CHAPTER 1

INTRODUCTION

1. Introduction

Tea is one of the most popular drinks due to its pleasant taste and perceived health effects. Although health benefits have been attributed to tea consumption since the beginning of its history, scientific investigation of this beverage and its constituents has been under way for about 30 years.

1.1 Origin and History of Tea

Tea, the beverage, is the second most widely consumed drink in the world, exceeded only by water. In many cases today, as in ancient times, tea is safer to drink than water because it is boiled first, killing any disease-carrying bacteria.

The discovery of tea in China can be traced back to the ancient time of Holy Farmer, who was thought as the God of Farming and Medicine. It is said that one day he got poisoned 72 times when gathering and tasting herbs on a mountain. Later he found a plant (tea) and brewed the leaves in a pottery tripod and drank the liquid. As a result, the toxins in his body disappeared. Since then, tea was treated as a precious medicine and later a vegetable and was specially used as a magical drink among a group of high-level scholars in the Han Dynasty (206B.C.-A.D.220). However, it was not until the Tang Dynasty (618-907) did the real Chinese tea culture, including tea art, the tea ceremony and a complete expression of cultural philosophy come into being. In the Tang Dynasty, the tea plant was cultivated in 42 prefectures of China, and the habit of drinking tea had filtered into the daily life of people of all social ranks and classes [1].

Its first use is believed to be about 5,000 years back and has remained popular as the most pleasurable and efficacious beverage in the world for medical properties [2]. The most commonly recognized varieties of *Camellia sinensis* used for tea are *C. sinensis var. sinensis* (China bush or Chinese Tea) and C. *sinensis var. assamica* (Assam bush or Assam Tea) [3]. China and Assam tea differ in quality and morphological features. As far as the Western tea trade is concerned, Assams have been regarded as producing the best fermented tea. Most sources, and Legends, acknowledge the Chinese Emperor Shen Nung (28th century B.C.) with the discovery of tea. The tea plant originated in South-East Asia, believably in the region incorporating sources and high valleys of the Brahmaputra, the Irrawaddy, the Salween and the Mekong rivers at the border separating India, Burma and China. The camellia leaves are familiar to Chinese, which they used as a part of medicinal compounds and in vegetable relishes. But, the leaves had never been considered an ingredient of a hot, refreshing drink until the emperor's discovery.

The cultivation of tea plant in other countries was started at different time historically. Introduction of the first cultivation to various countries was Indonesia in 1684, India in 1780, Russia in 1833, Sri Lanka in 1839, Malawi in 1875, Iran in 1900, Kenya in 1903, and Turkey and Argentina in 1924. Tea became a popular beverage served in numerous tea houses in London in the late 17th century.

1.2 Botany of Tea Plant

Tea grows in to a small tree about 10 m high with a conical shape, when left unpruned. It is pruned to form a hedge of convenient height for hand plucking or machine harvesting in cultivation. In tropical countries much of the tea produced is grown on steep hillsides at high elevations [4].

The tea shrub is a perennial evergreen plant. Tea comes under the Theaceae family and the Camellia species (Camellia sinensis). Indeed, in addition to the previous two types of varieties there are other varieties. Tea varieties differ in the height of the tea bush, characteristics of their leaves and the number of stems. On branches leaves are produced alternatively, which originate in the leaf axils lower in the canopy having a finely serrated margin. All tea leaves are somewhat shiny and they contain thickened stone cells (scleroids) and glabrous, these are important in the tea-trade because their presence in made tea determine its quality. Leaf growth is of central importance because the leaves provide the yield, with the tea crops. Tea flushes at regular frequency which is not strongly related to climatic changes, though the quantity of leaf produced at flush is highly affected by temperature and rainfall as well as by nutrition. The frequency of plucking depends on the growth rates and flushing; it will vary from one to two weeks in tropics, during the period of flushing. For quality of tea, in general, two leaves and a bud are the ones to be plucked [5]. For continued production, it is very important not to pluck the mature leaves below this; these are called maintenance leaves [6].

1.3 Soil and Climate for Tea Growth

Soil and climate characteristics are the most important ecological factors in growing tea. The variety of the tea plant is also another factor in growing tea. The Assam variety is less hardy than the China variety, for instance, which can tolerate a lower temperature or longer dry season. Under a variety of climate conditions it grows from the humid tropical lowlands to regions of high latitudes in Japan and Russia. Tea leaves are harvested all year around in tropical countries. Harvesting is seasonal in temperate countries. There are many different kinds of products of different quality arising from different cultivation practices, growing conditions and processing methods. For the quality of the black tea leaves and the growth of the tea plant application of fertilizer is also important [7].

For instance, an increase in the potassium application rate increases the amino acid content and polyphenol of the tea. The depletion of the organic matter status of the soil results from the failure to apply fertilizer [8].

1.4 Tea harvesting and processing

The processing method for tea varies, according to the kind of tea desired- white, green, oolong, or black. Every tea master, just like every wine master, has a unique way of creating a special product, but in general, the same basic steps are performed to make leaves into tea. For making tea, every step is not required making tea, for example, black tea involves every stage, while white tea involves only a few.

Once the buds and leaves are plucked, they are brought in from the field within two to three hours for the finest quality tea. If the picked leaves are bruised, left unattended for too long, or allowed to get too warm, the cell walls in the leaf break down and oxidation begins, resulting in an unpleasant, bitter flavour. The taste of tea depends very much on the methods of tea processing. Tea is traditionally classified based on the degree or period of "fermentation" the leaves have undergone. The freshly plucked leaves may undergo one or more of the following processes which is called as an orthodox method of tea processing.

Fig.1.1: Tea leaves plucking process

Tea harvesting is a laborious task that requires some training in order to yield the best results. When plucking the leaves for a high quality tea, they pluck the bud and the second and third leaves only. This is called fine plucking (this is known as "Orthodox" method). Another factor in the picking of young leaves is called a "flush." This is when there is a sprouting of new buds and leaves on a plant. These fresh young leaves and buds are then picked. Here is a general guideline of steps taken in processing tea leaves: Once the tea leaves are collected in baskets they are taken to the factory to be processed. The processing steps taken will depend on the type of tea desired. Common processing terms are withering, rolling, fermentation, and drying or firing.

