

Development of Sensor for Free Available Chlorine Estimation in Surface Water

by

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Master of Science in Chemistry



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Abstract

The development of portable sensors that can be used outside the lab is an active area of research in the electro analytical field. A major focus of such research is the development of low-cost electrodes for use in these sensors. Current electrodes, such as glassy carbon, platinum or gold electrodes, are costly and require time-consuming preparation. In this work an alternatives have been proposed, where pencil graphite electrodes (PGEs) has been used as sensing platform.

Surface of pencil has been used to make it suitable for estimating free chlorine in water sample. Chlorine is a common disinfectant in the water industry, and the residual free chlorine concentration in water distributed to the consumers must be lower than the value set by the regulatory bodies. The pencil graphite-electrode shows high selectivity, low detection limit and linear response to free chlorine in the relevant concentration range at the applied potential of 1.5V and no response to commonly interfering ions such as NO_3^- , SO_4^{2-} , CO_3^{2-} , Cl^- , HCO_3^- has been observed. Further investigation has been conducted on the storage stability and response time on FAC sensing. The sensitivity of free chlorine has been found to be $50\mu\text{AmM}^{-1}\text{cm}^{-2}$. The pencil graphite electrodes were also used for detection of chlorine with a relatively wide concentrations ranging up to 8 mM, with a limit of detection of 46 μM . It exposes that the stability of PGEs 97.93% after 14 days of its initial activity. This sensor is being proposed as a low cost device for determining free chlorine in water samples with short response time of t_{90} less than 5 sec.

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CHAPTER I

Introduction

1.1 General

Chlorine has been used for the disinfection of public water supplies for over 100 years. More than the allowed federal standard amount of (4 mgL⁻¹) free available chlorine in drinking water causes strong respiratory and dermal damage to human. [1,2]. Chlorine in aqueous solutions is used for a number of purposes, such as disinfection and bleaching, and also as a powerful oxidizing agent in various manufacturing processes. It is known that chlorine is highly toxic, and additionally it can further react with other substances, such as phenols to produce chlorophenols, that are suspected to be carcinogens. Furthermore, chlorine provides strong and persistent odor, even at low concentrations [4, 5]. A significant amount of work has been done on FAC detection based on classical volumetric techniques. Market demands encouraged the development of electrochemical transducer based sensor systems which are cost-effective, fast, reliable and portable in nature. Electrochemical sensors convert chemical information into an electrical signal through transducer. Appropriate choice of sensing materials would improve the transducing process and will enhance the sensitivity, selectivity and response time of the sensor. Majority of the current devices that measure free available chlorine are based on noble materials such as platinum, gold which are expensive. Researchers are working on the carbon based materials for decades on various part of the electrochemistry. However, very recently scientist and engineers are working on carbon based materials as sensing platform for FAC detection. In this work, I have studied commercial pencil graphite as sensing platform for FAC detection in water.

1.2 Historical perspective

Karl Scheele, a Swedish chemist, identified chlorine as a chemical element in 1774. Chlorine has an atomic number of 17 and atomic mass of 35.45. It is a member of the halogen family on the Periodic Chart. Other members of the family include fluorine,

Bromine and Iodine. Each of these compounds plays an important role in water treatment. It's a very dangerous toxin that has many uses, from disinfecting to bleaching.

In small quantities, liquid and gas form can be poisonous. In its gas form, chlorine is a pale greencolor and has a smelly odor and makes one's breathing labored. In its solid form, it's more of a yellow green color. It is abundant in nature in its chloride ion form found mainly at the earth as salt.

One of the first uses of chlorine in water and wastewater treatment was addition to sewers in London, England in the 1830's, not as a disinfectant but rather as a deodorant. It was believed controlling the odor from the sewers might help control the spread of the disease. The germ theory of disease and thus the practice of purposely adding chlorine for disinfecting water did not occur until nearly 70 years later. Disinfection of water is not the sole domain of a chemical such as chlorine. Whether for municipal drinking water, treatment of wastewater, or use of water for manufacture of another beverage, disinfection is the result of the proper application and operation of physical, biological and chemical treatment processes. In the practice of water treatment one should keep in mind proper operation and control of all the steps within the treatment process are important to achieving a properly disinfected effluent. The balance of this document will focus solely on use of chlorine for disinfection [11].

Chlorine is the most common primary disinfectant used in the treatment of swimming pool/spa water. Chlorine exists as gas, solid, and liquid. Each has advantages and disadvantages in its use and different ways of introduction to the water, which also plays a role in the management of chlorine and its effectiveness. The chemical reaction that occurs upon introduction of chlorine to pool water is important to understand to ensure proper water management and to reduce risk of recreational water illness. When chlorine is added to pool water, some of the chlorine reacts with organic materials and metals in the water, and will not be available for further disinfection. This is called the chlorine demand of the water. The remaining chlorine concentration is termed total chlorine.

$$TC = CC + FAC$$

Total chlorine (TC) consists of combined chlorine and free available chlorine (FAC; the chlorine available to inactivate disease causing organisms) [12].

1.3 The role of chlorine in water quality

When chlorine interacts with drinking water, it proceeds through a series of chemical reactions. After addition of chlorine in to the water, a portion of it reacts first with organic materials and metals in the water and is not available for disinfection (this is called the chlorine demand of the water). The remaining chlorine concentration after the chlorine demand is accounted for is called total chlorine. Total chlorine has two main elements:

- ❖ The combined chlorine which has reacted with nitrates and is unavailable for disinfection and
- ❖ The free chlorine, which is the chlorine available to inactivate disease-causing organisms, and thus a measure to determine whether the water is drinkable.

Generally in complete pure water for example, the free chlorine concentration equal to the chlorine concentration added initially, as the chlorine demand is zero. However, in natural water or surface water, organic material will exert a chlorine demand, and nitrates and other ions will form combined chlorine. Thus, the free chlorine concentration will be less than the concentration of chlorine initially added. Chlorine kills bacteria through following mechanism. For example, if using completing clean water the chlorine demand will be zero, and there will be no nitrates present, so no combined chlorine will be present. Thus, the free chlorine concentration will be equal to the concentration of chlorine initially added. In natural waters, especially surface water supplies such as rivers, organic material will exert a chlorine demand, and nitrates will form combined chlorine. Thus, the free chlorine concentration will be less than the concentration of chlorine initially added.

Chlorine kills bacteria through a simple chemical reaction. When chlorine solution is poured into water, it breaks down into many different chemicals, including hypochlorous acid (HOCl) and hypochlorite ion (OCl⁻). Both kill micro-organisms and bacteria by attacking the lipids in the cell walls and destroying the enzymes and structures inside the cell, rendering them oxidized and harmless. The difference between HOCl and OCl⁻ is the speed at which they oxidize. Hypochlorous acid HOCl is a much better disinfectant

compare to OCl^- , and is often referred to as active chlorine. HOCl is able to oxidize the organisms in several seconds, while the hypochlorite ion may take up to 30 minutes. As $\text{HOCl} / \text{OCl}^-$ equilibrium depends on pH, the disinfecting effect is strongly relative to the pH of water.

Chlorine addition flow chart in surface water

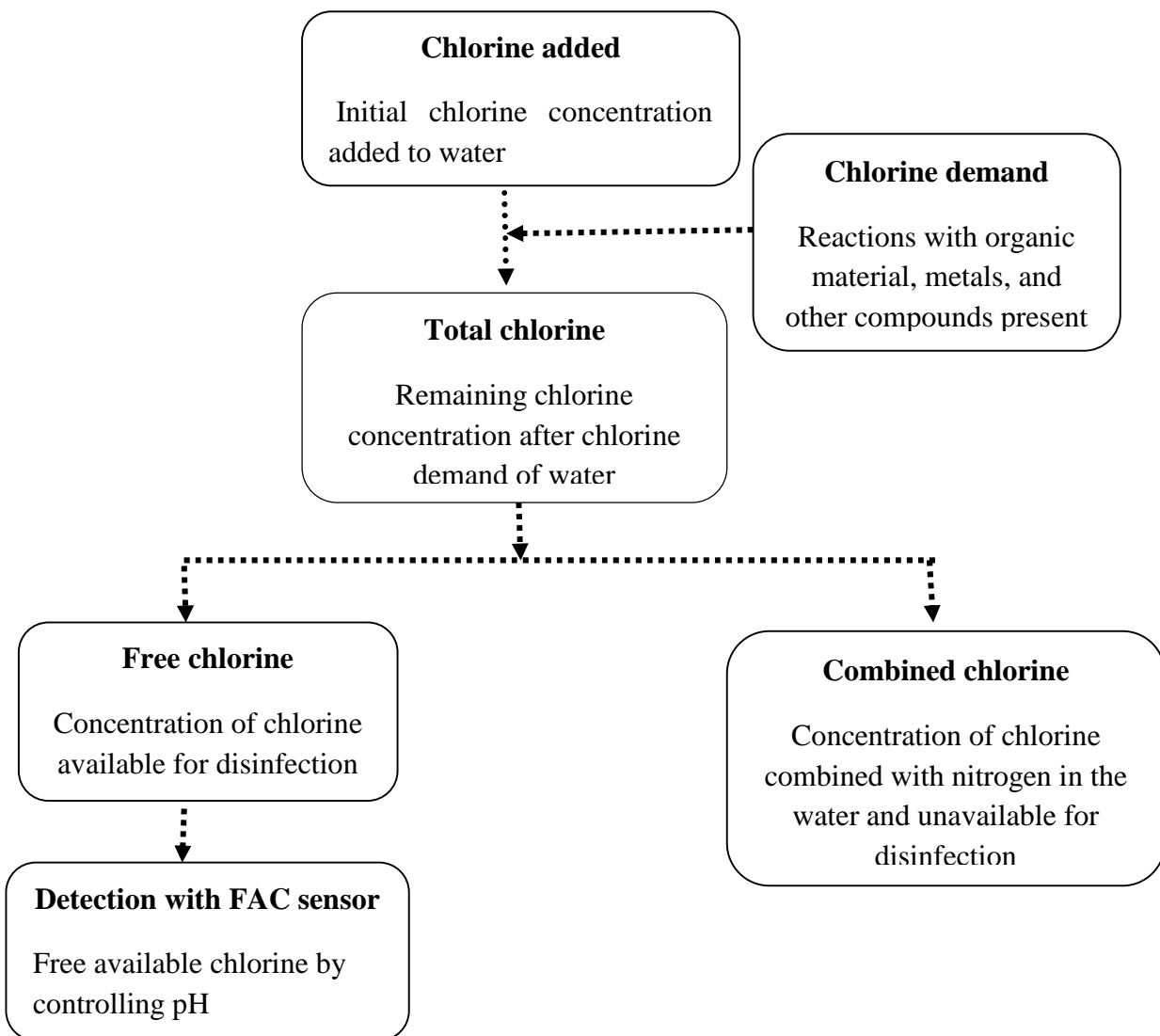


Figure 1.1: Flow chart of chlorine addition in surface water [13]

Disinfectant properties of chlorine

Chlorine is known to be a good disinfectant; it is able to kill living matter in water such as bacteria, cysts, and spores. Studies show that certain forms of chlorine are more effective than others. Whatever the chemical reaction, the relative efficiency of various disinfecting compounds is a function of the rate of diffusion of the active agent through the cell wall.

Factors which affect the efficiency of destruction are:

- ❖ Nature of disinfectant (type of chlorine residual fraction)
- ❖ Concentration of disinfectant
- ❖ Length of contact time with disinfectant
- ❖ Temperature
- ❖ Type and concentration of organisms
- ❖ pH

Hypochlorous acid is the most effective of all the chlorine forms, similar in structure to water. The germicidal efficiency of HOCl is due to the relative ease with which it can penetrate cell walls. This penetration is comparable to that of water, and can be attributed to both its modest size and to its electrical neutrality. The concentration of hypochlorous acid is dependent on the pH, which establishes the amount of dissociation of HOCl to H⁺ and OCl⁻ ions. Lowering the temperature of the reacting solution suppresses the dissociation; conversely, raising the temperature increases the amount of dissociation. The rate of dissociation of HOCl is so rapid that equilibrium between HOCl and the OCl⁻ ion is maintained, even though the HOCl is being continuously used up. The OCl⁻ ion form of chlorine is a relatively poor disinfectant because of its inability to diffuse through the cell wall of microorganisms; the obstacle being the negative electrical charge.

Types of chlorine used in disinfection

Public water systems use chlorine in the gaseous form, which is considered too dangerous and expensive for home use. Private systems use liquid chlorine (sodium hypochlorite) or dry chlorine (calcium hypochlorite). To avoid hardness deposits on equipment, manufacturers recommend using soft, distilled, or demineralized water when making up chlorine solutions.

