Quantitative and Qualitative Analysis of Green Tea, White Tea and Hibiscus Extract and Their Performances As Corrosion Inhibitors

Cyril Okhio* Ph.D., C.Eng., Mar Tia Adams** B.Sc.

ABSTRACT: Scientists have been trying to understand and control corrosion for as long as they have used iron and steel. A large number of nations spend about 6% of their total gross domestic product in addressing corrosion-related issues. In the United States alone, this amounts to over $550 billion a year. This is not economical, consequently, there is a need to investigate and produce cost-effective and non-toxic methods for reducing, preventing, and treating corrosion. The chemical process industry is one of the largest and most economically important groups of industries that are committed to this effort. The goal of this project is to contribute to the research on the development of materials and methods for corrosion protection using organics such as green, white, and hibiscus tea extracts. This is because organic resins are less contaminating than inorganic alternatives. This work describes the quantitative and qualitative analysis of the aforementioned plant extracts. A sample of each tea was extracted using ethanol, hexane and acetone respectively. After extraction, each sample was analyzed using gas chromatography. Samples of each tea were then boiled and applied to steel plates under laboratory conditions and allowed to dry well. They were then subjected to aggressive corrosive environments in accordance with the ASTM B117 corrosion testing conditions and evaluated thereafter. It was conclusive that the sorrel extract provided the most effective corrosion protection for the steel plates.

Keywords: Corrosion, Organic Extracts, Protection.

1.0 BACKGROUND

The corrosion process is one that occurs in metal as a result of oxidation and occurs over a period of time at almost all temperatures. The type of corrosion mechanism and its rate of attack depend on the exact nature of the atmosphere in which the corrosion takes place. Although the term is usually applied to metals, materials including ceramics, plastics, rubber, and wood, deteriorate at the surface to some extent when they are exposed to certain combinations of liquids and/or gases. Common examples of metal corrosion are the rusting of iron, the tarnishing of silver, the dissolution of metals in acid solutions, and the growth of patina on copper. Most research into the causes and prevention of corrosion involves metals since the corrosion of metals occurs much faster under atmospheric conditions than does the corrosion of nonmetals. Chemical corrosion is an important phenomenon to consider in the sectors of transportation (bridges, pipelines, cars, airplanes, trains and ships), utilities (electrical, water, telecommunications, and nuclear power plant), production and manufacturing (food industry), microelectronics, and petroleum refinery.

Since corrosion is the deterioration of a material as a result of reaction with its environment, especially with oxygen, it must not only be monitored but also be factored into the design of different components. For example, "A recent incident occurred at a nuclear power plant where significant corrosion led to a hole (approximately 6 inches deep, 5 inches long and 7 inches wide) in a holding tank where corrosion had occurred at an approximate rate of 2 inches per year. The corrosion was due to a leaking boric acid that was used as a coolant bath for uranium rods. If it were not detected and if it were not for the design of the stainless steel plate that held up under corrosive conditions and high pressures, a major nuclear accident could have occurred."[1] The trick to preventing corrosion is to either come up with a coating that can prevent direct contact with the reactant or apply a counter driving force to slow down the kinetics.

Corrosion is typically an electrochemical process in which the corroding metal behaves like a small electrochemical cell. Electrochemical corrosion is the most common form of attack of metals, and it occurs when metal atoms lose electrons and become ions. As

the metal is gradually consumed by this process, byproduct of the corrosion process typically forms. Electrochemical corrosion occurs most frequently in an aqueous medium, in which the ions are present in the solution, soil, or moist air. To illustrate the electrochemical nature of the process, a sheet of steel exposed to a water solution containing dissolved oxygen is the site of oxidation and reduction half-reactions, which occur at different locations on the surface. At anodic areas, steel is oxidized according to the reaction. At the same time, oxygen molecules in the solution are reduced at the cathodic areas. The two processes produce an insoluble steel hydroxide in the first step of the corrosion process: Generally, this steel hydroxide is further oxidized in a second step to produce the flaky, reddish-brown substance that is known as rust. Unfortunately, this new compound is permeable to oxygen and water, so it does not form a protective coating on the steel surface and the corrosion process continues. All metals exhibit a tendency to be oxidized, some more easily than others. A tabulation of the relative strength of this tendency is called the electromotive series of metals.