1.5 Tea Processing

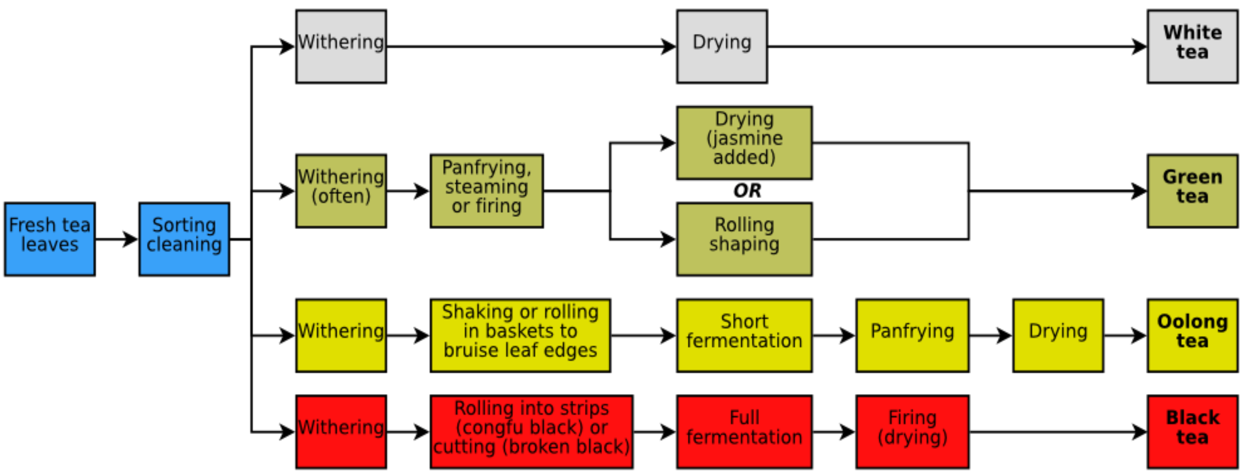

Fig. 1.2: Tea (Camellia sinensis) processing chart

1.5.1 Withering

It is a procedure which brings about physical and chemical changes in the shoots to produce quality, apart from conditioning the flush for rolling by reducing turgor, weight and volume. Previously the flush used to be withered under the sun. Now this process is generally achieved either by thinly spreading the flush on mats, or in thick layers in troughs for 8-18 hours depending on the condition of the leaves.

Fig. 1.3: Process of Withering

1.5.2 **Rolling**

From the withering racks, the leaves are now twisted and rolled so that the leaf cells are broken up. Sometimes shaking is done as well. Oils are released with this rolling process that gives the tea its distinctive aroma. The leaves can be rolled with machinery or by hand. The juices that are released remain on the leaf; a chemical change will occur shortly.

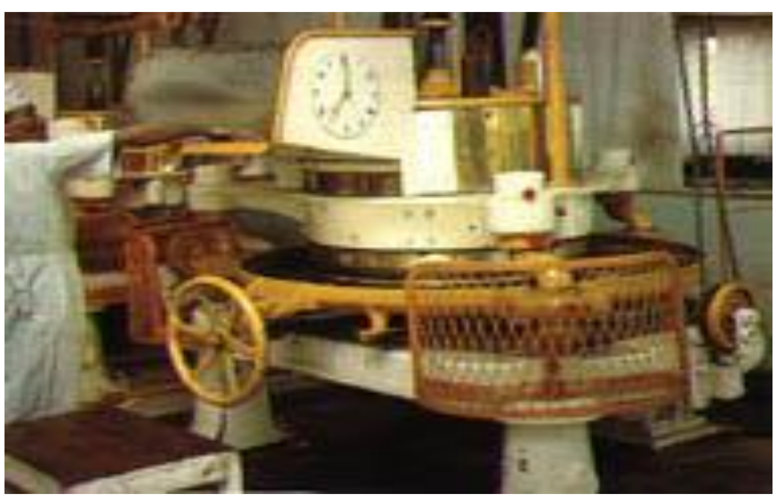

Fig. 1.4: Process of Rolling

1.5.3 Fermentation

It is the process of oxidation of leaves. The mechanical aspect involves spreading out of the leaves macerated by rolling a layer 5-8 cm thick, for 45 minutes to 3 hours, depending on the quality of the leaves. Fermenting machines make the process continuous, that is, every unit of macerated leaf has to be spread out for individual treatment.

Fig. 1.5: Process of Tea fermentation

1.5.4 Firing

The leaves are dried and the fermentation process is retarded. In this stage, the leaves move through hot air chambers to stabilize the leaves and lock in the flavour.

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Fig. 1.6: Process of firing of tea leaves

1.5.5 Grading

The tea will be packed after sorting, consisting of extracting the fibres with the aid of winnowing machines and grading the tea by volumetric weight and size. This is the final stage before longer leaves, such as orange pekoes, are used for loose tea. The left-over fannings and dust leaves are used for tea bags

Fig. 1.7: Process of grading

1.6: Types of Tea

Several major categories of tea are there which are distinguished by different processing methods and, consequently, different concentrations of the chemical components in tea. Prior to further heating and processing depending on the degree of fermentation tea are categorized in to three major varieties: Green tea, Oolong tea and Black tea. An enzymatic oxidation of polyphenols is involved in the fermentation process, leading to the formation of chemical compounds which generates the colour and aroma of black tea.

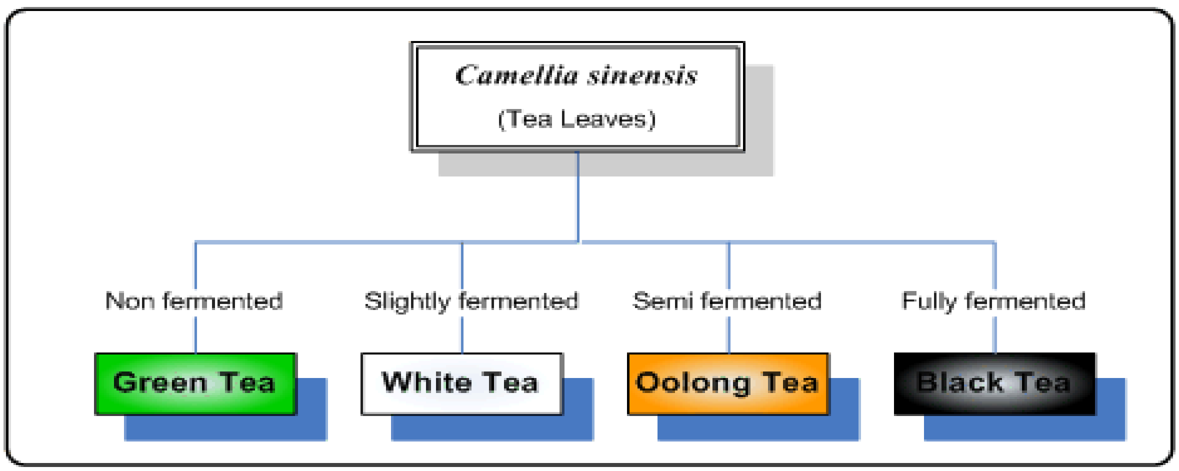


Fig. 1.8: Types of tea

1.6.1 Black tea

The Black tea process goes through the most stages. Once the leaves are picked, they are left to wither for several hours. After the leaves are rolled, oils from the leaves are brought to the surface. These aromatic oils aid in the oxidation process, which last for several hours. The last step consists of placing the leaves in an oven with temperatures reaching up to 200 degrees Fahrenheit. When the leaves are 80 percent dry, the leaves complete their drying over wood fires. The resulting product is brownish (sometimes black) in color and is sorted accordingly to size, the larger grade is considered "leaf grade," and smaller "broken grade" are usually used for tea bags. As compared to green tea and oolong tea, black tea brings a difference in the colour, aroma and chemical composition of the tea leaf, giving 20% of caffeine in a cup of coffee [9].