Table 1.1: Liquid chlorine vs. dry chlorine [31]

Liquid Chlorine	Dry Chlorine
household bleach most common form	powder dissolved in water
available chlorine range: 5.25% (domestic laundry bleach) 18% (commercial laundry bleach)	available chlorine: 4% produces heavy sediment that clogs equipment; filtration require
slightly more stable than solutions from dry chlorine	dry powder stable when stored properly dry powder fire hazard near flammable materials
protect from sun, air, and heat	solution maintains strength for 1 week • protect from sun and heat

1.4 Testing and FAC minimum level recommendations

Daily frequent monitoring and adjusting of chlorine residuals and other water parameters (pH) is necessary to ensure optimum chlorine effectiveness.

Table 1.2: FAC minimum level recommendations [14]

Surface water	Free Available Chlorine	
	Un-stabilized	Stabilized or used with cyanuric acid(outdoor pools)
Public Pool (and play features)	1.0 mg/L (ppm)	2.0 mg/L (ppm)
Hot tub/Therapy/ Spa	3.0 mg/L (ppm)	Not recommended

*Hypochlorous acid is approximately 80 times more effective than the hypochlorite ion as a disinfectant. It is important to maintain the pH below 7.8 to avoid disease transmission [15].

1.5 Impact of chlorine level in water on human health**1.5.1 Why is chlorine used so widely around the world?**

Chlorine is a simple, reliable, effective, relatively inexpensive and, above all else, safe, way to protect drinking water supplies against contamination by microbiological organisms. As it has been used for so many years the methods and equipment needed to use it safely are well designed, and its effectiveness is well understood. One other important benefit of using chlorine in drinking water is that once treated a small residual amount of chlorine remains in the water distribution system to provide continuing protection from microbiological contamination while the water is delivered to your tap. As chlorine is so effective and relatively easy to use it has become one of the most widely used disinfectants found in homes, industry and health care facilities. Chlorine based products are routinely used to sterilize baby feeding bottles, treat domestic and commercial swimming pools, spas and hydrotherapy pools.

1.5.2 How much chlorine is in our surface water?

The Bangladesh Drinking Water Guidelines state that the level of chlorine in scheme (piped) drinking water should be no more than 5mg/L. Normal chlorine concentrations in scheme drinking water pipeline systems will range from 0.5mg/L to 1.5 mg/L. It is quite normal for chlorine in southern Bangladesh drinking water to be at or below these levels. Chlorine levels may vary due to the flow rate of the water in the system, your proximity to the water treatment plant and during maintenance periods [17].

1.5.3 How am I exposed to chlorine?

Even taking a long bath or shower increases a person's risk for chlorine exposure because chlorine can enter the body through skin absorption or through the eyes, nose, and ears. Chlorine has long been used to disinfect our drinking water because it controls the growth of such unwelcome bacteria as Ecoli and Giardia. You have to be careful also, to take precautions even when showering or drinking tap water.

Common exposures to chlorine:

- Absorption through skin from water and from the air
- Drinking & Eating
- Breathing in the fumes that chlorine can create

It should be noted that the dangers of chlorine exposure also exist for people who do not normally swim, but instead choose to sit by the pool sunbathing or socializing. In some instances, non-swimmers have tested positive for high levels of trichloramine. What all of this means is that people need to be more aware of some of the seemingly innocent dangers that they are commonly exposed to. Chlorine, by many schools of thought, has become a dinosaur for swimming pool sanitation [18]. There are alternative methods that can be used to keep pools disinfected, including silver-copper ion generators.

1.6 Chlorine, cancer, and heart disease

The addition of chlorine to our drinking water began in the late 1800s and by 1904 was the standard in water treatment, and for the most part remains so today. We don't use chlorine because it's the safest or even the most effective means of disinfection, we use it because it is the cheapest. In spite of all our technological advances, we essentially still pour bleach in our water before we drink it. The long term effects of chlorinated drinking water have just recently been recognized.

According to the U.S. Council of environmental quality, "cancer risk among people drinking chlorinated water is 93% higher than among those whose water does not contain chlorine." Dr. Joseph Price wrote a highly controversial book in the late sixties titled *Coronaries/Cholesterol/Chlorine* and concluded that nothing can negate the incontrovertible fact, the basic cause of atherosclerosis and resulting entities such as heart attacks and stroke, is chlorine." Dr. Price later headed up a study using chickens as test subjects, where two groups of several hundred birds were observed throughout their span to maturity. One group was given water with chlorine and the other without. The group raised with chlorine, when autopsied, showed some level of heart or circulatory disease in every specimen, the group without had no incidence of disease. The group with chlorine under winter conditions, showed outward signs of poor circulation, shivering, drooped

feathers and a reduced level of activity. The group without chlorine grew faster, larger and displayed vigorous health. This study was well received in the poultry industry and is still used as a reference today. As a result, most large poultry producers use dechlorinated water. It would be a common sense conclusion that if regular chlorinated tap water is not good enough for the chickens, then it probably is not good enough for us humans! Research has shown, however, that long-term exposure to chlorine leads to the production of free radicals within the body. Free radicals are carcinogenic, and cause tremendous damage to our cells.

According to a Belgian study that was released in 2003, certain irritants called trichloramines are released any time chlorinated water reacts with organic materials (such as sweat or urine) from people [19]. Trichloramines are believed to initiate a biological process that effectively destroys the cellular barriers surrounding the lungs. Children exposed to large amounts of chlorine could potentially suffer asthmatic attacks. In one research study, rats exposed to chlorine and chloramines developed tumors in their kidneys and intestines. Chlorine can irritate severely, even burn, skin exposed directly to it. It can irritate and burn the eyes and throat as well.

There is a lot of well-founded concern about chlorine. When chlorine is added to our water, it combines with other natural compounds to form Trihalomethan(chlorination byproducts), or THMs. These chlorine byproducts trigger the production of free radicals in the body, causing cell damage, and are highly carcinogenic. “Although concentrations of these carcinogens (THMs) are low, it is precisely these low levels that cancer scientists believe are responsible for the majority of human cancers in the United States“.Simply stated chlorine is a pesticide, as defined by the U.S. EPA, whose sole purpose is to kill living organisms. When we consume water containing chlorine, it kills some part of us, destroying cells and tissue inside our body. Dr. Robert Carlson, a highly respected University of Minnesota researcher whose work is sponsored by the Federal Environmental Protection Agency, sums it up by claiming , “the chlorine problem is similar to that of air pollution”, and adds that “chlorine is the greatestcrippler and killer of modern times!”

Breast cancer, which now affects one in every eight women in North America, has recently been linked to the accumulation of chlorine compounds in the breast tissue. A study carried out in Hartford Connecticut, the first of its kind in North America, found that, “women with breast cancer have 50% to 60% higher levels of organochlorines (chlorination byproducts) in their breast tissue than women without breast cancer.”

One of the most shocking components to all of these studies is that up to 2/3s of our harmful exposure to chlorine is due to inhalation of steam and skin absorption while showering. A warm shower opens up the pores of the skin and allows for accelerated absorption of chlorine and other chemicals in water. The steam we inhale while showering can contain up to 50 times the level of chemicals than tap water due to the fact that chlorine and most other contaminants vaporize much faster and at a lower temperature than water. Inhalation is a much more harmful means of exposure since the chlorine gas (chloroform) we inhale goes directly into our blood stream. When we drink contaminated water the toxins are partially filtered out by our kidneys and digestive system. Chlorine vapors are known to be a strong irritant to the sensitive tissue and bronchial passages inside our lungs; it was used as a chemical weapon in World War II. The inhalation of chlorine is a suspected cause of asthma and bronchitis, especially in children which has increased 300% in the last two decades. “Showering is suspected as the primary cause of elevated levels of chloroform in nearly every home because of chlorine in the water.”

Chlorine in shower water also has a very negative cosmetic effect, robbing our skin and hair of moisture and elasticity, resulting in a less vibrant and youthful appearance. Anyone who has ever swam in a chlorinated pool can relate to the harsh effects that chlorine has on the skin and hair. What’s surprising is that we commonly find higher levels of chlorine in our tap water than is recommended safe for swimming pools [20].

Aside from all the health risks related to chlorine in our water, it is the primary cause of bad taste and odor in drinking water. The objectionable taste causes many people to turn to other less healthful beverages like soft drinks, tea or other sweetened drinks. A decreased intake of water, for any reason, can only result in a lower degree of health.

The good news is that chlorine is one of the easiest substances to remove from our water. For that reason it logically should serve its purpose of keeping our water free from harmful

bacteria and water borne diseases right up to the time of consumption, where it should then be removed by quality home water filtration.

No one will argue that chlorine serves an important purpose and that the hazards of doing away with chlorine are greater than or equal to the related health risks. The simple truth is that chlorine is likely here to stay. The idea that we could do away with chlorine any time in the near future is just not realistic. It is also clear that chlorine represents a very real and serious threat to our health and should be removed in our homes, at the point of use, both from the water we drink and the water we shower in.

1.7 Free available chlorine chemistry

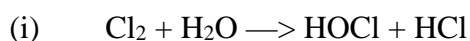
The different forms of chlorine are named as follows:

Cl_2 = chlorine

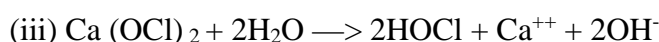
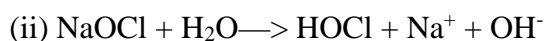
HOCl = hypochlorous acid

OCl^- = hypochlorite ion

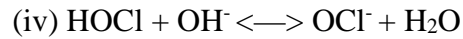
When chlorine gas is dissolved in water, it hydrolyzes rapidly according to equation (1). This reaction occurs very rapidly, in only a few tenths of a second at 18°C (64.4°F).



Since HCl, hydrochloric acid is a strong acid, addition of gaseous chlorine to water results in a lowering of the pH from the acidic HCl byproduct. The important product of reaction (i) is HOCl or hypochlorous acid. Hypochlorous acid is the killing form of chlorine in water. Hypochlorous acid is unstable because the chlorine molecule is lightly bound and therefore will react quickly. Free available chlorine, or free chlorine, is hypochlorous acid and is taste free and aggressive against germs and organic compounds [21, 22]. Chlorine supplied as sodium hypochlorite, calcium hypochlorite, or bleach is in alkaline or basic form. When a base is present, a different reaction sequence occurs:



In any hypochlorite solution, the active ingredient is always hypochlorous acid. Then once HOCl and OH⁻ are formed an additional reaction occurs:



The proportion of chlorine, hypochlorous acid, and hypochlorite ion in solution depends primarily on pH and somewhat on temperature.

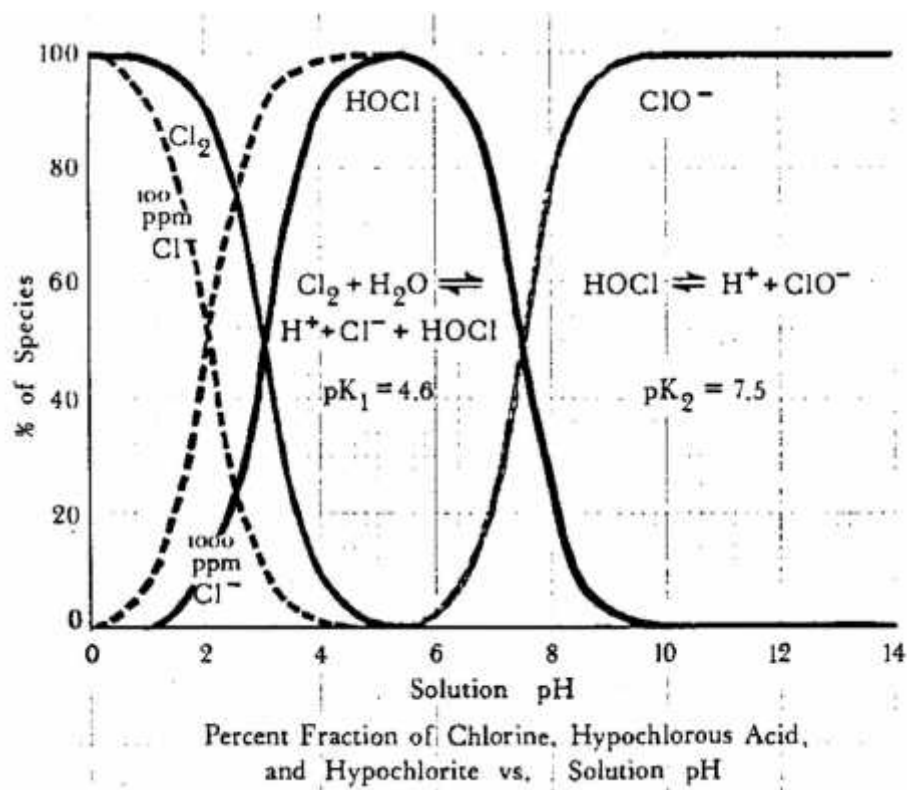


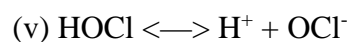
Figure 1.2: Chlorine species change vs. pH [41]

Disinfection of free chlorine in surface water

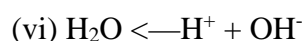
Various forms of chlorine are used to disinfect water. Each form of chlorine has benefits and limitations which help determine the specific application. The predominant categories used in disinfection are free chlorine, total chlorine and chlorine dioxide. Free chlorine is the sum of chlorine gas (Cl_2), hypochlorous acid (HOCl) and hypochlorite (OCl^-). Above pH 4.0 all of the molecular chlorine is converted to HOCl and OCl^- . Hypochlorous acid is a more potent disinfectant than hypochlorite and exists in a pH dependent. Free chlorine also combines with naturally occurring or human introduced nitrogen compounds in the water to form chloramines, also known as combined chlorine. Treatment operators introduce ammonia into the water to form monochloramine (NH_2Cl), dichloramines (NHCl_2) and trichloramine (NCl_3). Chloramines are a less effective disinfectant but have a longer residence time than the free chlorine species. Total chlorine is the sum of free chlorine (Cl_2 , HOCl and OCl^-) and combined chlorine (NH_2Cl , NHCl_2 , NCl_3) [16].

