band Range (Cm^{-1})	Band Reading (Cm^{-1})
1	C-H	3000-3100	3112.74
2	C-N	1300-1550	1548.81
3	C=O	1650-1690	1699.78
4	C=C	1600-1670	1653.97

RESULTS

Sr. No.	Source Name	Solvents	Time		
			30 min.	60 min.	90 min.
1	Tea Leaves	Di-chloromethane	0.75gm.	1.13gm.	1.37gm.
2		Ethyl Acetate	0.56gm.	0.8gm.	0.92gm.
3		Acetone	0.42gm.	0.58gm.	0.64gm.
4		Hexane	No Yield		

PART-2

EXTRACTION OF CAFFEINE FROM

COFFEE BEANS

MANUFACTURING PROCESS OF CAFFEINE FROM COFFEE BEAN'S

- Weight Accurately 15gm of given Coffee Bean's sample and crush it and then put it in a 250ml Conical flask.

- Add 5gms of Calcium Carbonate ($CaCO_3$) & 100ml Distilled water to the flask.

- Boil the Contain for 30 min., 60 min., 90min. With constantly Staring.

Figure 7- Heating Processing of Coffee Mixtures

- Cool the mixture at room temperature and filter the content.

- Add filtrate in a separating funnel and add 25ml of Solvent like Di-chloromethane, Ethyl Acetate, Acetone, Hexane, etc.

- Separate Two Layers by shaking for 2 minutes. Allow the layers to separate. Collect to the Solvent layer in a small beaker. Repeat the procedure 3 Times.

Figure8-Separating Column for Extraction of Caffeine by Coffee Liquid Mixture

- Add a pinch of Anhydrous Sodium Sulphate (Na_2SO_4) to this beaker and filter it.

- Collect the filtrate in a clean beaker. Evaporate solvent in water bath and collect the crude caffeine as greenish residue.

- Weight crude caffeine & Calculate amount of caffeine in the given sample.

- Then compared, which solvent is Economically and Environmentally good and provided highest yield in Extraction Process.

CONFIRMATIVE TEST FOR CAFFEINE DETECTION

❖ **Murexide test can be carried out for caffeine detection as follows:**

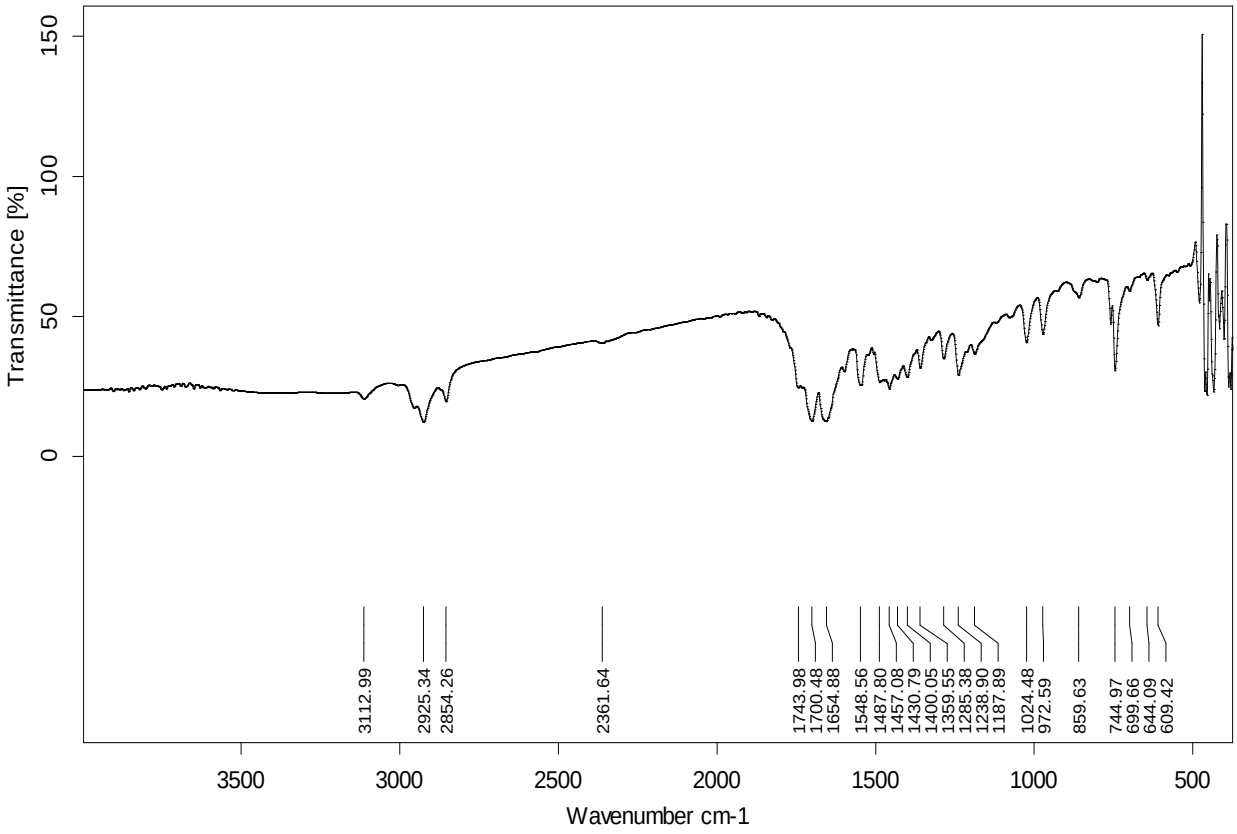
- In a watch glass, small amount of a sample with 2-3 drops of concentrated hydrochloric acid is mixing.
- Then we add a few small crystals of potassium chlorate and mix well.