1.6.2 Oolong tea

Oolong goes through a similar process that black tea goes through. The first two steps are withering and rolling. Instead of rolling, sometimes shaking is done to bruise the outer edges of the leaves. The oxidation period for oolong is half that of black tea. Once the veins become clear and the edges of the leaves become reddish brown, while the centre remains green, the oxidation process is stopped by firing. For oolong tea, the leaves are heated at a higher temperature so that they can be kept longer, due to the lower resulting water content. The chemical composition of Oolong tea is in between the black tea and the green tea.

1.6.3 Green Tea

The process for making green tea is the shortest. Withering is done first, but this step might be omitted. Rolling the leaves to break the membranes for oxidation is skipped, hence the oxidation process is also skipped. After withering, the leaves are pan fried or fired to prevent oxidation from occurring. The last step is to roll the leaves and dry them one last time for its final shape. The green tea leaves usually remain green.

There are other two types of tea in fact; the white and yellow tea regarded as two subclasses of green tea, due to differences in processing, variety, traditional and geographical distributions.

1.6.4 White Tea

White tea is the purest and least processed of all tea. This loose leaf tea has very little caffeine and brews a light brown colour and flavour. White tea also contains healthy antioxidants and is the best for skin and complexion.

1.6.5 Yellow tea

The yellow tea is a specially processed tea similar to green tea but slower with a drying phase, where the damp tea leaves are allowed to sit and yellow. The tea has generally a very yellow-green appearance and a smell different from both white and green tea.

1.6.6 CTC tea

CTC tea, called an unorthodox tea, takes its name from the mechanical "crush, tear, and curl" process used to get cheap, uniform, but inferior tea. Tea derived from this process is generally used for blends or tea bags, and it brews quickly, in two to three minutes. The CTC market is very strong; some estimates that more than 80% of India's tea production is CTC.

1.6.7 The different Grades of tea

Despite more or less intense sifting, bulk obtained after drying are still heterogeneous. Tea ranges in size from that of a speck of dust to a leaf approximately 4 cm long and 1cm wide. The fractions are to be brought to the desired forms and sizes with adequate uniformity and cleanliness conforming to trade requirement. Tea is, therefore, sorted into pieces of roughly equal size and to remove fibre and stalk in the tea. The electrostatically charged rollers are used to remove stalk and fibre, which attract the stalk and fibre preferentially. Four main sizes of tea are produced, namely, Whole Leaf Grades, Brokens, Fannings and Dusts. Within each of these sections tea is further split up into grades of varying qualities.

1.6.7.1 Whole leaf

Whole Leaf grades are the largest sizes produced and depending on the actual grade within the section may range from a long and wiry stem, 1cm to 2 cm in length, to a round and knobby twisted leaf similar in size and shape to that of a small garden pea.

1.6.7.2 Broken grades

Broken grades consist of smaller than the Whole Leaf grades, are generally about 1cm in length and are largely made up of leaf as opposed to stem.

1.6.7.3 Fannings Grades

Fannings grades are smaller still and sizes of more than 1/8 of an inch are rare. Fannings contain small parts of the leaf, which have broken off either during rolling or sorting.

1.6.7.4 Dust grades

Dust grades are self-explanatory regarding size.

1.7 Economic Importance of Tea

As stated in a Chinese document published in 347 A.D, people in Southwest China used tea for paying tribute to the Chinese emperors as early as 1066 B. C. In the essay "Tong Yue", written by a country landlord Wang Bao and published in 59 B.C., there mentioned the making and sale of tea. It showed that tea was commercially available in the local country market, suggesting that tea processing and marketing as early as 59 B.C. in Southwest China. The second most consumed beverage in the world is tea with an estimated 18-20 billion cups consumed daily. The principal tea produced and consumed in the world are black and green tea, with small amount of other types. Black tea represents approximately 78% of total consumed tea in the world, whereas green tea accounts for approximately 20%. India, China, Sri Lanka, and Kenya, are the major producers of tea while the major consumers are India, China, Turkey, and Japan.

The world production and consumption of tea has increased steadily with occasional fluctuation during the 1990s. With unique horticultural and processing methods Camellia sinensis has become a very important agricultural and commercial product. For instance, the leading export crop is tea in Kenya, which places Kenya to be the third largest producer of black tea after India and Srilanka and large amount of money is earned. Tea is regularly exported from Ethiopia to different countries nowadays

1.8 Health Benefits of Tea

It has been scientifically established that tea offers several health benefits to the consumer. Most of the health benefits of the tea are associated with the antioxidant properties of polyphenols called "flavanoids". While much of the research on flavanoids has been done with Green tea, Black tea too contains about the same amount of flavanoids as Green tea. The major difference between Green tea and Black tea is the fact that Green tea has more simple flavanoids called catechins as compared to Black tea, which contains more complex flavanoids called theaflavins and thearubigins. The black tea components have many health benefits to humans. Animal studies and epidemiological studies suggest that tea is protective against certain cancers, neurodegenerative diseases, and cardiovascular diseases [10].

The oxidization process modifies the type of flavonoid and antioxidant activity is similar in both green tea and black tea. Tea has been also used in folk medicine for headaches, pain, digestion, diuretics, enhancement of immune defence, body aches and detoxification, as an energizer to prolong life [11].

1.9 Antioxidative properties of tea

A free radical is an atom, molecule, or compound that is highly unstable because of its atomic or molecular structure (i.e., the distribution of electrons within the molecule). As a result, free radicals are very reactive as they attempt to pair up with other molecules, atoms, or even individual electrons to create a stable compound. These free radicals, unless removed, can cause immense damage to the DNA and other units of the cell. Under normal circumstances, the body is equipped to eliminate the free radicals by itself mainly through the presence of an enzyme called Super Oxide

Dismutase. However, when exposed to harmful conditions such as excessive UV exposure, exposure to smoke or pollution, the number of free radicals produced increases dramatically, which can be harmful to the body.