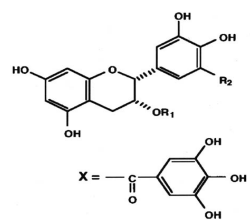
Another common type of corrosion is galvanic corrosion, which occurs at the contact point of two metals or alloys with different electrode potentials. An example of this is brass detail in contact with copper hot-water pipes. The brass becomes anodic and suffers the loss of its zinc atoms. Brass in contact with galvanized steel is protected, while the zinc coating on the steel is first dissolved, leaving the steel open to attack for the same reason. An area of concern is the use of one type of metal as bolts, screws, and welds to fuse together pieces of another metal. The combination to be desired is the large anode-small cathode combination. Bolts and screws should therefore be made of the metal that is less likely to be oxidized so that the bolt or weld is cathodically protected.

The conductivity of the corroding solution is of great importance. When large areas of the surface are in contact with a water solution of high conductivity, such as seawater, the attack on the anodic metal may spread far from its contact point with the cathodic metal. This is a less severe situation than that which occurs in soft water or under atmospheric conditions in which the attack is localized in the vicinity of the contact. In the absence of dissolved oxygen or hydrogen ions to maintain the cathode process, galvanic corrosion does not occur. However, in order to fully understand how metal corrodes, one must comprehend that most metals are crystalline in nature, they generally are not continuous single crystals, but rather are collections of small grains or domains of localized order. Metal objects are formed from melts in which microcrystal form as the liquid cools and solidifies. In the final state, these microcrystal have different orientations with respect to one another. The edges of the domains form grain boundaries, which are examples of planar defects in metals. These defects are usually sites of chemical reactivity. The boundaries become anodic, while the grains themselves are the cathodes. The boundaries are also weaknesses, the places where stress cracking begins.

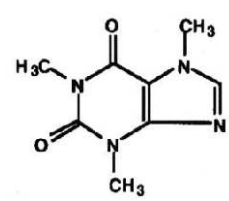
The rate of corrosion can be calculated from the amount of metal plated on the cathode in electroplating, or removed from the metal by corrosion, and can be determined from Faraday's equation:

$$w = \frac{I \times t \times M}{n \times F} \quad \text{----------} \quad (1)$$

where w is the weight plated or corroded in grams (g), I is the current in Amperes (A), M is the atomic mass of the metal, n is the valence number of the metal ion, t is time in seconds (s), and F is Faraday's constant (96,500 Coulombs). It is possible to combine different metals such as copper and steel in closed hot-water systems with little corrosion.

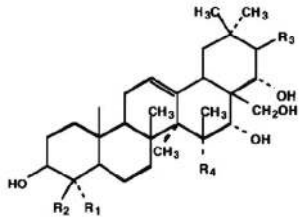


Catechins[13]

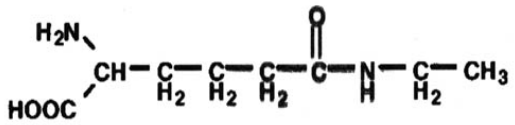


Caffeine[13]

Compound	Concentration (mg/kg)
Terpenes and alcohols	350
Polyphenols	30
Carboxylic acids	2100
Nitrogen containing compounds	240
Alkaloids	5-50



Saponins[13]



Theanine[13]

Corrosion can be prevented or contained using different techniques that include the use of coating, and anodic and cathodic protection. These coatings act by isolating the anode and cathode regions. Coatings also prevent the diffusion of oxygen or water vapor which are usually initiators of corrosion or oxidation. Paint is the most common coating used to slow the rate of atmospheric corrosion. Many other materials, such as plastics, ceramics, rubbers, and even electroplating, can be used as protective coatings. The corrosion resistance of a metal can be greatly increased by the proper choice of alloys. Many of the coatings used to prevent or slow metallic corrosion are organic resins. Temporary coatings, such as grease or oil, provide some protection, but are easily disrupted. Organic compounds such as paint or ceramic coatings, such as enamel or glass, provide better protection. However, if the coating is disrupted, a small anodic site is exposed that undergoes rapid, localized corrosion.

The first step in preventing material corrosion is to understand its specific mechanism. The second more complex step is in designing a type of prevention. Some metals produce corrosion byproducts that are insoluble, which are about the same molecular size as the parent metal, and crystallize in the same type of lattice structure. These are often able to become attached to the metal surface and form protective coats against further corrosion. The patina that forms on copper is an example of this type of coating. Other preventive measures involve the use of protective coatings and modification of the environment. Some trace impurities can significantly reduce the rate of corrosion and can be added in low concentration to the surrounding medium.

Studies on Tobacco demonstrate that Tobacco extracts represent a major new initiative in corrosion inhibition with the advantages of low costs and high effectiveness, combined with the absence of toxicity and polluting effects." Tobacco was first developed by John Rolfe in the 17th century, and its commercial exploitation has continued ever since. Despite its popularity, the tobacco plant does not have many other uses aside from human consumption. The tobacco plant consists of at least 2549 individual constituents that have been identified in tobacco products. It has fairly high concentrations of alkaloids, fatty acids, nitrogen, sulfur, and oxygen-containing compounds, as well as poly-nuclear aromatic hydrocarbons.