1.8 Chlorine and the effect of pH

The most important reaction in the chlorination of an aqueous solution is the formation of hypochlorous acid, a form of chlorine very effective for killing germs. Hypochlorous acid is a 'weak' acid, meaning that it tends to undergo partial dissociation to form a hydrogen ion (H^+) and a hypochlorite ion (OCl^-) in a water environment HOCl tends to dissociate into these ions.



In water between 5 pH and 8.5 pH, the reaction is incomplete and both species are present to some degree [23]. Since H^+ is one of the ions formed and its concentration is expressed as pH, changing pH levels will influence the balance of this reaction and with it, the availability of hypochlorous acid for reaction. Therefore, in an aqueous environment, the water pH will affect the chemistry of chlorine through its pH sensitivity; this is important as the pH value increases.



Three things follow from this form of ionization:

- (i) Since the tendency of these two ions to react and form H_2O is much stronger than the tendency of water to break down into the ions, as the pH increases there are fewer H^+ ions and more OH^- ions.
- (ii) The H^+ released by the breakdown of HOCl (equation v), react to form water (equation vi) and leave behind residual OCl^- ions. Hypochlorite does not react readily so the chlorine is weaker.
- (iii) If the pH goes down and H^+ ions become readily available again, the OCl^- ions revert to HOCl , which is the killing form of chlorine.

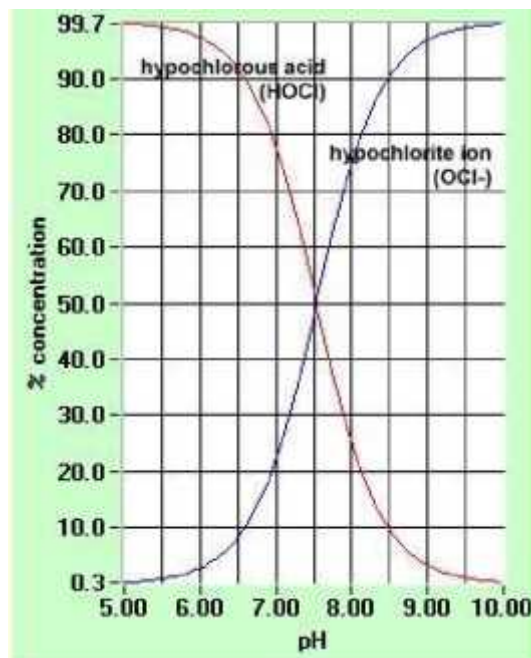


Figure 1.3: % Chlorine concentration vs. pH

- ❖ At pH 8.0, only 20% of the FAC is immediately available as hypochlorous acid there by making any measurable FAC less effective.
- ❖ At pH 7.5, about 50% of the FAC is immediately available as hypochlorous acid making the FAC more effective.

Terminology:

In the industry, there are a number of terms used to indicate the various forms of chlorine that are of interest. These terms tend to be used rather loosely and not necessarily consistently. For that reason, the following terms are defined:

Total free chlorine refers to the sum of hypochlorous acid (HOCl) and hypochlorite ion (OCl⁻). The hypochlorite ion is not effective for disinfection, but it is in a free form. All of the total free chlorine would be in the form of hypochlorous acid if the pH was low enough [27].

Total residual chlorine refers to the sum of total free chlorine and combined chlorine. The concentration of chlorine species present in water after the oxidant demand has been satisfied. Low total residual chlorine is of particular interest to ensure there are no downstream consequences for aquatic life.

Combined chlorine rationale

Combined chlorine is the sum of the species resulting from the reaction of free chlorine with ammonia (NH₃), including monochloramine (NH₂Cl), dichloramine (NHCl₂), and trichloramine (nitrogen trichloride, NCl₃). Combined Chlorine forms when chlorine chemically bonds with materials containing nitrogen including, but not limited to urine (ammonia), dead algae, and skin. This reduces the chlorine available for disinfection, which reduces disinfection power. CC can be determined using an appropriate test kit and utilizing this formula [25].

$$\text{Combined chlorine} = \text{Total chlorine} - \text{Free available chlorine}$$

High CC levels in surface water

Levels above 0.4 mg/L (ppm) can indicate that the bathing load or contaminant load (from swimmers) is high. High CC can cause complaints of a strong chlorine smell, eye and possible breathing irritation after exposure to pool water and air, particularly for indoor pools. These complaints are further exacerbated when water becomes agitated from patron

activity, pool features (wave pools, spray features), or hot tubs as all of these by nature aerosolize the water and corresponding CC into the aquatic venue's air. [18] High levels of CC, poorly positioned air vents, and inadequately designed and maintained ventilation systems increase potential health effects and equipment corrosion [26].

Primary disinfection: the application of a disinfectant at the drinking water treatment plant, with a primary objective to achieve the necessary microbial inactivation.

Secondary disinfection: the subsequent application of a disinfectant, either at the exit of the treatment plant or in the distribution system, with the objective of ensuring that a disinfectant residual is present throughout the distribution system [27, 28].

1.9 Why do we test free chlorine in water?

Drinking - tap water:

The goal of dosage testing is to determine how much sodium hypochlorite solution to add to water that will be used for drinking to maintain free chlorine residual in the water for the average time of storage of water in the household (typically 4-24 hours). This goal differs from the goal of infrastructure-based (piped) water treatment systems, whose aim is effective disinfection at the endpoints (i.e., water taps) of the system: defined by the WHO (1993) as: "a residual concentration of free chlorine of greater than or equal to 0.5 mg/litre after at least 30 minutes contact time at pH less than 8.0." This definition is only appropriate when users drink water directly from the flowing tap. A free chlorine level of 0.5 mg/litre of free chlorine will contain a sufficient level of residual to maintain the quality of water through the distribution network, but is probably inadequate to maintain the quality of the water when this water is stored in the home in a bucket or jerry can for 24 hours.

Thus, it is recommended to maintain a dosage as:

(i) At 30 minutes, after the addition of sodium hypochlorite there should be no more than 2-4 mg/l of free chlorine residual present (this ensures the water does not have an unpleasant taste or odour).

(ii) At 24 hours after the addition of sodium hypochlorite to containers that are used by families to store water there should be a minimum of 0.2 mg/l of free chlorine residual present (this ensures microbiologically clean water).

FAC in surface water

Chlorine generators avoid the need for constant handling of sanitizing chemicals, and can generate sanitizing power at a lower cost than the equivalent chemicals, but they have a large up-front cost for the apparatus and for the initial loading of the pool with salt. Being closer to isotonic salinity than fresh water, saltwater pools have an easier feel on the eyes, and a touch typically characterized as "silky", not unlike bath salts. Maintaining a safe concentration of disinfectant is critically important in assuring the safety and health of swimming pool users

Recommended minimum free available chlorine:

- Residential Pools: 1-3 ppm (1-3 mg/l)
- Residential Spas: 3-5 ppm (3-5 mg/l)
- Commercial pools: provincial and/or municipal regulations must be followed.

The presence of organic matter in swimming pool water reduces the effectiveness of sanitizers. In some cases, the label directions of swimming pool sanitizers and algicides may instruct residential pool owners to maintain a minimum chlorine level of 0.6 ppm. Reducing sanitizer levels from 1-3 ppm (as recommended above) to 0.6 ppm is possible only when the organic matter content in swimming pool water is controlled, using UV-light for example. The levels of HOCl and OCl⁻ vary with the pool's pH level. If the pH is too high, not enough HOCl is present and pool cleaning can take much longer than normal. Ideally, the level of pH in the pool should be between 7.2 and 7.8; 7.4 is ideal which is the pH of human tears as higher pH drastically reduces the sanitizing power of the chlorine due to reduced ORP, while lower pH causes bather discomfort, especially to the eyes. Chlorine reacting with urea in urine from bathers can create nitrogen trichloride, which has an effect similar to tear gas. Once the HOCl and OCl⁻ have completed cleaning the pool, they either combine with another chemical, such as ammonia, or are broken down into single atoms. Both of these processes render the chlorine harmless. Sunlight speeds these processes up. You have to keep adding chlorine to the pool as it breaks down.

Pool sanitation, which necessarily involves toxic or mechanical means of killing microbes, can sometimes unintentionally irritate the swimmers, especially if poorly maintained, especially a too high level of chlorine and/or too low pH. Non-chlorine sanitizing chemicals and devices are promoted as being less harsh, but any sanitizer is harsh if overused. Water circulating through a pipe can be sterilized with UV light instead of chemicals, but some level of chemical sanitizer is still needed, because only a small portion of the pool water passes through the circulation system at any given time, and the circulation system typically only runs for a few hours each day. UV sterilization also does not inhibit algae from growing on pool surfaces, and it does not break down dissolved nitrogenous nutrients that feed algae growth, so some type of oxidizing sanitizer is still needed to check these trends, although it need not be dosed during bathing hours for this purpose.

Ionization systems using copper and silver, destroying bacteria and algae, are optional replacements for chlorine systems. In this method no chemicals are added apart from the metals. The pool water runs through the ionization cells and is disinfected using a low electrical current. A control unit can decide how much copper and silver to release into the pool, reducing manual maintenance. The cost for such a system is higher than that of a saltwater generator, which already is much more expensive than standard chlorine disinfection systems.

Health effects of bad surface water disinfection

Disinfectants used for surface water disinfection water can affect human health. Too much chlorine can cause eczema and rashes. Water that has a high pH value increases susceptibility to these kinds of ailments. When water is mobile, it comes in contact with a sufficient amount of air. Carbon dioxide is released into the water, causing the pH value to decrease. When one applies chlorine, chlorine gas will evaporate.

Free active chlorine in surface water

Hypochlorous acid (HOCl) and hypochlorite (OCl⁻) are the main components of free active chlorine. The surface water has a high pH value and the amount of dissolved chlorine gas as free active chlorine is negligible. Free active chlorine hardly ever causes eye irritations. These only occur above concentrations of 20 mg/L. Dissolved chlorine and chlorine substances dehydrate hair and skin. The air above the pool contains chlorine gas concentrations between 0.01 and 0.1 mg/L. These concentrations are far below the level that irritates respiratory tracts. Through the formation of combined active chlorine, free active chlorine can cause irritation.

Combined active chlorine in surface water

Combined active chlorine is the generic term for reaction products produced by free active chlorine with organic and inorganic nitrogen pollutants. These pollutants are made of swimmers excreta. Combined active chlorine is a complex mixture of partly unknown substances, such as chlorine urea combinations, chloramines and chlorine kreatines. The irritating effects of combined active chlorine are often ascribed to chloramines (NH₂Cl, NHCl₂, NCl₃). Chloramines are volatile substances that partly escape from water as gas. Like chloroform, chloramines cause the well known 'chlorine smell' in swimming pools. The formation of di- and trichloramines increases when the free active chlorine concentration is increased and the pH value is lowered. The typical 'chlorine smell' in swimming pools arises at urea levels of 0.5 mg/L and free active chlorine concentrations of 1.0 mg/L. There is no relation between chloramine formation and urea concentration. Monochloramines cause eye irritations. At normal pH levels in swimming pools, monochloramine is produced predominantly. Both di- and trichloramines irritate eyes. These substances reach the eyes through water and through the air above the pool. Trichloramine also irritates air tracts. Other chlorinated organic substances are suspected to irritate as well, particularly chlorinated ammonia, creatinine and uric acid. The combined active chlorine concentration in swimming pools should be below 1 mg/L.

1.10 Chlorination chemistry of surface water



Seawater contains about 65- 80ppm dissolved bromides most of which are sodium bromide. When you put chlorine in water it displaces (because it's more reactive) the bromine from the bromide and becomes a chloride. So for up to about 70ppm of total chlorine dosed what you actually have in the water is free bromine and combined bromine (NOT free and combined chlorine) so it is the total bromine that actually does the disinfection [29]. Mainly most people don't know this interesting bit of chemistry. Normally it makes no difference at all in that bromine is an effective disinfectant, however there can be a lot of confusion when it comes to monitoring residuals and controlling dosing. Choosing the correct sensor to control the dosing is crucial.