Figure 9-EvaporateinWater bath

- Heat the watch glass over a boiling water bath until the sample is dry.
- Allow to cool.
- Moisten with a drop of 'bench' (2 mol dm^{-3}) ammonia solution. The sample should turn purple.

Figure 10-Color Change

ANALYSIS GRAPHS (IR SPECTROSCOPY)



Graph.2- IR graph of Caffeine Extracted by Coffee Beans

Table.2- Reading of IR spectroscopy

Sr. No.	Bond	Band Range (Cm^{-1})	Band Reading (Cm^{-1})
1	C-H	3000-3100	3112.99
2	C-N	1300-1550	1548.56
3	C=O	1650-1690	1700.48
4	C=C	1600-1670	1654.88

RESULTS

Sr. No.	Source Name	Solvents	Time		
			30 min.	60 min.	90 min.
1	Coffee Bean's	Di-chloromethane	1.8gm.	2.06gm.	2.84gm.
2		Ethyl Acetate	1.1gm.	1.3gm.	1.7gm.
3		Acetone	0.08gm.	0.11gm.	0.17gm.
4		Hexane	No Yield		

PART-3

EXTRACTION OF CAFFEINE FROM

GREEN TEA LEAVES

MANUFACTURING PROCESS OF CAFFEINE FROM GREEN TEA LEAVE'S

- Weight Accurately 15gm of given Green Tea Leaves sample and crush it and then put it in a 250ml Conical flask.

- Add 5gms of Calcium Carbonate ($CaCO_3$) & 100ml Distilled water to the flask.

- Boil the Contain for 30 min., 60 min., 90min. With constantly Staring.

Figure 11- Heating Processing of Green Tea Leaves Mixture

- Cool the mixture at room temperature and filter the content.

- Add filtrate in a separating funnel and add 25ml of Solvent like Di-chloromethane, Ethyl Acetate, Acetone, Hexane, etc.

- Separate Two Layers by shaking for 2 minutes. Allow the layers to separate. Collect to the Solvent layer in a small beaker. Repeat the procedure 3 Times.

Figure 12-Separating Column for Extraction of Caffeine by Green Tea Liquid Mixture

- Add a pinch of Anhydrous Sodium Sulphate (Na_2SO_4) to this beaker and filter it.

- Collect the filtrate in a clean beaker. Evaporate solvent in water bath and collect the crude caffeine as greenish residue.

- Weight crude caffeine & Calculate amount of caffeine in the given sample.

- Then compared, which solvent is Economically and Environmentally good and provided highest yield in Extraction Process.