Inhibiting corrosion with Tobacco: The corrosion problem is widespread, costly, and has no easy solution. The need for better protective coatings and linings will provide the impetus to those industries that deal with materials development for years to come. Particular importance is the relatively high concentrations of alkaloids, fatty acids, and nitrogen-, sulfur-, and oxygen-containing compounds, as well as poly-nuclear aromatic hydrocarbons in tobacco. These compounds contain active groupings or chemical structures that suggest they may be electrochemically active that suggest that they may react with a metal surface and inhibit metallic corrosion. As shown in Table 1, the relatively high concentrations of large molecules with possible electrochemical activity within tobacco products led to preliminary studies on their possible use in corrosion inhibition.

Table 1-1 Concentrations of Electro-active Compounds in Tobacco

"Other than venerability, there would appear to be little connection between the electrochemical phenomenon of metallic corrosion and the tobacco plant until one considers what is present in tobacco."

In this effort, tobacco has been used as a standard for tea because tobacco contains some of the electrochemical compounds needed to inhibit corrosion.

Green tea products have also become increasingly common on the market today. Used for thousands of years in both China and Japan, green tea is reputed to provide major health benefits. *Green tea comes from a tea plant native to Asia called,* ***Camellia sinensis***. What makes green tea different, and green, is not the plant used to make the tea, but how the plant is processed. Green teas are the least processed of commercial teas and the method used preserves more nutrients. Green tea leaves are picked and then immediately fired, a tea processing term which means that the leaves are either steamed or heated. The tea leaves are then dried and prepared for either sale or further processing. Other teas are picked and dried by a process commonly called "withering", rolled or broken which induces oxidation, and then dried.

Hibiscus, or Rosemallow, is a large genus of about 200–220 species of flowering plants in the family Malvaceae aka the mallow family, along with members like cocoa, cotton, okra, baobab and durian. The hibiscus plant is a native of warm temperate, subtropical and tropical regions throughout the world. The genus includes both annual and perennial herbaceous plants and woody shrubs and small trees.

White tea is tea manufactured by a process that uses relatively low heat and no rolling. The formative stage is an extended period of withering, during which enzymatic reactions progress under the right temperature, humidity and airflow. The key is to get the fresh leaves to mature properly with minimal oxidation.[2] White tea usually contains buds and young tea leaves, which have been found to contain lower levels of caffeine than older leaves, suggesting that the caffeine content of some white teas may be slightly lower than that of green teas. [3]

White tea is a specialty of the Chinese province Fujian. [4] The leaves come from a number of varieties of tea cultivars. The most popular are *Da Bai* (Large White), *Xiao Bai* (Small White), *Narcissus* and *Chaicha* bushes. According to the different standards of picking and selection, white teas can be classified into a number of grades, further described in the varieties section.

Table 1-2 The Teas contain six primary Catechin compounds and three alkaloids

Catechin compounds and Alkaloids
catechin
gallaogatechin
epicatechin
epigallocatechin
epicatechin gallate
apigallocatechin gallate (also known as EGCG
Alkaloids:
caffeine
theobromine
theophylline

2.0 INTRODUCTION

Tea (green, hibiscus and white) was chosen as an inhibitant because they have been analyzed to have high concentrations of alkaloids and polyphenols which act as reducing agents used to slow the electrochemical process in corrosion. Tea is also environmentally friendly, having less environmentally damaging effects than most other contaminants.

Type A	Characteristics
Type IA	Reduce corrosion rate but do not completely prevent corrosion
Type IIA	Provide temporary immunity be delaying onset of corrosion
Type IIIA	Form passive film (oxide or insoluble salt) on metal surfaces

Table 2-1 Type-A Corrosion Inhibitors

Many nitrogen and polyphenols compounds are able to inhibit corrosion in metals but they vary depending on the mode of action and their effectiveness in diverse conditions. One major class of a corrosion inhibitor is known as Type A. Type A inhibitors react with metal, typically by forming a protective layer or film on the surface.