Table 1.3: Shows concentrations of the major constituents in surface seawater [30]

At Salinity (PSS 1978):S =35.000%				
	g/kg	ppm (mg/L)	Mmol/kg	mM
Na⁺	10.781	10781	468.96	480.57
K⁺	0.399	399	10.21	10.46
Cl⁻	19.353	19353	545.88	559.4
Br⁻	0.0673	67	0.844	0.865
F⁻	0.0013	1	0.068	0.07

1.11 Fundamentals of electrochemical sensor

Electrochemical Sensors are the devices, which are composed of an active sensing material with a signal transducer. The role of these two important components in sensors is to transmit the signal without any amplification from a selective compound or from a change in a reaction. These devices produce any one of the signals as electrical, thermal or optical output signals which could be converted into digital signals for further processing. One of the ways of classifying sensors is done based on these output signals. Among these,

electrochemical sensors have more advantage over the others because; in these, the electrodes can sense the materials which are present within the host without doing any damage to the host system. On the other hand, sensors can be broadly classified in to two categories as chemical sensors and biosensors. The biosensors can be defined in terms of sensing aspects, where these sensors can sense biochemical compounds such as biological proteins, nucleotides and even tissues [39].

At the same time the major disadvantage of the electrochemical methods became obvious: lack of selectivity. Practically, all the electroactive species can be reduced or oxidized from a sample or from a matrix and the simultaneous detection in the same sample is possible only in the case when two species possess redox potentials sufficiently separated in the investigated domain of potential. The reduced selectivity was the main issue that pointed the researchers' attention towards the delicate area of the electrode surface, where essential phenomena take place and trigger the race that still continues today having the goal of increasing the selectivity (specificity) for certain analytes. A new domain has been born, the field of modified electrochemical sensors. There are several possibilities today to modify the electrode material or its surface; the general strategies of electrochemical sensor technology will be discussed later. According to IUPAC a chemical sensor is “a device that transforms chemical information, originating from a chemical reaction of the analyte or from a physical property of the investigated system, ranging from the concentration of a specific sample component to total composition analysis, into an analytically useful signal.

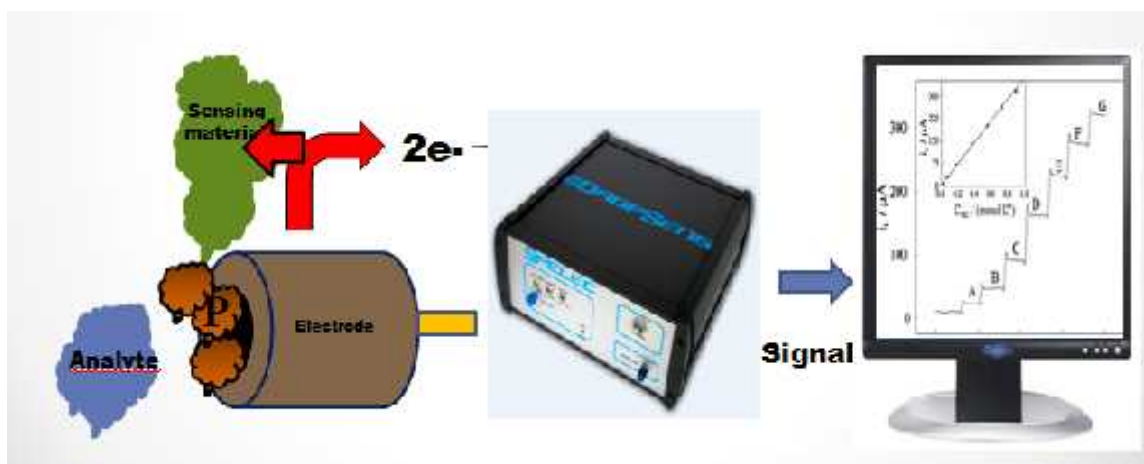


Figure1.4: Mechanism of electrochemical sensor [39]

Generally, chemical sensors contain two basic functional units connected in series: a chemical (molecular) recognition system, named receptor, which transforms the chemical information into a measurable form of energy and a physicochemical transducer capable of transforming the energy carrying the chemical information about the sample into a useful analytical signal.

A modern sensor system generally incorporates besides the receptor and the transducer other two key components: a sample delivery unit and a data processor [39]. The receptor part of the chemical sensors is based on three various basic principles of stimulus: physical, where no chemical reaction takes place (e.g., measurement of absorbance, refractive index, conductivity, temperature or mass change); chemical, in which a chemical reaction with participation of the analyte gives rise to the analytical signal and biochemical, in which a biochemical process is the source of the analytical signal (e.g. enzyme amperometric sensors, microbial potentiometric sensors, or immunosensors). The last category consists of the well known biosensors and they can be differentiated according to the biological elements used as receptor, namely enzymes, nucleic acids, aptamers, antibodies, organelles, membranes, cells, tissues, or even whole organisms.

The main function of the receptor is to provide the sensor with a high degree of selectivity for the analyte to be measured. While most chemical sensors are more or less selective (specific) for a particular analyte, some are, by design and construction, only class specific, e.g. sensors or biosensors for phenolic compounds, or whole-cell biosensors used to measure the biological oxygen demand.

Depending on the exact mode of signal transduction, electrochemical sensors can use a range of modes of detection such as potentiometric, voltammetric and conductimetric. Each principle requires a specific design of the electrochemical cell. Potentiometric sensors are very attractive for field operations because of their high selectivity, simplicity and low cost. They are, however, less sensitive and often slower than their voltammetric counterparts. Examples of transduction techniques include:

- ❖ Potentiometric – The measurement of the potential at zero current. The potential is proportional to the logarithm of the concentration of the substance being determined.

- ❖ Voltammetric – Increasing or decrease the potential that is applied to a cell until the oxidation or reduction of the analyte occurs. This generates a rise in current that is proportional to the concentration of the electroactive potential. Once the desired stable oxidation/reduction potential is known, stepping the potential directly to that value and observing the current is known as amperometry.

- ❖ Conductiometric – Observing changes in electrical conductivity of the solution [129].

The selection and development of an active material is a challenge. The active sensing materials may be of any kind as whichever acts as a catalyst for sensing a particular analyte or a set of analytes. The recent development in the nanotechnology has paved the way for large number of new materials and devices of desirable properties which have useful functions for numerous electrochemical sensor and biosensor applications [127].

Basically by creating nanostructure, it is possible to control the fundamental properties of materials even without changing their chemical composition. In this way the attractive world of low dimensional systems, together with the current tendencies on the fabrication of functional nanostructured arrays could play a key role in the new trends of nanotechnology [128, 130, 131].

Continuous, real-time monitoring of the level of free chlorine in drinking water is of great importance to public health. However, it is challenging when conventional analytical instruments, such as bulky pH electrodes and expensive free chlorine meters, are used. These instruments have slow response, are difficult to use, prone to interference from operators, and require frequent maintenance. In contrast, microfabricated electrochemical sensors are cheaper, smaller in size and highly sensitive. Therefore, these sensors are desirable for online monitoring of free chlorine in water. we discuss different physical configurations of microfabricated sensors. These configurations include potentiometric electrodes, ion-sensitive field-effect transistors, and chemo-resistors/transistors for

electrochemical chlorine sensing. Also, we identified that micro-amperometric sensors are the dominant ones used for free chlorine sensing. We summarized and compared the structure, operation/sensing mechanism, applicable materials and performance parameters in terms of sensitivity, sensing range, response time and stability of each type of sensor. We observed that novel sensor structures fabricated by solution processing and operated by smart sensing methodologies may be used for developing pH and free chlorine sensors with high performance and low cost. Finally, we highlighted the importance of the concurrent design of materials, fabrication processes, and electronics for future sensors.

Electrochemical chlorine sensor

Chlorine in aqueous solutions is used for a number of purposes such as disinfection, taste and odor control, bleaching, and as a powerful oxidizing agent in various manufacturing processes. Chlorine is a costly chemical and requires large amounts of energy to produce. As energy becomes more expensive, so inevitably will chlorine. If for no other reason than cost, it is important to measure and control chlorine concentration. Perhaps more important is the fact that the bleaching and disinfecting ability of chlorine depends on concentration. Too little chlorine is ineffective. Too much chlorine is wasteful and may create other problems in the process. A good illustration is the chlorination of drinking water. Underfeeding chlorine results in incomplete disinfection with consequent danger to the public health. Overfeeding chlorine may produce water with an objectionable odor. Overfeeding may also increase the levels of trihalomethanes (THMs) in the finished water. THMs are suspected carcinogens. In certain applications, such as the chlorination of drinking water, it is important to know the chemical form of the chlorine. Certain forms of chlorine are 80 to 100 times more effective in disinfecting water than other forms. The reactivity of chlorine and its complex chemistry in aqueous solution make the measurement of chlorine difficult. Even under ideal laboratory conditions, results vary with the method used. With process instruments the situation is even more complicated. Calibration, drift, reliability and maintenance become important issues. Emerson Process Management has developed a series of accurate, easy to use, low maintenance Rosemount Analytical amperometric sensors for the determination of chlorine.

The tip of the chlorine sensor consists of a membrane stretched over a noble metal cathode. The chlorine in solution diffuses through the membrane to the surface of the cathode. A voltage applied to the cathode reduces the chlorine to chloride. The process consumes electrons, which come from a second electrode (the anode) inside the sensor. The number of electrons consumed at the cathode, i.e., the current, is directly proportional to the concentration of chlorine in the sample. The sensors are relatively free from interference. Manganese, iron, nitrate, silicon, magnesium, calcium and chromate substances that interfere with other methods--have little influence on amperometric sensors. The sensors are fairly low maintenance, although they do require periodic cleaning to wash away solids that slowly accumulate on the membrane. The chemistry of chlorine is complex, and we will confine ourselves in the following discussion to a summary of what happens when chlorine is added to water. Water is chlorinated by treating it with chlorine gas (Cl_2) or sodium hypochlorite (NaOCl) solution (bleach). When chlorine gas dissolves in water it produces hypochlorous acid (HOCl). $\text{Cl}_2 + \text{H}_2\text{O} = \text{HOCl} + \text{H}^+ + \text{Cl}^-$ (i) Sodium hypochlorite solution is a source of hypochlorite ions (OCl^-). Hypochlorous acid and hypochlorite ion are both forms of active chlorine and are related to one another by the following equation. $\text{HOCl} = \text{H}^+ + \text{OCl}^-$ (ii). The important thing about equation (ii) is that any solution of chlorine gas or bleach in water is a mixture of hypochlorous acid and hypochlorite ions. The relative amount of hypochlorous acid or hypochlorite present depends on pH and to a slight extent on temperature.

1.12 Fundamentals of electrochemistry and various electro-analytical techniques

The science of electrochemistry is concerned with the interrelation of electrical and chemical effects. Broadly speaking, electrochemistry is fundamental to numerous phenomena, such as metallic corrosion, electroplating technologies, batteries, the production of aluminium and chlorine, and electrochromic displays. Electrochemistry, the study of the exchange between electrical and chemical energy, has important applications in everyday life stretching from the battery that powers your portable radio to the electro refining that produces the copper pipes carrying your drinking water. Those electrochemical processes utilize oxidation and reduction reactions. An oxidation involves the loss of one or more electrons from a chemical species while a reduction is the gain of one or more electrons by a chemical species. When an oxidation and a reduction are paired

together in a redox reaction, electrons can flow from the oxidized species, the reducing agent or reductant, to the reduced species, the oxidizing agent or oxidant. That electron flow can either be spontaneously produced by the reaction and converted into electricity, as in a galvanic cell, or it can be imposed by an outside source to make a non-spontaneous reaction proceed, as in an electrolytic cell. Electrochemical cells are usually classified as either galvanic or electrolytic.

Dynamic electrochemistry is the study of electron transfer reactions between electrodes and reactant molecules, which are normally in solution. Typical factors to affect the dynamics of an electrode reaction include:

- i. the transport of material to and from the electrode and solution
- ii. the electrode potential and temperature of the system
- iii. the physical and chemical properties of the electrode surface (e. g. activity)
- iv. the reactivity of the species in solution
- v. the nature of the interfacial region over which the electron transfer occurs

In order to understand the principle of dynamic electrochemistry, equilibrium electrochemistry and the process of electrolysis must first be considered [32].

1.12.1 Faradaic currents

The Faradaic current is the current that flows through an electrochemical cell that is generated by the change in oxidation state of the electroactive species occurring at the electrode surface, combined with the current contribution due to the charge transfer between the electrode and the background analyte present in solution. The faradic current obeys Faraday's law.