CONFIRMATIVE TEST FOR CAFFEINE DETECTION

❖ **Murexide test can be carried out for caffeine detection as follows:**

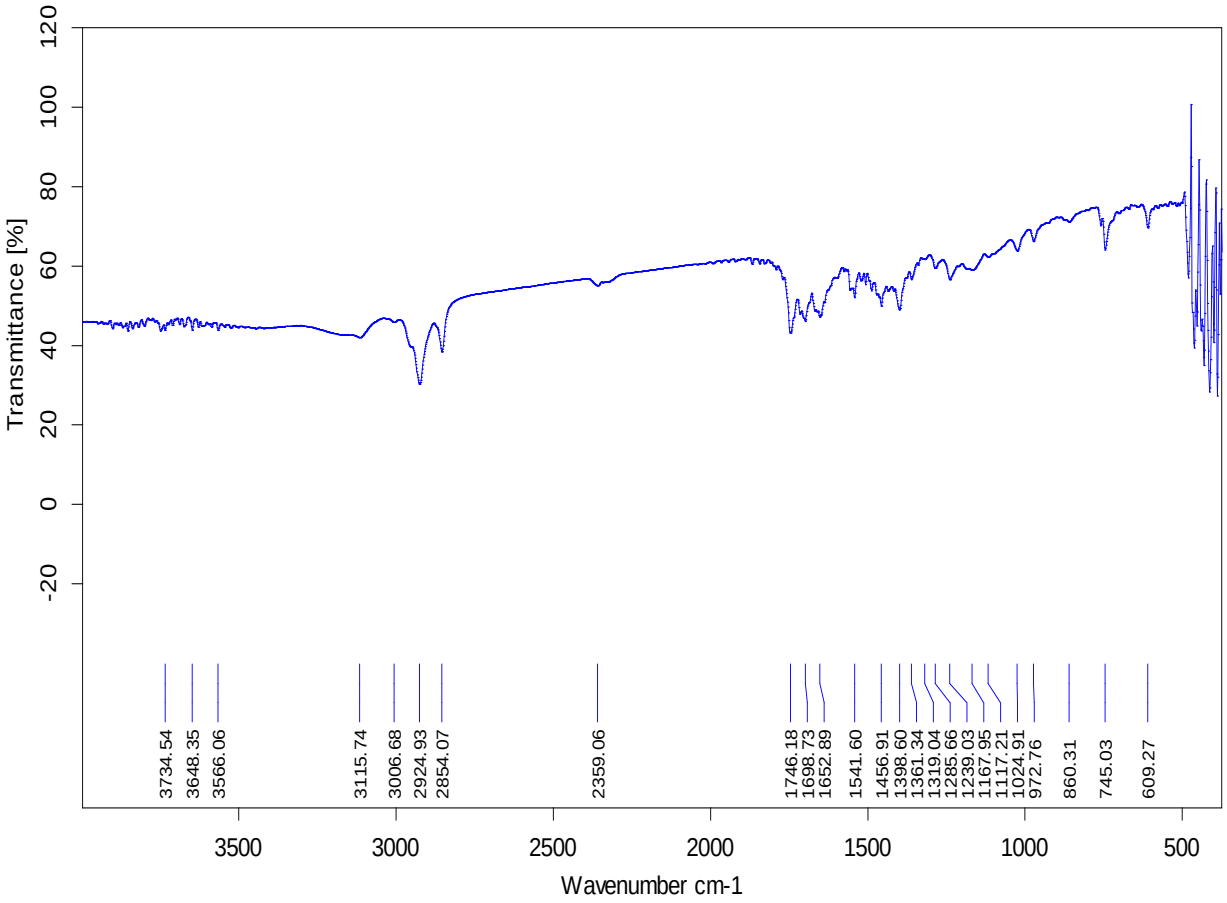
- In a watch glass, small amount of a sample with 2-3 drops of concentrated hydrochloric acid is mixing.
- Then we add a few small crystals of potassium chlorate and mix well.

Figure 13-Evaporate in Water bath

- Heat the watch glass over a boiling water bath until the sample is dry.
- Allow to cool.
- Moisten with a drop of 'bench' (2 mol dm^{-3}) ammonia solution. The sample should turn purple.

Figure 14-Color Change

ANALYSIS GRAPHS (IR SPECTROSCOPY)



Graph.3- IR Graph of Caffeine Extracted by Green Tea Leaves

Table.3- Reading of IR spectroscopy

Sr. No.	Bond	Band Range (Cm^{-1})	Band Reading (Cm^{-1})
1	C-H	3000-3100	3115.74
2	C-N	1300-1550	1541.60
3	C=O	1650-1690	1698.73
4	C=C	1600-1670	1652.89

RESULTS

Sr. No.	Source Name	Solvents	Time		
			30 min.	60 min.	90 min.
1	Green Tea Leaves	Di-chloromethane	0.20gm.	0.32gm.	0.46gm.
2		Ethyl Acetate	0.08gm.	0.21gm.	0.28gm.
3		Acetone	0.12gm.	0.34gm.	0.44gm.
4		Hexane	No Yield		

BENEFITS OF CAFFEINE

Caffeine has several potential benefits when consumed in moderation, which include:

Figure 15- Benefits of Caffeine

A. Increased alertness and concentration: Caffeine is a stimulant that can help to improve cognitive function, including alertness, concentration, and reaction time.