3.0 DESCRIPTION OF APPROACH

***Experimental Procedure*:**

Phase 1: Extraction

(1) Three 20ml samples of hexane was measured and placed in three separate flasks
(2) The same was done for samples of acetone and ethanol
(3) Weighed 2.0g of the green tea, white tea and sorrel
(4) Each sample of tea was placed in each of the flask that were prepared in number 1 and 2 above
(5) Samples were allowed to sit for twenty four hours

Phase 2: Vial Preparation

(1) A vial was prepared for each from the extraction phase
(2) A syringe was used to measure 1µl of each sample, a filter was placed over the tip of each syringe before the samples were injected into the vials
(3) The syringe was rinsed several times between each transfer with its base solvent
(4) Each vial was recapped and placed in the gas chromatography instrument to be analyzed, results of the analysis were recorded and can be seen in the results section of this report

Phase 3: Sea water and Corrosion

(1) Three beakers of 3% salt water solutions were prepared by placing 3.0g of salt into 100ml of water
(2) 2.0g of each tea was allowed to boil for 15minutes to prepare the coat for each steel plate
(3) After boiling, each steel plate was coated both back and front with the tea
(4) Each plate was then placed in the salt water solution and allowed to sit for 48 hours, observations were made and recorded at both 24 and 72 hour intervals

The Instrumentation for the analysis of Green tea and tobacco was a Gas-liquid chromatography (GLC), or simply gas chromatography (GC). It is a type of chromatography in which the mobile phase is a carrier gas, usually an inert gas such as helium or an un-reactive gas such as nitrogen, and the stationary phase is a microscopic layer of liquid or polymer on an inert solid support, inside glass or metal tubing, called a column.

Gas Chromatography GC Analysis: In a GC analysis, a known volume of gaseous or liquid analyte is injected into the "entrance" (head) of the column, usually using a micro-syringe, (solid phase micro-extraction fibers, or a gas source switching system). As the carrier gas sweeps the analyte molecules through the column, this motion is inhibited by the adsorption of the analyte molecules either onto the column walls or onto packing materials in the column. The rate at which the molecules progress along the column depends on the strength of adsorption, which in turn depends on the type of molecule and on the stationary phase materials. Since each type of molecule has a different rate of progression, the various components of the analyte mixture are separated as they progress along the column and reach the end of the column at different times (retention time). A detector is used to monitor the outlet stream from the column; thus, the time at which each component reaches the outlet and the amount of that component can be determined. Generally, substances are identified (qualitatively) by the order in which they emerge (elute) from the column and by the retention time of the analyte in the column.

A detector is used to monitor the outlet stream from the column; thus, the time at which each component reaches the outlet and the amount of that component can be determined. Generally, substances are identified (qualitatively) by the order in which

they emerge (elute) from the column and by the retention time of the analyte in the column.

Sample Size and Injection Technique: The real chromatographic analysis starts with the introduction of the sample onto the column. The development of capillary gas chromatography resulted in many practical problems with the injection technique. The technique of on-column injection, often used with packed columns, is usually not possible with capillary columns. The injection system, in the capillary gas chromatograph, should fulfill the following two requirements: The amount injected should not overload the column. The width of the injected plug should be small compared to the spreading due to the chromatographic process. Failure to comply with this requirement will reduce the separation capability of the column. As a general rule, the volume injected, V_{inj}, and the volume of the detector cell, V_{det}, should be about 1/10 of the volume occupied by the portion of sample containing the molecules of interest (analytes) when they exit the column.

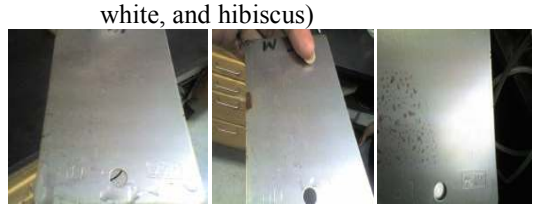
The output data were recorded as a series of peaks, each one representing a compound in the mixture passing through the detector. As long as care was taken to control the conditions on the column, the retention times can be used to help to identify the compounds present, provided, of course, pure samples of the various compounds under those identical conditions have been previously measured and identified.

Figure 13. Experimental Data Peaks

But you can also use the peaks as a way of measuring the relative quantities of the compounds present. This is only accurate if you are analyzing mixtures of similar compounds, for example, of similar hydrocarbons. The areas under the peaks are proportional to the amount of each compound which has passed the detector, and these areas can be calculated by suitable software in the computer connected to the data display. The areas it would measure are shown in green in the (very simplified) diagram. Note that it is not the peak height that matters, but the total area under the peak. There might be a lot of one compound present, but it might emerge from the column in relatively small amounts over quite long periods. Therefore, measuring the area rather than the peak height is essential.