1.12.2 Charging currents and the electrical double layer

The application of a potential to the electrode surface causes ions near the electrode surface to migrate towards or away from the electrode depending on the respective charge of the electrode and the ions. This forms an electrical double layer, comprised of the electrical charge at the surface of the electrode and the charge of the ions in the solution near the electrode. This double layer leads to the generation of a non-faradic charging current.

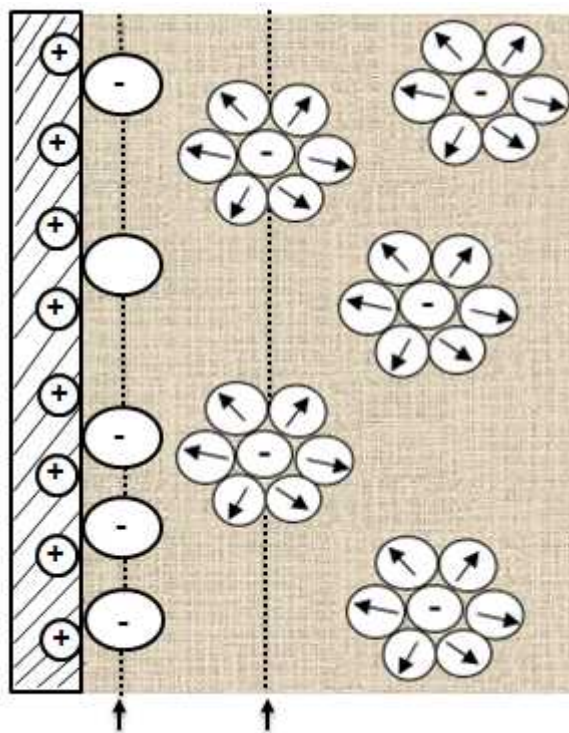


Figure 1.5: Schematic representation of the electrical double layer

The electrical double layer is an array of charged particles and orientated dipoles. It is composed of two layers; the layer closest to the electrode is known as the inner Helmholtz plane (IHP) and the outer Helmholtz plane (OHP) (figure-1.5). The planes were discovered by Hermann von Helmholtz in 1853. The IHP is composed of solvent molecules and specifically adsorbed ions, whilst the OHP represents the imagined outer layer closest to the electrode that passes through the centre of solvated ions, but is separated by the molecules at the IHP [33]. These layers are both held at the surface of the electrode. The behaviour of the interface between the electrode and the solution is similar to that of a capacitor. Beyond the double layer, is a diffuse layer of scattered ions that extend into the bulk solution? These ions are ordered relative to the coulombic forces acting upon them and the random motion of the solution by thermal motion. This causes a non-uniform distribution of ions near the electrode surface. As a result, the field strength of the potential applied to the electrode diminishes rapidly, thereby causing the double layer to be extremely thin at 10 – 20 nanometers in thickness [33, 34]. It is also essential to use a high electrolyte concentration, typically a 100 fold greater than that of the analyte, as this concentrates the charge at the Helmholtz planes, therefore ensuring that diffusion is the dominant mechanism for mass transport [35].

1.12.3 Mass transfer process in voltammetry

Mass transfer is the movement of material from one location to another in solution. In electrochemical systems, three modes of mass transport are generally considered which a substance may be carried to the electrode surface from bulk solution including diffusion, convection and migration. Any of these or more than one might be operating in a given experiment which is depended on the experimental conditions.

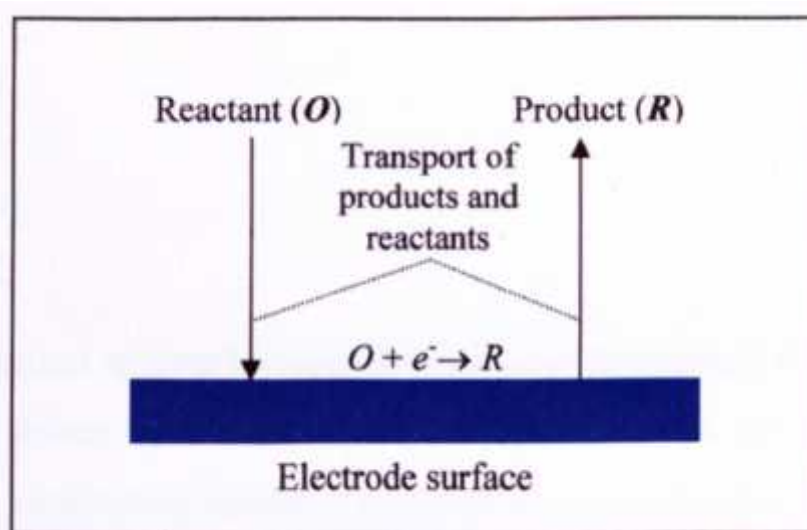


Figure 1.6: Mass transfer to and from the electrode surface

In general, there are three types of mass transfer processes:

-) Migration
-) Diffusion
-) Convection

Migration

Migration is the movement of ions through a solution as a result of electrostatic attraction between the ions and the electrodes. It is the primary cause of mass transfer in the bulk of the solution in a cell. This motion of charged particle through solution, induced by the charges on the electrodes is called migration. This charge movement constitutes a current. This current is called migration current. The larger the number of different kinds of ions in a given solution, the smaller is the fraction of the total charge that is carried by a particular

species. Electrolysis is carried out with a large excess of inert electrolyte in the solution so the current of electrons through the external circuit can be balanced by the passage of ions through the solution between the electrodes and a minimal amount of the electroactive species will be transported by migration. Migration is the movement of charged species due to a potential gradient. In voltammetric experiments, migration is undesirable but can be eliminated by the addition of a large excess of supporting electrolytes in the electrolysis solution. The effect of migration is applied zero by a factor of fifty to hundred ions excess of an inert supporting electrolyte.

Diffusion

Diffusion refers to the process by which molecules intermingle as a result of their kinetic energy of random motion. Whereas a concentration difference between two regions of a solution, ions or molecules move from the more concentrated region to the dilute and leads to a disappearance of the concentration difference.

Diffusion is a natural mixing process facilitated by the natural vibration of atoms and molecules. It is driven by entropy which seeks to even out any inhomogeneities in a system, thereby eliminating localised concentrations as disorder is spread through the system. The rate of diffusion, first described mathematically by Fick, is dependent upon the concentration gradient [36]. In this model it is assumed that the electrode is perfectly flat and of infinite dimensions. The direction of mass transport to and from the electrode occurs in a direction normal to the electrode surface. Ignoring any electrostatic effects, the rate of diffusion at a given point in the solution is dependent on the concentration gradient at that point. Fick's first law of diffusion terms this flow of material flux.

$$flux = j = -D_B \frac{\delta[B]}{dx}$$

The one kind of mode of mass transfer is diffusion to an electrode surface in an electrochemical cell. The rate of diffusion is directly proportional to the concentration difference. When the potential is applied, the cations are reduced at the electrode surface

and the concentration is decreased at the surface film. Hence a concentration gradient is produced. Finally, the result is that the rates of diffusion current become larger.

Convection

By mechanical way reactants can also be transferred to or from an electrode. Thus forced convection is the movement of a substance through solution by stirring or agitation. This will tend to decrease the thickness of the diffuse layer at an electrode surface and thus decrease concentration polarization. Natural convection resulting from temperature or density differences also contributes to the transport of species to and from the electrode [36]. At the same time a type of current is produced. This current is called convection current. Removing the stirring and heating can eliminate this current. Convection is a far more efficient means of mass transport than diffusion.

1.12.4 Electrodes

An electrode is an electrical conductor used to make contact with a nonmetallic part of a circuit (e.g. a semiconductor, an electrolyte or a vacuum). Types of electrode

- ❖ Working electrode
- ❖ Reference electrode
- ❖ Counter electrode

Working electrode

The Working Electrode is the electrode where the potential is controlled and where the current is measured. The working electrode makes contact with the analyte and transfer charge to and from the analyte. The Working Electrode is an "inert" material such as gold, platinum, or glassy carbon.

Advantages of working electrode:

- ❖ Available wire, flat plate & tube, large range of sizes.
- ❖ Larger cathodic potential range.
- ❖ Wide potential range low background current inexpensive



Figure1.7: Gold disk working electrode

Function of Working Electrode: It serves as a surface on which the electrochemical reaction takes place.

Reference Electrode:

A reference electrode is an electrode which has a stable and well-known electrode potential. The high stability of the electrode potential is usually reached by employing a redox system with constant (buffered or saturated) concentrations of each participants of the redox reaction.

A reference electrode is used in measuring the working electrode potential. A Reference Electrode should have a constant electrochemical potential as long as no current flows through it. The reference electrode acts as reference in measuring and controlling the working electrode's potential.



Figure1.8: Ag/AgCl reference electrode

Function of R.F: The most common lab Reference Electrodes are the Saturated Calomel Electrode (SCE) and the Silver/Silver Chloride (Ag/AgCl) electrodes.

Counter electrode:

The Counter, or Auxiliary, Electrode is a conductor that completes the cell circuit. The Counter Electrode in lab cells is generally an inert conductor like platinum or graphite. In field probes, it's generally another piece of the Working Electrode material. The current that flows into the solution via the Working Electrode leaves the solution via the Counter Electrode. The auxiliary electrode passes all the current needed to balance the current observed at the working electrode. Auxiliary electrodes are often fabricated from electrochemically inert materials such as gold, platinum, or carbon.



Figure 1.9: Platinum electrode (Pt)

Function of CE: Remove the solution resistance and measure only the electrode potential.

1.12.5 Cyclic voltammetry (CV)

Cyclic voltammetry is a very versatile electrochemical technique which allows to probe the mechanics of redox and transport properties of a system in solution. This is accomplished with a three electrode arrangement whereby the potential relative to some reference electrode is scanned at a working electrode while the resulting current flowing through a counter (or auxiliary) electrode is monitored in a quiescent solution. The technique is ideally suited for a quick search of redox couples present in a system; once located, a couple may be characterized by more careful analysis of the cyclic voltammogram. More precisely, the controlling electronic is designed such that the potential between the reference and the working electrodes can be adjusted but the big impedance between these two components effectively forces any resulting current to flow through the auxiliary electrode. Usually the potential is scanned back and forth linearly with time between two extreme values – the switching potentials using triangular potential waveform (see Figure 1.10). When the potential of the working electrode is more positive than that of a redox couple present in the solution, the corresponding species may be oxidized (i.e. electrons going from the solution to the electrode) and produce an anodic current. Similarly, on the return scan, as the working electrode potential becomes more negative than the reduction potential of a redox couple, reduction (i.e. electrons flowing

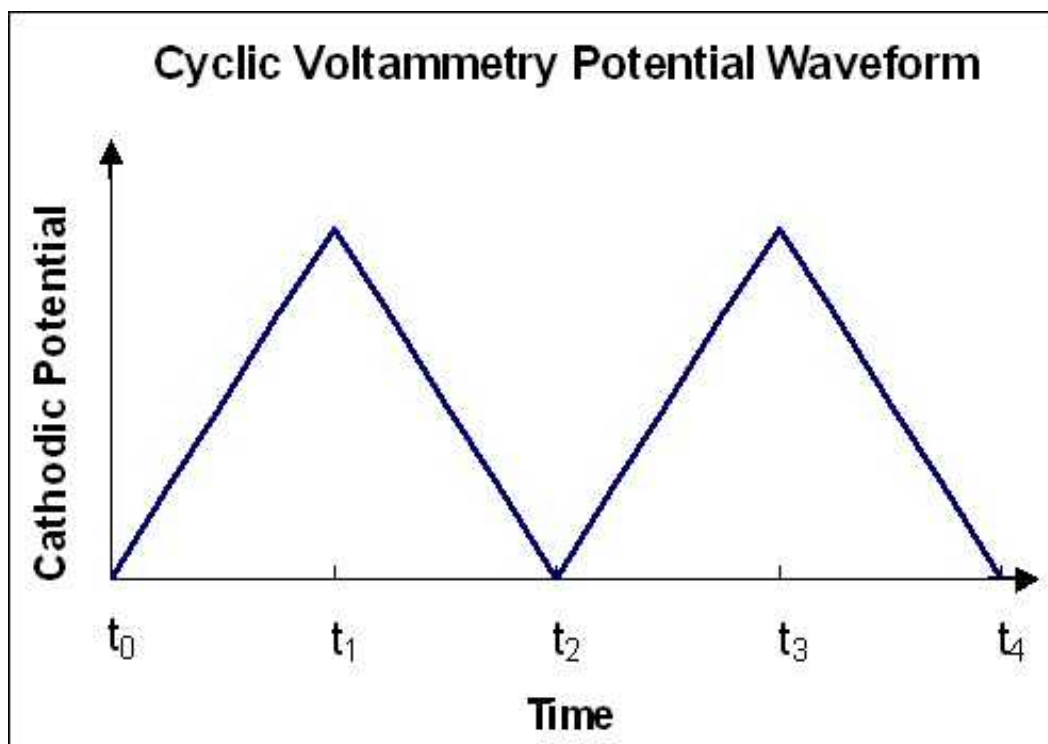
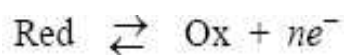


Figure 1.10: A cyclic voltammetry potential waveform with switching potentials

away from the electrode) may occur to cause a cathodic current. By IUPAC convention, anodic currents are positive and cathodic currents negative. The magnitude of the observed faradic current can provide information on the overall rate of the many processes occurring at the working electrode surface. As is the case for any multi-step process, the overall rate is determined by the slowest step. For an redox reaction induced at a working electrode, the rate determining step may be any one of the following individual step depending on the system: rate of mass transport of the electro-active species, rate of adsorption or desorption at the electrode surface, rate of the electron transfer between the electro-active species and the electrode, or rates of the individual chemical reactions which are part of the overall reaction scheme.