1.10 The Chemical Composition of Tea

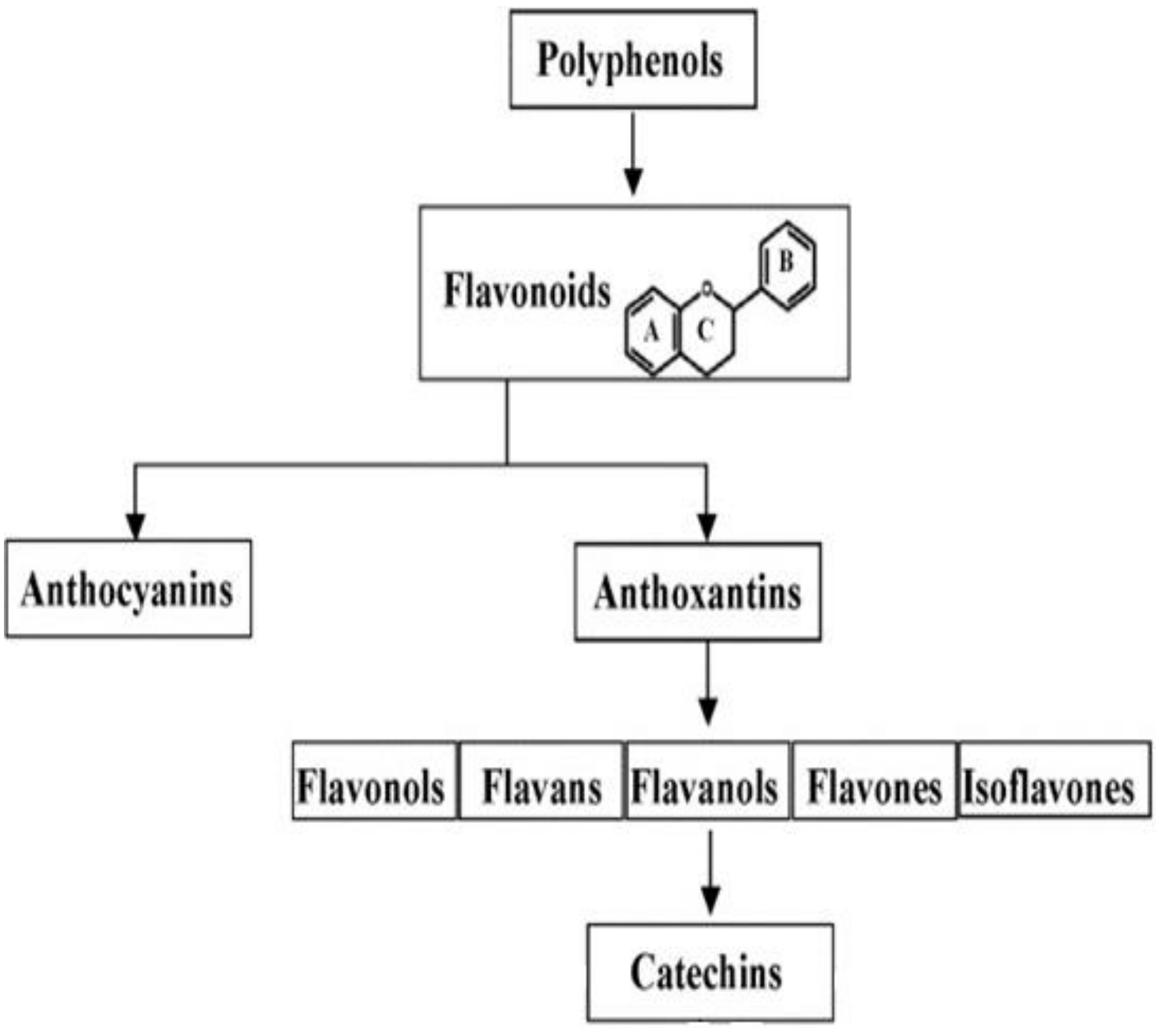


Fig. 1.9: Chemical compounds of tea

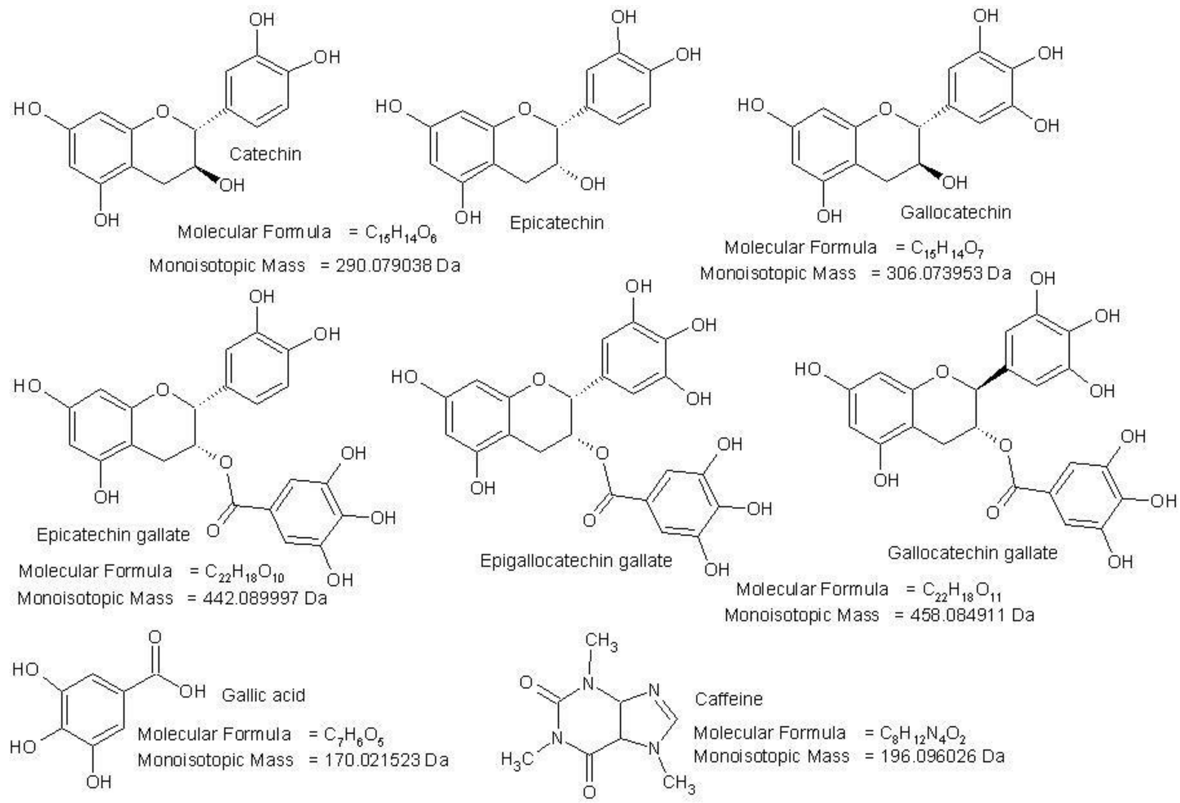


Fig. 1.10: Structures of some biologically active compounds in tea

Depending on different parameters such as the variety of leaf, growing environment, application of fertilizers, manufacturing, particle size of ground tea leaves and infusion preparation the chemical composition of tea may vary. The tea leaves consists of many compounds, such as polysaccharides, volatile oils, vitamins, minerals, purines, alkaloids (eg. caffeine) and polyphenols (catechins and flavonoids). Whereas, all three types of tea have free radical capturing (antioxidising) and antibacterial activities and when the tea becomes darker the efficacy decreases substantially which results due to lower contents of anti-oxidising polyphenols remaining in the leaves.

1.10.1 Flavonoids (polyphenols)

Proven medicinal properties include anti-inflammatory, anti-allergic, antibacterial, antioxidant and antiviral effects and also have the ability to strengthen veins and decrease their permeability. It is widely believed that the antioxidising effects of both black and green varieties are reduced when taken with milk, which is thought to be due to the effective binding of flavonoids by proteins [12].

According to a recent ex vivo study the flavonols are absorbed from tea and their bioavailability is not affected by milk [13].