B. Improved physical performance: Caffeine can enhance physical performance by increasing endurance, reducing fatigue, and improving muscle strength and power.

C. Weight loss: Caffeine can help to suppress appetite and increase metabolism, which may aid in weight loss.
D. Mood enhancement: Caffeine can have a positive effect on mood, improving feelings of well-being and reducing symptoms of depression.

E. Reduced risk of certain diseases: Some studies suggest that caffeine consumption may reduce the risk of developing certain diseases, such as Parkinson's disease, Alzheimer's disease, type 2 diabetes, and liver cancer.

F. Headache relief: Caffeine can be an effective pain reliever for headaches and migraines, as it can help to constrict blood vessels in the head.

Figure 16- Benefits of Caffeine

It is important to note that excessive consumption of caffeine can lead to negative effects, such as anxiety, insomnia, jitteriness, and heart palpitations. Additionally, individual tolerance and sensitivity to caffeine can vary, so it is important to monitor caffeine intake and consume in moderation.

APPLICATION'S OF CAFFEINE

Caffeine is widely used in various industries and applications, including:

I. Food and beverage: Caffeine is a common ingredient in many beverages, including coffee, tea, energy drinks, and soft drinks. It is also used as a flavouring agent in food products such as chocolate, candy, and baked goods.

II. Pharmaceuticals: Caffeine is used in several over-the-counter and prescription medications, such as pain relievers, cold and flu remedies, and weight loss supplements.

Figure 17- Application of Caffeine

III. Cosmetics: Caffeine is a common ingredient in skin care products, such as eye creams and anti-aging serums, due to its antioxidant and anti-inflammatory properties.

IV. Agriculture: Caffeine can be used as a natural pesticide and herbicide, as it can help to repel insects and inhibit the growth of certain weeds.

V. Personal care products: Caffeine is also used in some hair care products, such as shampoos and conditioners, as it can help to stimulate hair growth and prevent hair loss.

VI. Industrial applications: Caffeine can be used in industrial applications, such as in the production of certain plastics and textiles.

Overall, caffeine is a versatile compound that has many potential applications in various industries and products.

CONCLUSION

The extraction of caffeine from natural sources is a well-established process that has been used for centuries. Caffeine is a natural stimulant found in many plants, including coffee, tea, and green tea. It is extracted from these sources using a variety of methods, including solvent extraction, supercritical fluid extraction, and subcritical water extraction.

The extraction of caffeine from natural sources has many benefits, including its natural origin and potential health benefits. Additionally, the use of natural sources reduces the need for synthetic production, which can have negative environmental impacts.

Overall, the extraction of caffeine from natural sources is a valuable process that can be used in a variety of industries, including the food, beverage, and pharmaceutical industries. However, it is important to ensure that the extraction process is sustainable and environmentally friendly, and that the sources of caffeine are obtained ethically and responsibly.

REFERENCES

1. Andrzejak, R., et al. *"Comparison of extraction methods of caffeine from tea leaves."* Food Chemistry, vol. 132, no. 2, 2012, pp. 1045-1052.
2. Ardhana, M.M., et al. *"Extraction of caffeine from tea waste using subcritical water."* Journal of Environmental Chemical Engineering, vol. 4, no. 3, 2016, pp. 2623-2630.
3. Ashraf-Khorassani, M., et al. *"Supercritical fluid extraction of caffeine from tea."* Journal of Chromatography A, vol. 1033, no. 2, 2004, pp. 259-265.
4. Bhat, R., et al. *"Extraction of caffeine from tea waste using microwave energy."* International Journal of Research in Pharmacy and Chemistry, vol. 3, no. 3, 2013, pp. 601-609.
5. Brzezowska, A.M., et al. "*The use of subcritical water extraction for isolation of caffeine from tea."* Journal of Chromatography A, vol. 1381, 2015, pp. 197-205.
6. Chu, Q., et al. *"Extraction and characterization of caffeine from tea waste."* Food Science and Biotechnology, vol. 22, no. 5, 2013, pp. 1375-1380.
7. Dubey, S.P., et al. *"Natural sources of caffeine: a review."* Journal of Food Science and Technology, vol. 49, no. 6, 2012, pp. 724-731.
8. Han, X., et al. *"Optimization of extraction conditions for caffeine from tea waste using response surface methodology."* Journal of Food Science and Technology, vol. 54, no. 6, 2017, pp. 1491-1500.
9. Hasan, M.A., et al. *"Ultrasound-assisted extraction of caffeine from tea waste using aqueous ethanol."* Journal of Chemical Engineering and Process Technology, vol. 7, no. 4, 2016, pp. 1000317.