For the oxidation reaction involving n electrons



The Nernst Equation gives the relationship between the potential and the concentrations of the oxidized and reduced form of the redox couple at equilibrium (at 298 K):

$$E = E^{0'} + \frac{0.059}{n} \log_{10} \frac{[\text{Ox}]_i}{[\text{Red}]_i}$$

Where E is the applied potential and $E^{0'}$ the formal potential; $[\text{OX}]$ and $[\text{Red}]$ represent surface concentrations at the electrode/ solution interface, not bulk solution concentrations. Note that the Nernst equation may or may not be obeyed depending on the system or on the experimental conditions.

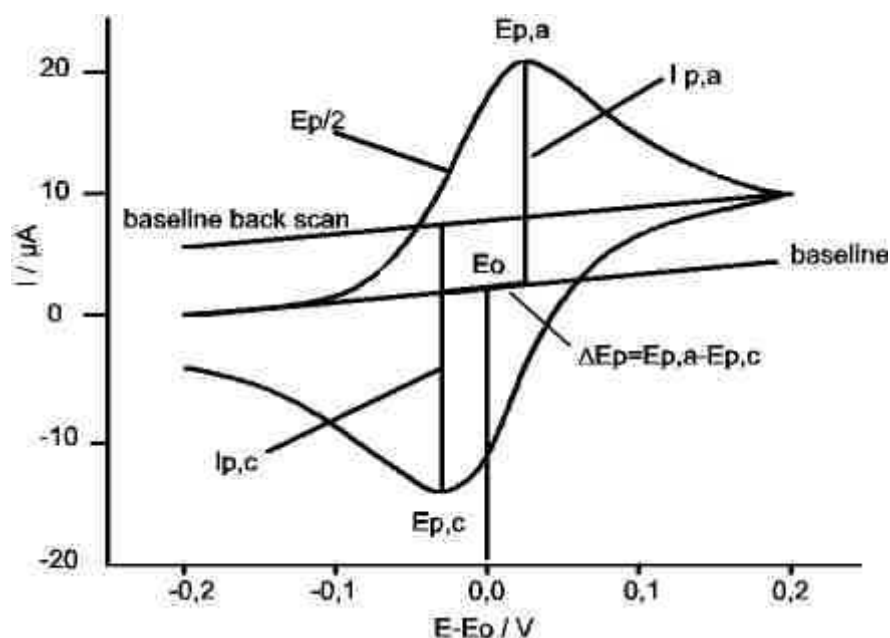


Figure 1.11: The expected response of a reversible redox couple during a single potential cycle

A typical voltammogram is shown in Figure 1.2.8. The scan shown starts at a slightly negative potential, (A) up to some positive switching value, (D) at which the scan is reversed back to the starting potential. The current is first observed to peak at E_{pa} (with value i_{pa}) indicating that an oxidation is taking place and then drops due to depletion of the reducing species from the diffusion layer. During the return scan the processes are

reversed (reduction is now occurring) and a peak current is observed at E_{pc} (corresponding value, i_{pc}).

Providing that the charge-transfer reaction is reversible, that there is no surface interaction between the electrode and the reagents, and that the redox products are stable (at least in the time frame of the experiment), the ratio of the reverse and the forward current $i_{pr}/i_{pf}=1.0$ (in Figure 1.11 $i_{pa}=i_{pf}$ and $i_{pc}=i_{pr}$). In addition, for such a system it can be shown that:

- ❖ the corresponding peak potentials E_{pa} and E_{pc} are independent of scan rate and concentration
- ❖ the formal potential for a reversible couple E^0 is centered between E_{pa} and E_{pc} : $E^0 = (E_{pa} + E_{pc})/2$
- ❖ the separation between peaks is given by $\zeta E_p = E_{pa} - E_{pc} = 59/n$ mV (for a n electron transfer reaction) at all scan rates (however, the measured value for a reversible process is generally higher due to uncompensated solution resistance and non-linear diffusion. Larger values of ζE_p , which increase with increasing scan rate, are characteristic of slow electron transfer kinetics).

It is possible to relate the half-peak potential ($E_{p/2}$, where the current is half of the peak current) to the polarographic half-wave potential, $E_{1/2}$: $E_{p/2} = E_{1/2} \pm 29\text{mV}/n$ (The sign is positive for a reduction process.) Simply stated, in the forward scan, the reaction is $O + e^- \rightarrow R$, R is electrochemically generated as indicated by the cathodic current. In the reverse scan, $R \rightarrow O + e^-$, R is oxidized back to O as indicated by the anodic current. The CV is capable of rapidly generating a new species during the forward scan and then probing its fate on the reverse scan. This is a very important aspect of the technique [37].

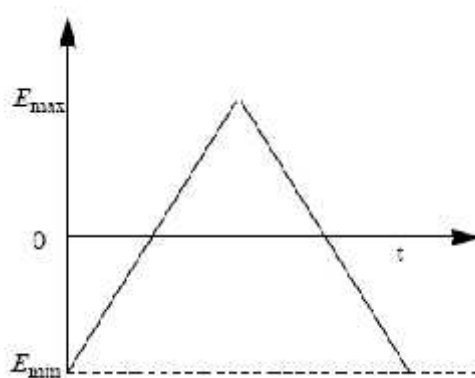


Figure 1.12: Variation of potential with time in cyclic voltammetry

A characteristic feature is the occurrence of peaks, identified by the peak potential E_p , which corresponds to electron transfer reactions. The repetitive triangular potential excitation signal for CV causes the potential of the working electrode to sweep backward and forward between two designate values (the switching potentials). In cyclic voltammetry of reversible system, the product of the initial oxidation or reduction is then reduced or oxidized, respectively, on reversing the scan direction.

Adsorbed species lead to changes in the shape of the cyclic voltammogram, since they do not have to diffuse from the electrode surface. In particular, if only adsorbed species are oxidized or reduced, in the case of fast kinetics the cyclic voltammogram is symmetrical, with coincident oxidation and reduction peak potentials [38].

1.12.6 Amperometry

A fixed potential is applied to an electrode against a reference electrode (Figure 1.13 (a)) until a steady state current is generated. This is achieved more readily in a stirred solution due to the greater efficiency of mass transport. Stirring also ensures that the concentration gradient at the working electrode is constant. Once steady state is achieved, standard additions of the analyte of interest are added into the voltammetric cell. The additions result in increases in current, with each addition occurring after steady state has been achieved, the magnitude of the current is proportional to the concentration of the analyte,

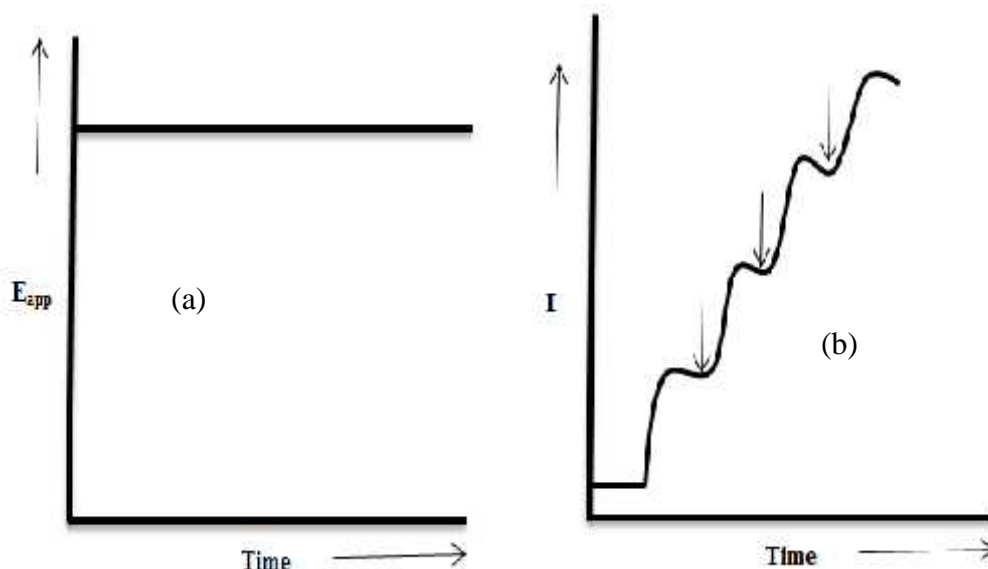


Figure 1.13: (a) Current waveform for amperometric experiments. (b) A typical amperometric plot in stirred solution. Arrows indicate additions of the target analyte

which in turn is proportional to the rate of the redox reaction at the working electrode surface. An example of a typical amperometric plot is shown in Figure 1.13. (b).

1.12.7 Chronoamperometry (CA)

As with all pulsed techniques, chronoamperometry (CA) is one of the simplest potential wave forms. The potential is changed instantaneously from the Initial Potential to the First Step Potential, and it is held at this value for the First Step Time. This is a single potential step experiment. In CA, the current is monitored as a function of time. The Faradaic current--which is due to electron transfer events and is most often the current component of interest--decays as described in the Cottrell equation. Since the current is integrated over relatively longer time intervals, CA gives a better signal to noise ratio in comparison to other amperometric technique. A chronoamperometric curve at a disk microelectrode varies from the Cottrell behavior to the steady state current.

Chronoamperometric techniques involve the polarisation of the working electrode at a fixed potential in a quiescent solution. The potential is stepped from E_1 , where no reaction takes place, to one at which all species which reach the electrode surface react (E_2), as

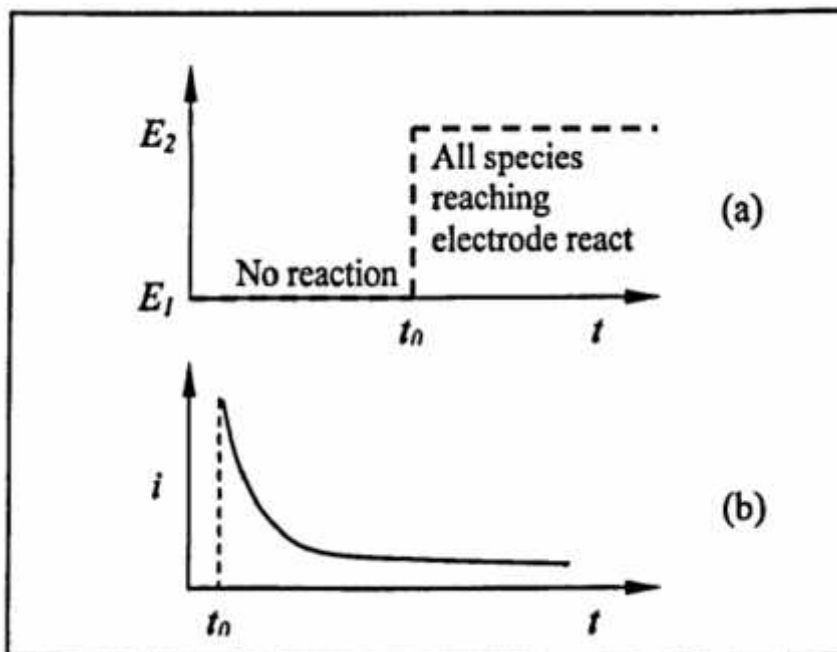


Figure 1.14: Chronoamperometry: (a) the potential step (b) current response to the applied potential as a function of time

Shown in Figure 1.14 (a). Current flow is recorded against time (t), as shown in Figure 1.14 (b). Immediately following the application of potential, E_2 , a large current is observed resulting from the relatively high (bulk) concentration of reactant at the electrode surface. As the reactant is consumed, and the concentration gradient extends into solution, the current can be seen to decay to a steady-state value controlled by the rate of diffusion given by the case of a planar electrode in a quiescent solution.

For an electrode of normal dimensions in static conditions, the current flow is described by the Cottrell Equation (Cottrell, 1902), which is derived from Fick's second law of diffusion:

$$i = \frac{nFA[B]_{bulk} D_B^{1/2}}{(\pi t)^{1/2}}$$

Where i is the current measured at time (t), n is the number of electrons transferred per mole, F is the faraday constant, A is the electrode area, $[B]_{bulk}$ is the bulk concentration of the measured species, D_B is the diffusion coefficient of species B.