1.10.2 Tea tannins - called catechins (polyphenols)

Seems to be the most potent therapeutic plant-derived chemicals, aside from their antioxidant and antiseptic properties, they are able to form complexes with other molecules, hence detoxifying the system. Catechins include gallocatechin, epicatechin (EC), epigallocatechin (EGC), epicatechin gallate (EGC) and epigallocatechin gallate (EGCG). Catechins make up approximately one-quarter of fresh dried green tea leaves, among which 60% is comprised of EGCG.

1.10.3 Vitamin C

Du Toit et al., in their recent studies stated that the Black, Green and Oolong tea are all extremely good sources of vitamin C [14].

They stated that one or two cups a day provide the equivalent of three glasses of orange juice or two capsules.

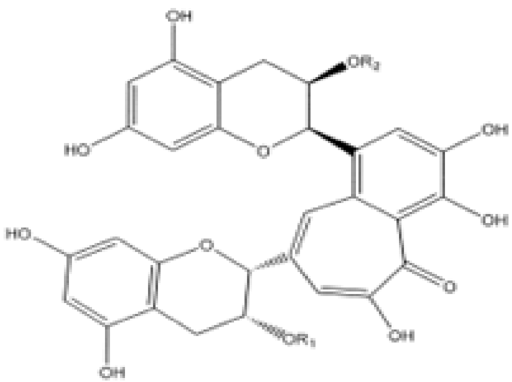
The chemical entities in tea that are generally believed to cause variations in colour and bitterness are mainly the theaflavins (3-6%) and thearubigins (12-18%) of tea solids by weight, respectively. The quantities of each theaflavins and thearubigins, and the ratio of their quantities, both are said to determine the colour characteristics of the tea beverage (tea infusion). For example, a tea with a low level of thearubigins and a high level of theaflavins would tend to give a beverage with a high degree of briskness and a yellow-orange colour. Whereas, a tea with low level of theaflavins and high level of thearubigins would be expected to give a tea infusion with a brown colour and little briskness (a soft tea). An optimum level of each of these chemical groups in a tea may give a tea infusion with a rosy color and appropriate briskness. [15].

Compound	**Description**	**Reaction**	**Health effects**	**Mostly found tea type**
Polyphenol	**Antioxidant**	**Taste**	**Antiviral and antibacterial properties, anti-cholesterolemic**	**Green**
Vitamins	**A (carotene) B (B1,B2, B6,Niacin and Folic acid)**	**Colour**		**Black**

Theaflavin, thearubigins	**Antioxidant**	**Colour and taste**	**Have effects against infection, strengthen human circulatory system, Capillary walls, stroke prevention**	**Black**
Minerals	**Zinc, magnesium, potassium and calcium**	**Colour and taste**	**Boosts immune system, helps prevent cancer and blindness in old age and fights cold, Zinc also helps maintain our senses smell, taste and vision. Important in fighting osteoporosis, high blood pressure, high cholesterol and arthiritis.**	
Tea fibre				
Amino acids		**Taste**	**Tranquilizing effect on the brain for anti-stress.**	**Black**
Carbohydrates				
Caffiene		**Taste**	**Mental clarity and awakeness, excessive amounts are harmful.**	**Black**
Lipid				

Table 1.1: Chemical composition of tea in tabulate form

1.10.4 Theaflavin and thearubigins



		R1	R2
Theaflavin	TF	H	H
Theaflavin 3-gallate	TF3G	Gallate	H
Theaflavin3'-gallate	TF3'G	H	Gallate
Theaflavin3,3'gallate	TFDG	Gallate	Gallate

Fig. 1.11: Structure of theaflavins

During fermentation, the characteristic black tea polyphenols, theaflavins and thearubigins, are generated. Four major theaflavins have been identified from black tea, including theaflavin, theaflavin-3-gallate, theaflavin-3'-gallate, and theaflavin-3,3-digallate (Fig.1.11) [16] .Thearubigin is known as a heterogeneous mixture of pigment.

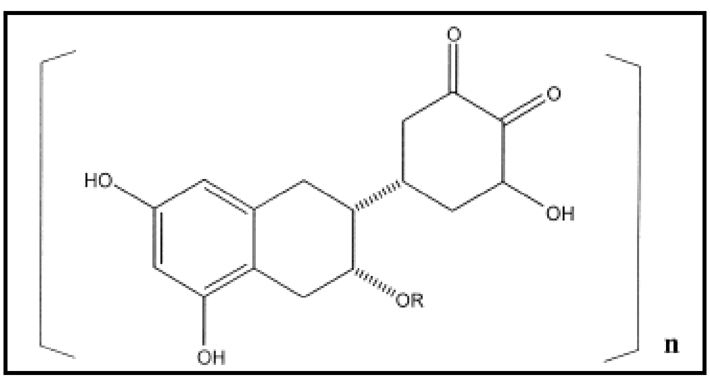


Fig. 1.12: Structure of thearubigins

Thearubigins are polymeric polyphenols that are formed during the enzymatic oxidation (called fermentation by the tea trade) of tea leaves. Thearubigins are red in colour. Therefore, black (fully oxidized) tea gives reddish liquor while a green or white tea gives a much clearer one. The colour of black tea, however, is affected by many other factors as well.