4.0 EXPERIMENTAL RESULTS

1.) Initially coated steel plates with tea (green, white, and hibiscus)



Figures 1-3 Initial Coating of Plates

2.) 24hours after seating in 3% salt solution

Figures 4-7 Plates after 24 hrs

Corrosion resin has formed above the area slightly below the steel plate coated with tea extract. The most effective tea extract was the sorrel (on the far right). The first plate is white tea. Both middle plates are green tea.

3.) 48hours after seating in 3% salt solution

Figures 8-10 More Corrosion Results

Figures 11: Experimental Setup.

Figures 12: Data Analysis Tools [13]

More corrosion resin has formed above the and slightly below the steel plate coated with tea extract. The most effective tea extract is still the sorrel with very little corrosion at the bottom of the plate at 100 ml measurement (on the far left). Middle and last plate is white tea.

5.0 DISCUSSION

After the extractions, each sample was analyzed using gas chromatography. Then samples of each tea were boiled and applied to steel plates and allowed to dry for 48 hours. After which time it was observed that the sorrel had presented itself as the most effective in preventing the onset of corrosion of the steel plates. Based on the results that were presented in the previous section, the sorrel portrayed the greatest efficiency as an inhibitor of corrosion when compared to both green and white teas. All the samples that were analyzed had active phenols and alkaloids, however, the sorrel had very high concentrations of alkaloids and polyphenols which may have been the contributing factor to its ability to better prevent corrosion. The teas ability to prevent corrosion is evident.

6.0 CONCLUSION

This project was designed to develop non-toxic, organic, renewable solutions for corrosion prevention using green and white tea and hibiscus flower extracts. The use of ethanol, hexane, and acetone to extract each tea contributed to a significant reduction in the cost of acquiring the polyphenols and alkaloids which are the active components. The solvents (ethanol, hexane and acetone) were used to extract soluble compounds from a mixture in order to examine the teas polar and non-polar characteristics. This experiment contributes to producing a more cost-efficient method for reducing, preventing, and treating corrosion. Many different approaches could be applied that may change the outcome of the rate of corrosion on the steel plate and the concentration of extracted tea coated on them. There are several coating techniques that may be applied to enhance the efficiency of the results that were obtained such as grease and oil. However, grease and oil were not applied in the best interest of this design because they are known to be easily disrupted with time.

7.0 REFERENCES

[1] The Science and Engineering of Materials, Thompson Brooks and Cole (2003), Donald R. Askland and Pradeep P. Phule': Prentice Hall. ISBN 0-534-953-5

[2] Studies: Green Tea May Help Prolong Life, Senay: Research Also Shows Benefits For Skin, Few Drawbacks - CBS News

[3] Efficacy of a green tea extract rich in catechin polyphenols and caffeine in increasing 24-h energy expenditure and fat oxidation in humans - Dulloo et al. 70 (6): 1040 - American Journal of Clinical Nutrition

[4] Amazing-green-tea, "Chinese White Tea - The Complete Guide"., amazing-green-tea.com

[5] PubMed Medline, "National Taiwan University - PubMed"., Institute of Biochemistry, College of Medicine, National Taiwan University, Taipei, Taiwan

[6] Jane Pettigrew, "The Tea Companion". page 129, Running Press Book Publishers (September 7, 2004)

[7] Kit Chow, "All the Tea in China". page 129, China Books & Periodicals Inc. (September 1990)

[8] Puerh Cha, "China's Luxurious White Puerh Tea".

[9] IUPAC Nomenclature for Chromatography IUPAC Recommendations 1993, Pure & Appl. Chem., Vol. 65, No. 4, pp.819-872, 1993.

[10] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* 1978, *43(14)*, 2923-2925. (doi:10.1021/jo00408a041)

[11] Pascal Bailon, George K. Ehrlich, Wen-Jian Fung and Wolfgang Berthold, An Overview of Affinity Chromatography, Humana Press, 2000. ISBN 978-0-89603-694-9, ISBN 978-1-60327-261-2.

[12] International Organization for Standardization, Procedure 719 (1985) Jones, Denny (1996). *Principles and Prevention of Corrosion*, 2nd edition, Upper Saddle River, New Jersey: Prentice Hall. ISBN 0-13-359993-0.

[13] Tea Components by H. Takayanagi et al., Tea Res. J., No.61, 20, (1985)

http://www.o-cha.net/english/cup/pdf/38.pdf

[14] Inhibiting Corrosion with Green Tea, Sheyreese M. Vincent, Okhio, C. The Journal of Corrosion Science & Engineering, Vol. 7, #36, 2005.

Acknowledgement:

We acknowledge with thanks the contributions made by Ms. Beverly C. Okhio in the detail review of this publication and the very many meaningful contributions to its contents.