10. Ho, C.L., et al. *"Comparison of supercritical fluid extraction and steam distillation for the extraction of caffeine from tea leaves."* Journal of Food Science, vol. 62, no. 3, 1997, pp. 534-537.
11. Huang, D., et al. *"Comparison of three extraction methods for the determination of caffeine in tea by high-performance liquid chromatography.*" Journal of Separation Science, vol. 34, no. 8, 2011, pp. 847-852.
12. Jaiswal, P., et al. *"Extraction of caffeine from tea leaves using supercritical carbon dioxide."* Journal of Food Science and Technology, vol. 53, no. 7, 2016, pp. 2914-2922.
13. Li, H., et al. *"Extraction of caffeine from tea by supercritical carbon dioxide."* Food Science and Technology Research, vol. 23, no. 6, 2017, pp. 833-839.
14. Liang, Y., et al. *"Optimization of microwave-assisted extraction of caffeine from tea using response surface methodology."* Food Analytical Methods, vol. 6, no. 6, 2013, pp. 1749-1757.
15. Fernandes, T. A. C., et al. "*Extraction of caffeine from guaraná seeds using supercritical CO2."* The Journal of Supercritical Fluids, vol. 88, 2014, pp. 85-92.
16. Wu, J. M., et al. *"Extraction and purification of caffeine from tea leaves by ultra-high-performance liquid chromatography."* Food Chemistry, vol. 194, 2016, pp. 1264-1270.
17. González-Gómez, D., et al. *"Comparison of three extraction techniques for the determination of caffeine in green coffee beans."* Food Chemistry, vol. 124, no. 2, 2011, pp. 582-587.
18. Yuan, M., et al. *"Extraction of caffeine from tea leaves using microwave-assisted pyrolysis and activated carbon adsorption."* Journal of Analytical and Applied Pyrolysis, vol. 135, 2018, pp. 137-143.

19. Jiménez-Moreno, N., et al. *"Comparison of two different methods for caffeine extraction from yerba mate leaves (Ilex paraguariensis)."* Journal of Food Composition and Analysis, vol. 33, no. 1, 2014, pp. 83-89.
20. Barbosa, J., et al. *"Green Coffee Oil Obtained by Supercritical CO2 Extraction and Characterized by High-Resolution Mass Spectrometry."* Journal of Agricultural and Food Chemistry, vol. 63, no. 28, 2015, pp. 6427-6436.
21. Belay, A., et al. *"Optimization of green tea extraction parameters for maximum total phenolic content and antioxidant activity using response surface methodology."* Food Science & Nutrition, vol. 7, no. 9, 2019, pp. 2996-3006.
22. Benassi, M. T., et al. *"Extraction of caffeine from mate (Ilex paraguariensis) leaves using different solvents."* Journal of Food Engineering, vol. 75, no. 1, 2006, pp. 19-23.
23. Dugo, P., et al. *"Supercritical fluid extraction of caffeine from coffee beans: Kinetics and yield."* The Journal of Supercritical Fluids, vol. 56, 2011, pp. 70-75.
24. Granja, A., et al. *"Extraction of caffeine from yerba mate using supercritical CO2 and ethanol."* The Journal of Supercritical Fluids, vol. 72, 2012, pp. 135-140.
25. Hernández-Sánchez, J. F., et al. *"Effect of extraction methods on antioxidant activity of coffee residues."* Food Chemistry, vol. 216, 2017, pp. 114-121.
26. Iglesias-Carres, L., et al. *"Extraction of caffeine from guarana seeds using supercritical carbon dioxide."* Journal of Food Engineering, vol. 107, no. 2, 2011, pp. 222-229.
27. Jin, H., et al. *"Optimization of ultrasound-assisted extraction of caffeine from tea leaves using response surface methodology."* Food and Bioprocess Technology, vol. 6, no. 9, 2013, pp. 2453-2463.

28. Kivilompolo, M., et al. *"The effect of temperature on the extraction yield and composition of spruce needle essential oil using supercritical carbon dioxide."* The Journal of Supercritical Fluids, vol. 97, 2015, pp. 63-68.
29. Li, M., et al. *"Extraction of caffeine from green tea leaves by ultrasonic-assisted CO2."* Journal of Food Science and Technology, vol. 55, no. 11, 2018, pp. 4619-4626.
30. Mazzone, G., et al. *"Extraction of caffeine from cocoa shells using supercritical CO2."* The Journal of Supercritical Fluids, vol. 132, 2018, pp. 103-109.