Most drinking water treatment plants in the world use chlorine as a disinfectant. The use of chlorine in the treatment of drinking water has virtually eliminated waterborne diseases, because chlorine can kill or inactivate most microorganisms commonly found in water. We designed, fabricated and tested a disposable micro sensor for free chlorine monitoring in water. The developed micro sensor is a low cost device that is applicable to a portable on-site instrument for monitoring free chlorine in the water treatment process.

1.13 Objectives of the present work

FAC sensor is one of the important sensors with a high environmental impact which will facilitate sourcing pure water; however, its improvement associates few challenges. The objectives of this research are to develop a chlorine sensor and also to study the sensitivity, selectivity, stability of this sensor using various electrochemical techniques.

The specific aims are:

- ❖ Fabrication of graphite based sensor platform
- ❖ Development of free available chlorine sensor
- ❖ Electrochemical characterization of chlorine sensor
- ❖ Fictionalization of graphite electrode for estimation of free chlorine
- ❖ A prototype free available chlorine sensor

CHAPRWER II

Literature Review

2.0 General

Chlorine dissolved in liquid, is one of the most effective and economical germ-killers for the treatment of water to make it potable or safe to drink. Chlorine's powerful disinfectant qualities come from its ability to bond with and destroy the outer surfaces of bacteria and viruses. Drinking water chlorination is one of the most widely used methods to safeguard drinking water supplies. In addition to water disinfection, chlorine and its derivatives are used to treat sewage and industrial effluent, and as household and industrial bleaches (e.g., to control biological agent growth in water filled industrial systems) to maintain and improve hygiene standards [40,41].

2.1 Various analytical methods for free available chlorine detection

Platinum electrodes that is commonly used and commercially available for estimating FAC in water. On the other hand, carbons electrodes have are widely used in electrochemistry and are a well established [42]. A number of different carbon based materials and technologies have been commonly utilized such as glassy cabon [43], carbon paste [44] or screen printed [45]. All of these approaches require some degree of expertise, preparation and care. As a result, a number of alternative sources for the manufacture of carbon electrodes have been investigated, such as utilization of pencil leads as electrodes [[46-47]. The pencil lead is actually a mixture of graphite, wax and clay, the proportions of which impart different properties to the pencil with increasing amounts of clay making the pencil harder, hence the designation 'H'. Increasing the level of graphite make the pencil softer, and their marks darker or black and so the designation 'B'. This allows for an extremely facile, green, low cost, rapid method to fabricate electrode prototype, as illustrated in Table 2.1.

Table 2.1: Recent application of pencil electrodes

Analyte	Fabrication	Analytical Technique	Reference
Glucose	Pencil working electrode with Ag ink reference and counter electrode	Glucose biosensor using voltammetric analytical technique	48
Ascorbic acid, dopamine	Pencil dual electrode	Thin layer chromatography and dual electrode redox system	49
p-nitrophenol	6B pencil drawn on paper	Solvent vapour measured at pencil drawn chemiresistor	50
H ₂ O ₂	Doped pencil leads	Cobalt (II) modified pencil electrode	51
Lead	6B pencil drawn carbon electrode	Anodic stripping voltammetry	133
Carbohydrate antigen	Entirely hand drawn with commercially available crayon and pencils	electrochemiluminescence	134

There are various other methods also involve in detecting FAC in water, such as colorimetric methods. The DPD (N, N-diethyl-p-phenylenediamine) colorimetric method for residual chlorine was first introduced by Palin in 1957 [52]. Over the years it has become the most widely used method for determining free and total chlorine in water and waste water. Hach Company introduced its first chlorine test kit based on the DPD chemistry in 1973. The chemical basis for the DPD chlorine reaction is depicted in Figure 2.1. The DPD amine is oxidized by chlorine to two oxidation products. At a near neutral pH, the primary oxidation product is a semi-quinoid cationic compound known as a Würster dye. This relatively stable free radical species accounts for the magenta color in the DPD colorimetric test. DPD can be further oxidized to a relatively unstable, colorless imine compound. When DPD reacts with small amounts of chlorine at a near neutral pH, the Würster dye is the principal oxidation product. At higher oxidant levels, the formation

of the unstable colorless imine is favored — resulting in apparent “fading” of the colored solution [53-57].

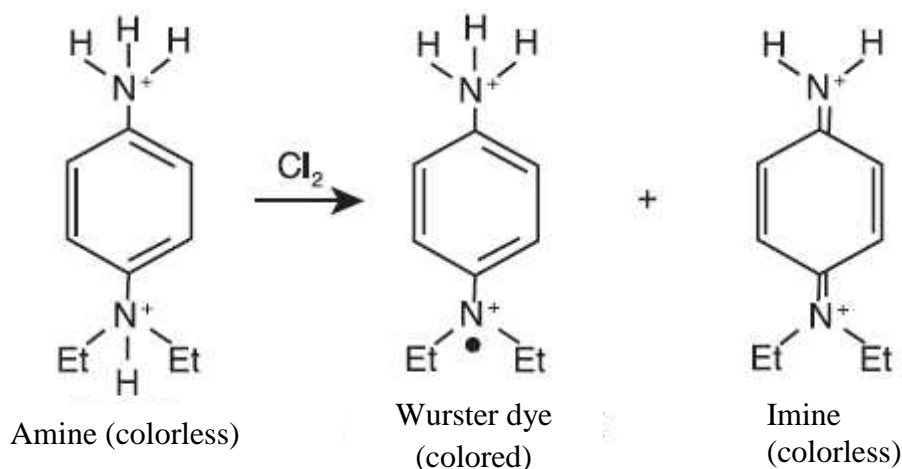


Figure 2.1: DPD-chlorine reaction products

Hach Company has developed a procedure to determine the reagent blank for the ULR-DPD method. The procedure dechlorinates the sample without affecting the color contributed by the indicator reagent. In the reagent blank compensation procedure, a non-reducing agent is added to the sample to remove free and combined chlorine. Next, indicator and buffer reagents are added to the dechlorinated sample, following the normal test procedure. The resulting color is used to correct the sample analysis results. Consistent reagent blank values, equivalent to less than 3 μ g/L chlorine, are obtained when using the ULR-DPD reagents.

Hach Company's method for ULR totals chlorine testing, chlorine residuals as low as 2 μ g/L can be determined [58]. This level of detection was determined using the U.S. Environmental Protection Agency (USEPA) procedure for estimating the method detection limit (MDL) [58, 59]. The upper range for the test is 500 μ g/L as Cl₂.

Monitoring uses for the ULR-DPD method for total chlorine include dechlorination of feed water to reverse osmosis membranes or ion-exchange resins, make-up water for the pharmaceutical and beverage industries, and in wastewater treated to meet NPDES requirements. The ULR-DPD method is USEPA-accepted for total chlorine determinations in drinking water and wastewaters.

2.2 Titration method for estimation of FAC

The DPD titration method is based on the same chemistry as the DPD colorimetric method in that DPD is oxidized by chlorine (or iodine in the case of chloramines) to the magenta-color species. The red color then is titrated with a ferrous reducing agent to the colorless end point. The reaction chemistry is depicted in Figure 2.2.

Standard methods and ISO DPD titration procedures both use the same buffer and indicator reagent formulations as those specified in the referenced DPD colorimetric methods. Hence, the inherent problems of reagent instability and buffering of hard water samples cited above also are applicable to the reference titration procedures.

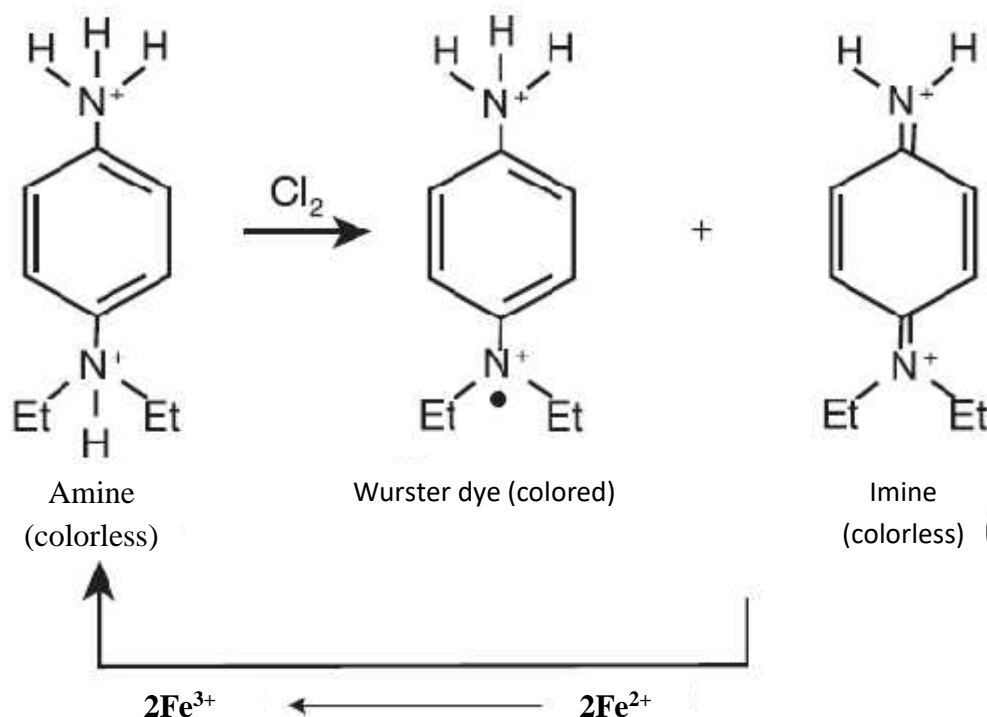


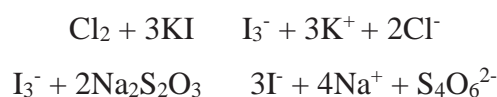
Figure 2.2: Chemistry of DPD-FAS titration

The ferrous iron titrant reagent used in the Standard methods and ISO DPD titration methods is prepared from ferrous ammonium sulfate. This titrant solution is very unstable, susceptible to oxidation, and must be frequently standardized against standard potassium dichromate. The titrant generally is used for only one month.

In DPD titration methods, a DPD free or total chlorine reagent powder pillow is added to 25 mL of sample. After full development of the Würster dye, the reacted sample is titrated to the colorless end point using FEAS with the Digital Titrator. The number of digits required to the end point is divided by 100 to obtain the mg/L chlorine. For most samples, there is no clear advantage to using the DPD titration method over Hach's DPD colorimetric method.

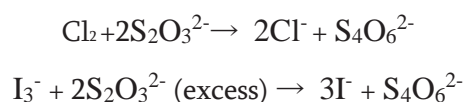
2.3 Iodometric titration

The starch-iodide titration method, one of the oldest methods for determining chlorine, is very non-specific for oxidants and generally is used for total chlorine testing at levels above 1 mg/L Cl₂. The method is based on reaction with thiosulfate solution:



The end point of the titration is indicated by the disappearance of the blue-colored, starch-iodide complex. The titration usually is performed at a sample pH between 3-4. Research by Hatch and Yang [60] has shown sample temperatures above 20 °C can produce significant errors if starch is used as the titration end-point indicator. Their studies indicate the release of triiodide from the starch helix is temperature-dependent. For maximum accuracy, iodometric titrations using starch indicator should be performed at sample temperatures less than 20 °C (68° F).

A "back titration" is recommended for waters containing potential chemical interferences. In this case, a known amount of thiosulfate is added in excess of the chlorine in the sample. The amount of unreacted thiosulfate is titrated with a standard iodine solution. Then, the total chlorine is calculated, based on the Thiosulfate equivalency in the sample. The chemical reactions are:

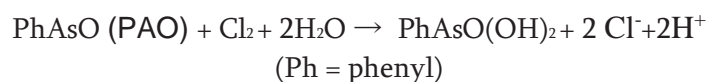


Hach Company offers several total chlorine systems using the iodometric titration method. Typically, the application range is from 1 to 70,000 mg/L chlorine. Hach Company's

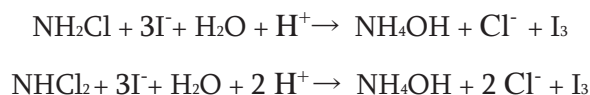
iodometric procedures are used to assay chlorine in commercial bleach solutions and in chlorinated wastewaters.