1.11 Geographical distribution of tea in India

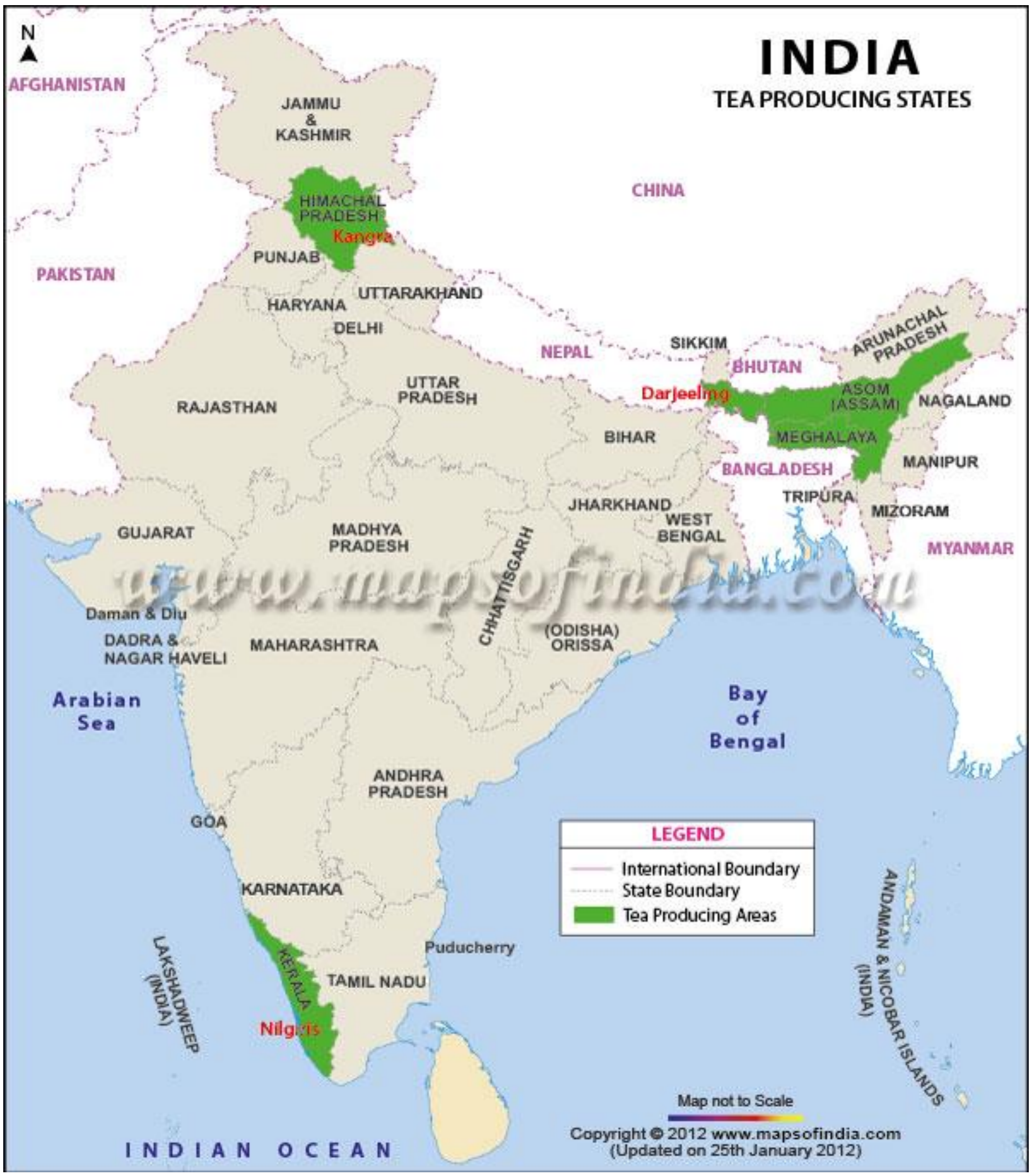


Fig. 1.13: Geographical distribution of tea in India

Indian Tea Industry is about 172 years old. In 1823 Robert Bruce observed tea plants growing wild in upper Brahmaputra Valley.

The first Indian tea from Assam was sent to United Kingdom for Public Sale. Then later it extended to other parts of country between 50's and 60's of the last century.

Tea plantations are mainly located in rural hills and backward areas of Northern Eastern and Southern states. The major tea growing areas in India are concentrated in Assam, West Bengal, Tamilnadu and Kerala. The other areas growing tea to the extent is Karnataka, Tripura, Himachal Pradesh, Uttaranchal, Arunachal Pradesh, Manipur, Sikkim, Nagaland, Meghalaya, Mizoram and Bihar. In India Tea is indigenous and is an area where the country can take a lot of pride. It is mainly due to its pre-eminence as a foreign exchange earner and its contributions to the country's gross national product.

India has emerged as world leader in all aspects of tea production, consumption and export mainly because it accounts for 31% of global production. For last 150 years perhaps the Tea Industry is the only one where India has retained its leadership. The range of tea offered by India - from the original Orthodox to CTC and Green Tea, from the aroma and flavour of Darjeeling Tea to the strong Assam and Nilgiri Tea- remains unparalleled in the world.

1.12 Tea Quality Assessment techniques

Various analytical tools have been reported for estimation of tea quality in terms of colour, tone strength, briskness, astringency and other characteristics attributed to Theaflavins and other factors. In the past few years, tea quality had been assessed using different analytical tools such as, high-performance liquid chromatography [17] , gas chromatography [18], capillary electrophoresis [19], plasma atomic emission spectrometry [20], electronic tongue and lipid membrane taste sensors [21-24].

However, these techniques are complex and have certain limitations and not widely used commercially due to high cost and requirement of skilled personnel and laboratory setup. At present, the assessment of the tea quality is commonly made by sensory evaluation from tea experts, but this is unfortunately susceptible to influence of the environment and subjectivity. To make the evaluation more efficient and objective, several tea experts are usually summoned to assess the tea quality [25]. Thus both for the customers and the tea industry, developing technologies to objectively assess tea quality using a low-cost instrument and discriminate between different tea types is highly desired.

Electronic sensor technology is an application of multi-sensor system which is applied particularly to analyze liquid phase foodstuffs, and had started finding applications in the last decade. Different tasks such as discrimination, classification, quality control and process monitoring have been successfully performed using electronic sensors. The low cost, easy-to-handle measurement set-up and rapidness are the advantages over the well-established analytical methods such as liquid chromatography and spectroscopy.

The main principle used in electronic sensor devices is the application of the array of non-specific chemical sensors with wide sensitivity toward several components. Therefore, the electronic sensor output contains the overlapped information about the sample due to cross-sensitivity of sensors. Several outputs can be derived from this overlapped information with the help of multivariate data analysis. Electronic sensor coupled with multivariate data analysis has proved to be a powerful analytical tool applied widely in foodstuff and beverage. In recent years, intensive studies have been carried out regarding the sensory activity of the individual components of food and alcoholic beverage odours, and the dependence between the odour and the chemical composition of the volatile fraction of these products. The majority of the accomplishments within this area can be attributed to the combination of gas chromatography with olfactometric detection [26].

Testing and developing food uses the results from sensory experiments in which products are systematically presented to people, trained panellists, or random consumers, who score them in various ways. The understanding of the aroma profile will help technologists to enhance the sensory quality of this beverage [27].

The taste sensors introduced by Toko [28] are composed of eight lipid/polymer membranes, and are claimed to be applicable for the qualitative discrimination of mineral waters, beverages (beers and shake), and foodstuffs (tomatoes, sake mash, soybean paste, etc.). These taste sensors have been demonstrated to be useful for the quantitative taste representation. Since 2000, electronic sensors has been attempted to classify different tea categories. The influence of different applied waveforms on discrimination ability between green and black tea by means of pulse voltametric electronic sensor has also been investigated [29].

An application of disposable all-solid-state potentiometric electronic sensor micro-system for the discrimination of Korean green tea was reported [30- 31]. State of the art in the field of Electronic and Bioelectronic Tongues – Towards the Analysis of Wines was reported by Zeravik et al. [32]

The above mentioned studies show that the electronic sensor technique can be employed for tea classification, but no discussion has been undertaken in these studies regarding the classification results obtained by different pattern recognition methods and even an independent sample set was not used in these studies to test the robustness of the identification models. Moreover, a very few studies on the application of electronic sensor technology for the identification of the tea grade level have been reported till date in literature.

In view of the above, this work proposes to employ the electronic sensor based on AC impedance technique for identifying different grades of black tea coupled with pattern recognition through actual sensorial analysis of tea as well as other preformulated and commercially available beverages.

1.13 AC Impedance technique

Electrochemical impedance (also known as AC impedance or the electrochemical impedance) is an electrochemical technique that has gained wide acceptance for quality control, product development and sensory evaluation food technology applications, food quality assurance, corrosion research etc.

AC impedance applications have become a very useful tool in the field of metal packaging with the base materials steel and aluminium, aiming to enhance the corrosion stability and to minimize metal migration into food.

There are few reports available detailing the impact of artificial processes such as commonly-used food processing techniques on the electrical impedance characteristics of fruits and vegetables. The use of AC impedance analysis would provide a new approach to the evaluation of the freshness or quality of processed agricultural products [33]. Main applications are foreseen as the replacement of long-term storage tests to establish the compatibility of food and package material and to work out the specific influence of individual food components [34]. The technique itself is conceptually rather simple [35].

Low amplitude alternating potential (or current) wave is imposed on top of a DC potential (often the corrosion potential with zero imposed current). The frequency is varied from as high as 10^5 Hertz to as low as about 10^{-3} Hertz in one experiment in a set number (often between 5 and 10) steps per decade of frequency [36]. Varying frequency from low to high frequency is also possible. Dividing the input voltage by the output current furnishes the impedance. The variation in impedance values which are also related with the working surface (electrode) is used for the interpretation [37].

For this purpose, metal electrodes, Glassy Carbon electrode standard configuration has been used while two electrodes of conducting polymers have been in house fabricated. The brief introduction of conducting polymers is given below.

1.14 Conducting polymers

Electronically conducting polymers possess a variety of properties related to their electrochemical behaviour and are therefore active materials whose properties can be altered as a function of their electrochemical potential. The importance and potential impact of this new class of material was recognized by the world scientific community when Hideki Shirakawa, Alan J. Heeger and Alan G. MacDiarmid were awarded the Nobel Prize in Chemistry in 2000 for their research in this field [38-39].

Although these materials are known as new materials in terms of their properties, the first work describing the synthesis of a conducting polymer was published in the nineteenth century. At that time 'aniline black' was obtained as the product of oxidation of aniline, however, its electronic properties were not established [40].

The conducting polymers may be divided into three categories:

1. Redox polymer.
2. Ion conducting polymer.
3. Inherently conducting polymers.

Ionically conducting polymers (polymer/salt electrolytes) are of great interest because they exhibit ionic conductivity in a flexible but solid membrane. Ionic conductivity is different than the electronic conductivity of metals and conjugated conducting polymers, since current is carried through the movements of ions. They have been critical to the development of devices such as all-solid-state lithium batteries.

In 'conjugated conducting polymers', the redox sites are delocalized over a conjugated π system, however, 'redox polymers' have localized redox sites. The redox polymers are well known to transport electrons by hopping or self-exchange between donor and acceptor sites. The redox conductivity is comparatively lower than that of conjugated conducting polymers, likely due to slow electron transport to from the redox centre [41].

An organic polymer that possesses the electrical and optical properties of a metal while retaining its mechanical properties and processability, is termed as an 'intrinsically conducting polymer' (ICP). These properties are intrinsic to the 'doped' form of the polymer. The conductivity of ICPs lies above that of insulators and extends well into the region of common metals; therefore, they are often referred to as 'synthetic metals'. The common feature of most ICPs is the presence of alternating single and double bonds along the polymer chain, which enable the delocalization or mobility of charge along the polymer backbone. The conductivity is thus assigned to the delocalization of π-bonded electrons over the polymeric backbone, exhibiting unusual electronic properties, such as low energy optical transitions, low ionization potentials and high electron affinities of the many interesting conducting polymers that have been developed over the past 30 years, such as polyaniline/ polypyrrole/ polythiophenes/polyphenylene and poly (*p)* phenylene vinylene have attracted the most attention. In order to make conjugated polymers electronically conductive, it is necessary to introduce mobile carriers into the conjugated system; this is achieved by oxidation or reduction reactions and the insertion of counter ions (called ‘doping’).

During the doping process, an organic polymer, either an insulator or semiconductor having small conductivity, typically in the range of 10^{-10} to 10^{-5} S/cm, is converted to a polymer which is in a ‘metallic’ conducting regime (1 -10^4 S/cm).

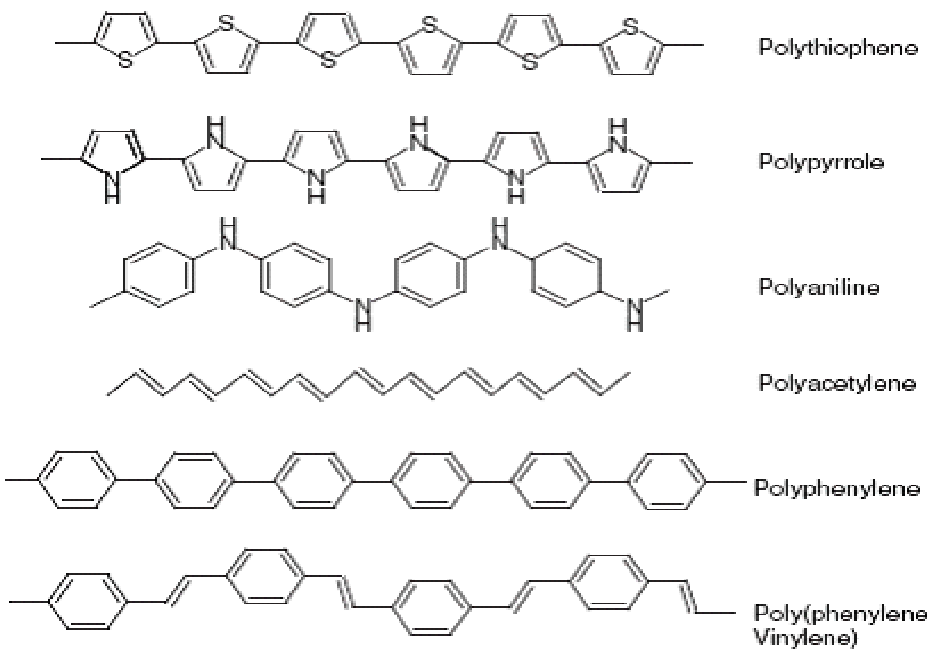


Fig.1.14: Structure of conjugated polymers

The highest value reported to date has been obtained in iodine-doped polyacetylene (>10^5 S/cm) and the predicted theoretical limit is about 2×10^7, more than an order of magnitude higher than that of copper. Conductivity of other conjugated polymers reaches up to 10^3 S/cm [42].

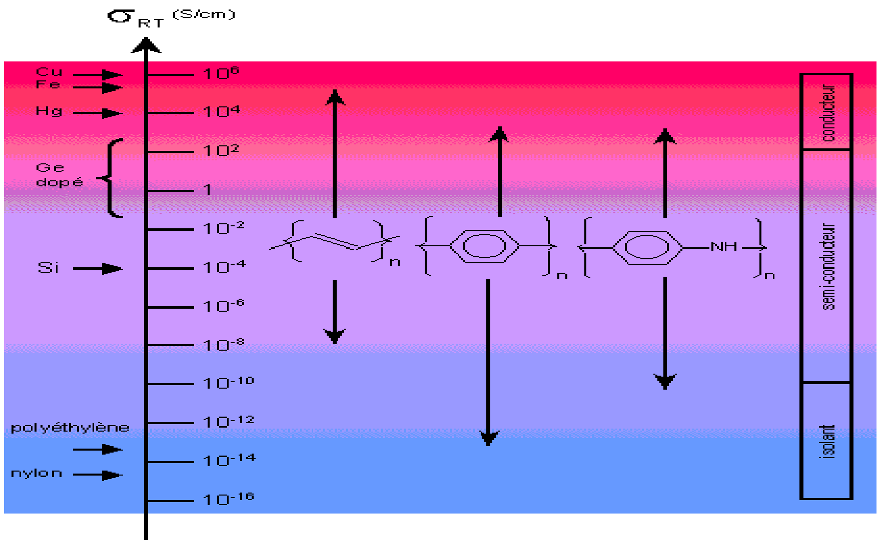


Figure 1.15: Conductivity range of different materials

Conducting polymers are unusual in that they do not conduct electrons *via* the same mechanisms used to describe classical semiconductors and hence their electronic properties cannot be explained well by standard band theory. The electronic conductivity of conducting polymers results from mobile charge carriers introduced into the conjugated π-system through doping. To explain the electronic phenomena in these organic conducting polymers, new concepts including solitons, polarons and bipolarons have been proposed by solid-state physicists. The electronic structures of π-conjugated polymers with degenerate and nondegenerate ground states are different. In π-conjugated polymers with degenerate ground states, applications are important and dominant charge storage species. Polyacetylene, $(CH)x$, is the only known polymer with a degenerate ground state due to its access to two possible configurations as shown in Figure 1.16. The two structures differ from each other by the exchange of the carbon–carbon single and double bonds. While polyacetylene can exist in two isomeric forms: cis and trans, the trans-acetylene is thermodynamically more stable [43].

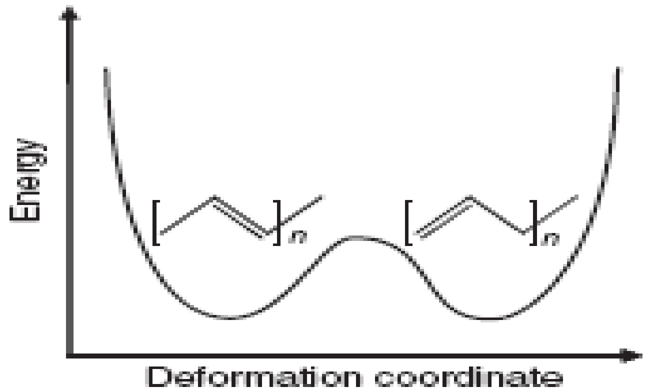


Fig.1.16: Energetically equivalent forms of degenerate polyacetylene

Oxidative (p-type) doping of polyacetylene involves the chemical or anodic oxidation of the polymer to produce carbonium cations and radicals with simultaneous insertion of an appropriate number of anions between the polymer chains that neutralize the charge as shown in Fig.1.17 [44]. Two radicals can then recombine to give a spinless dication referred to as a positive soliton, which can act as the charge carrier [45].

Each soliton constitutes a boundary which separates domains that differ in the phase of their π-bonds. In solid-state physics a charge associated with a boundary or domain wall is called a soliton, because it has the properties of a solitary wave that can move without deformation and dissipation [46].

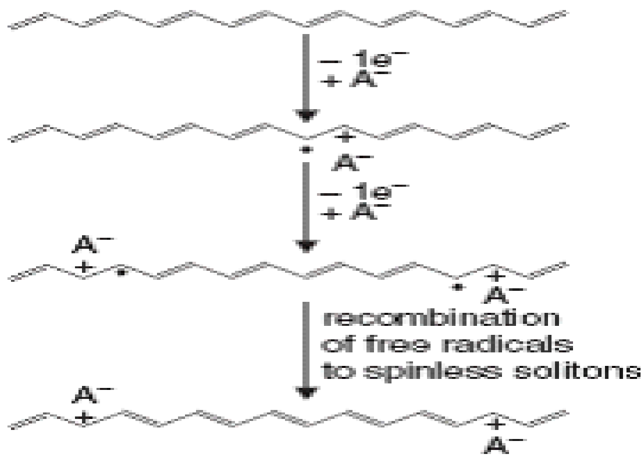


Fig.1.17: p-type doping in polyacetylene

The π-conjugated systems based on aromatic rings, such as polythiophene, polypyrrole, polyaniline, polyparaphenylene and their derivatives have non-degenerate ground states. In these polymers, the ground-state degeneracy is weakly lifted so that polarons and bipolarons (confined soliton pairs) are the important and dominant charge storage configurations.

1.15 Data Analysis using chemometric technique Principal Component Analysis

Classification of tea from electronic sensor data is complex primarily due to the fact the data set obtained is small compared to other applications of classification. As a first step, exploratory data analysis has been performed using principal component analysis (PCA) to identify underlying clusters in the electronic sensor signatures. PCA is a statistical technique for the reduction of input data dimension and is largely used for feature extraction. It captures the relevant information in a set of input data providing a lower dimension, but informative representation of the original data. It sequentially creates a set of principal components from the original data. The first principal component (PC1) maps the maximum variance and information of the input data followed by the other principal components (PC2, PC3 and so on) in descending order of the variance. Generally a good discrimination is mapped by the first two principal components i.e. PC1 and PC2 [47-49].

1.16 Gap in Current Studies

Various methods based on techniques like potentiometry, voltametry and conductivity has been generally employed for the quantification of the some of the parameters of ready tea for quality classification. However each method has some limitation in terms of either lower in sensitivity or tedious procedures for sample preparation/handling and use of number of costly instrumentation/data interpretation. Therefore further research in this field is required in terms of development of new and more efficient sensors and techniques. A method involving AC Impedance technique based on a multi sensor response (non specific) has been proposed for the classification of different types of Indian black tea. The AC Impedance method is used to record the impedance plots or the part of it (possibly at only one or more frequencies) for qualitative and quantitative analysis. The samples which are measured are often complex matrices, and certainly non-ideal, so that the filming of simple equivalent circuits to the experimental data is not easy or obvious. The data has been obtained in the form of Nyquist and Bode plots to get various parameters like real impedance, virtual impedance, resistance and others. The bulk data has been analyzed using chemometric methods in which PCA has deployed as main tool in our studies. The pattern generated will be able to classify the tea liquor and behaviour how these tastants behave which has been computed with the known data available with tea tastes or from the existing literature.

1.17 Objectives of the present study

To study the response of 6 different sensing/working electrodes for various tea liquors/DI water in impedance mode & to generate a specific pattern.

1. Develop conducting polymer sensors of Polyaniline and Polypyrrole adding different dopants and their characterization.
2. To make an array of sensors of Metal Electrode, Glassy Carbon and Conducting Polymer.
3. To conduct AC Impedance Studies using this array of Sensors.
4. To find significant sensorial parameter using PCA.
5. Validation of Impedance based output with conventional Sensorial Analysis.