2.4 Amperometric titration methods to detect chlorine in surface water

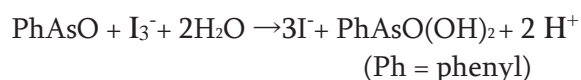
In the amperometric determination of free chlorine, chlorine is titrated with a standard reducing agent such as thiosulfate or phenylarsine oxide (PAO) at pH 7. A small potential is applied across the electrodes before the titration begins. Current cannot flow between the electrodes unless two substances are present — one that can be oxidized at the anode and another that can be reduced at the cathode. During the course of the titration, chlorine is reduced at the cathode to chloride (Cl^-) from the reaction with PAO. PAO is oxidized from the +3 to the +5 oxidation state at the anode:



As long as the oxidant (free chlorine) is present in the titrated sample, a current flows through the cell. When all of the oxidant is reacted, the rate of current change is zero, signaling the end point of the titration. After the end point is reached, the solution cannot conduct current even though excess PAO is added. The amount of PAO used at the titration end point is proportional to the chlorine concentration in the sample. In the case of chloramine determination, the pH is lowered to 4 and potassium iodide is added to convert the chloramine species to an equivalent amount of triiodide ion:



The triiodide is titrated with PAO with the current change measured amperometrically



Standard methods [61] differentiate between monochloramine and dichloramines by performing the monochloramine titration in the presence of potassium iodide at pH 7. After titration, the pH is lowered to 4, additional iodide is added and the titration is continued to resolve the dichloramine fraction. Because an amperometric titration typically must be “over-shot” to determine the end point, the volume of titrant must be corrected for the over-shot increment.

The direct amperometric titration of chlorine or chloramines with a standard reducing agent is known as a “forward” titration. Back titration with an amperometric end point also is used widely for the determination of total chlorine in water.

Amperometric titrations require a higher level of skill and care than the colorimetric methods for chlorine analysis. Standard methods state the amperometric method “is the standard of comparison for the determination of free or combined chlorine” [62]. However, the amperometric method is no longer accepted by ISO methods for the determination of chlorine species [63]. There is considerable conflicting information about interferences with amperometric methods for chlorine in treated wastewater and effluents.

Hach Company offers both forward and backward amperometric methods for determination of free and total chlorine in water. Hach’s Dropsens 4000 Amperometric Titrator (Figure 2.3) is based on a biamperometric system that uses a dual platinum electrode (DPE) probe. The Dropsens 4000 software controls the delivery of titrant from a glass burette driven by a step motor. The step motor requires 18,000 individual steps to deliver the full 5.0 mL of titrant that it contains. This allows a volume resolution of 0.0003 mL per step.



Figure 2.3: Hach company's dropsens amperometric titrator

Even when a Class A 5mL buret is used, dispensation of one small droplet of 0.00564 N PAO could relate to as much as 20 $\mu\text{g/L}$ Cl_2 in a forward titration using 200 mL of sample. Typical titration plots for Hach's Dropsens 4000 forward and back amperometric method. A comparison of currently available commercial amperometric systems shows lower detection levels are possible with the Dropsens 4000 because of microdispensation and automatic determination of the endpoint. Method detection limits for the total chlorine forward titration are 0.0012 mg/L (1.2 $\mu\text{g/L}$) Cl_2 and 0.0051 mg/L (5.1 $\mu\text{g/L}$) for the back titration [62].

2.5 Interferences in the DPD methods

Calibration non-linearity

The non-linearity of the DPD colorimetric method calibration using the standard methods procedure has been reported by Gordon and Ellms [63-65] and confirmed by Hach Company chemists. The concentration range is stated to be 0 - 4.0 mg/L Cl_2 , using either chlorine standards or secondary standards made from potassium permanganate. Gordon

reported the Standard Methods procedure using permanganate exhibited a non-linear response above 1.0 mg/L equivalent chlorine. Hach Company also has confirmed the non-linearity of the standard methods procedure using free chlorine standards.

The non-linearity of the standard methods calibration (Figure 2.7) is attributed to the increased formation of the colorless imine product at higher oxidant concentration. In the standard methods formulation, the amount of DPD added to the sample is insufficient to optimize the oxidation to the würster product stage. The instability of the liquid DPD reagent is also a contributing factor to the non-linear chlorine calibration. As the DPD indicator solution ages, less active DPD free amine is available to react with sample chlorine, there by shifting the DPD oxidant ratio. This would lead to increasing nonlinearity at the higher chlorine levels as the DPD reagent solution ages and becomes oxidized.

Hach Company has optimized its DPD reagent formulations to obtain a linear response to chlorine over the test range. Hach DPD reagents are controlled to assure linearity over the specified range. Because Hach DPD powdered formulations offer superior stability over the liquid reagent formulations, a reproducible and linear response to chlorine will be obtained for a longer period of time.

It should be noted that in the DPD titration method, both DPD oxidation products are titrated by the ferrous titrant. As a result, the titration method does not suffer from the “color fading” phenomenon.

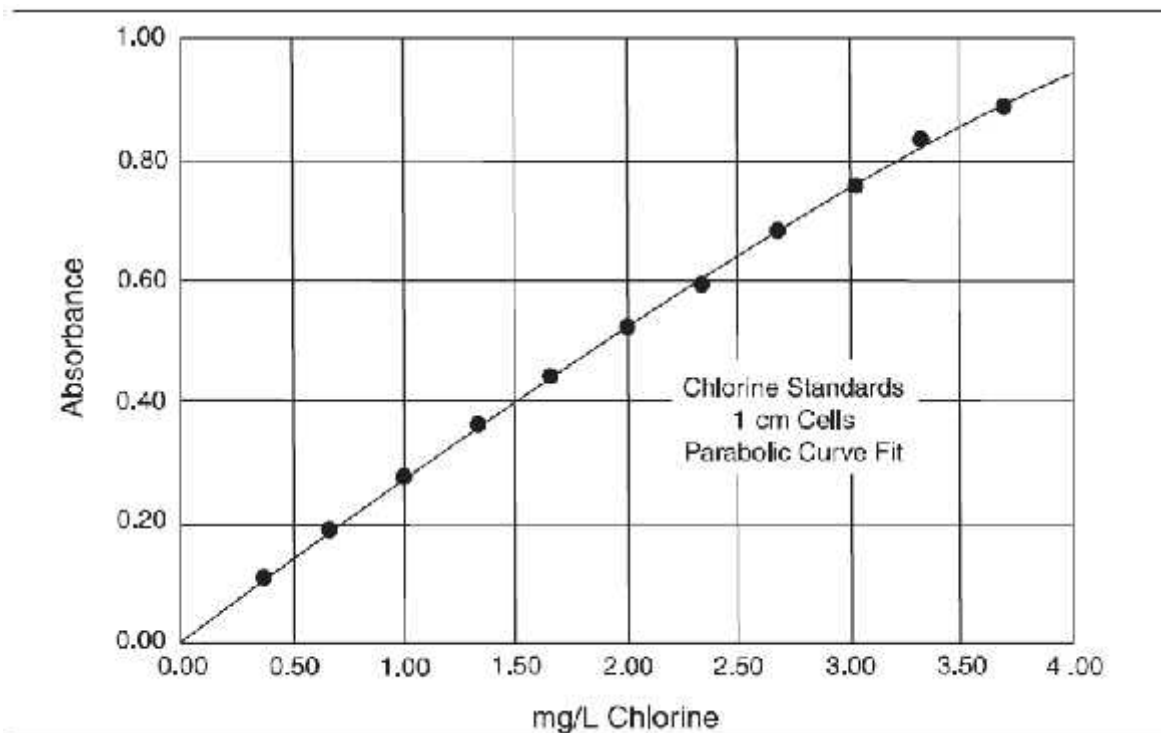


Figure 2.4: Standard methods calibration - DPD colorimetric method

Using permanganate as an equivalent standard method

Dilute solutions of potassium permanganate are used in standard methods as equivalent standards for establishing a chlorine calibration. Gordon, et al. [65] permanganate oxidizes DPD to both the colored and colorless oxidation product. Hach Company researchers have noted the order of adding reagent to sample also will affect the ratio of oxidized DPD products.

In practical terms, the differences between reagent to sample and sample-to-reagent additions using permanganate standards and Hach's DPD reagent are relatively small. Table 2.2 shows the differences obtained over a series of permanganate standards in the range of 0.2-1.8 mg/L as chlorine. The average difference between the two addition techniques was 0.03 mg/L as chlorine. The greatest discrepancies were noted at concentrations greater than 1.0 mg/L.

Table 2.2 Order of sample-to-reagent addition using permanganate equivalent standards method [67, 67]

Equivalent mg/L Cl ₂	Reagent-to-Sample		Sample-to-Reagent		Difference	
	Abs.	Conc.mg/L	Abs.	Conc.mg/L	Abs.	Conc.mg/L
1.00	0.530	0.99	0.543	1.02	0.013	0.03
1.20	0.613	1.15	0.643	1.19	0.019	0.04
1.40	0.727	1.36	0.743	1.39	0.016	0.03
1.60	0.764	1.43	0.791	1.49	0.027	0.06

The Chlorine Voluette standards are pure aqueous free chlorine standards prepared in two ranges 20 - 30 mg/L or 50 - 75 mg/L chlorine. The actual value is provided for each lot of standards [68].

Monochloramine interference in the free chlorine sensor

There is considerable controversy about monochloramine interference in the free chlorine DPD test. Some studies [69] have indicated the percent interference in the free chlorine results can vary from 2.6 to 6.0%, depending on the monochloramine concentration and sample temperature.

The amount of monochloramine must be substantial in comparison to the free chlorine concentration to indicate interference in the DPD colorimetric free chlorine determination. The reaction of DPD with free chlorine is rapid. If the color is measured within one minute, the monochloramine breakthrough will be minimal. A concentration of 3.0 mg/L monochloramine (as Cl₂) will cause an increase of less than 0.1 mg/L free chlorine when using Hach DPD colorimetric tests.

Monochloramine breakthrough is more of a problem in the DPD titrimetric method for free chlorine because of the additional time necessary to perform the test. Standard methods recommends the use of thioacetamide to “completely stop further reaction with combined

chlorine in the free chlorine test.”The thioacetamide modification is recommended for the DPD titration of free chlorine in the presence of more than 0.5 mg/L chloramines.

Free chlorine is to be tested in the presence of a significant amount of monochloramine, the free chlorine DPD colorimetric test is the recommended procedure. Some published reports [70, 71] indicate mercuric chloride, added to the Standard methods liquid phosphate buffer, has an inhibitory effect on monochloramine breakthrough in the DPD free chlorine determination. The mercuric salt may scavenge trace iodide, thereby minimizing monochloramine oxidation. Here again, because this phenomenon is not completely understood and because of the toxicity of mercury salts, Hach company does not recommend or use mercury in any of its DPD reagent formulations.

2.6 Interferences in the amperometric methods

Standard method states the amperometric method “is the method of choice because it is not subject to interference from color, turbidity, iron, and manganese or nitrite nitrogen” [72]. In reality, several of these factors do affect the determination of chlorine species when using amperometric methods. A brief review of some of the common sources of errors encountered with real world samples follows:

Deposition on electrode surfaces

Clean and regularly conditioned electrodes are necessary for sharp amperometric titration end points. Because the electrodes contact the sample, certain species in the sample may plate out or coat the electrode’s metallic surface. Metallic ions such as copper (+2), silver (+1) and iron (+3) have been reported as either interferences in the forward amperometric method or may diminish the electrode response. In some waters, foaming or oily surface active agents will coat the metallic electrodes, resulting in decreased sensitivity.

Hach company’s dual platinum electrodes (DPE), regular cleaning and conditioning are necessary to remove any oxidation of the metal surfaces and to sensitize the electrodes to chlorine. Cleaning involves soaking the electrode surfaces with a 1:1 nitric acid solution for a short period of time and then rinsing the probe repeatedly with distilled or deionized

water. The cleaned probe is stabilized by soaking the platinum electrodes in chlorinated tap water or a dilute (1-5 mg/L chlorine) solution of commercial bleach, while stirring. Allow at least 10 minutes for probe stabilization in the chlorinated water. Performing a couple of test titrations with chlorine or iodine standards prior to actual sample titration will further stabilize the probe.

2.7 Nitrite interference for FAC sensor

Nitrite can exist as a transitory compound in certain waters, due to the biological oxidation of ammonia:



There is conflicting information about the interference of nitrites in either the forward or backward amperometric methods for total chlorine. According to Standard Methods, nitrites do not interfere in the forward titration methods [73]. The iodometric method, states that nitrite interference can be minimized by buffering to pH 4.0 before addition of iodide. It also states that interference from more than 0.2 mg/L of nitrites can be controlled by the use of a phosphoric acid and sulfamic acid reagent. This reagent is used in conjunction with iodate as titrant because higher acidity is required to liberate free iodine. White [74] indicates nitrites can oxidize KI to iodine, similar to the reaction of KI with chlorine or chloramines. The reaction of KI with nitrite apparently is accelerated by acidity, especially when the pH is less than 4. White recommends the addition of sulfamic acid to the sample containing nitrites and allowing it to stand for 10 minutes prior to the addition of standard reducing agent. This procedure does not, however, address the possible loss of chloramines or side reactions during the delay period.

Monochloramine was selected since it is slow to react with nitrites [75] and represents the primary disinfectant form in treated wastewater. Free chlorine has been shown to react directly with nitrites [76] according to:



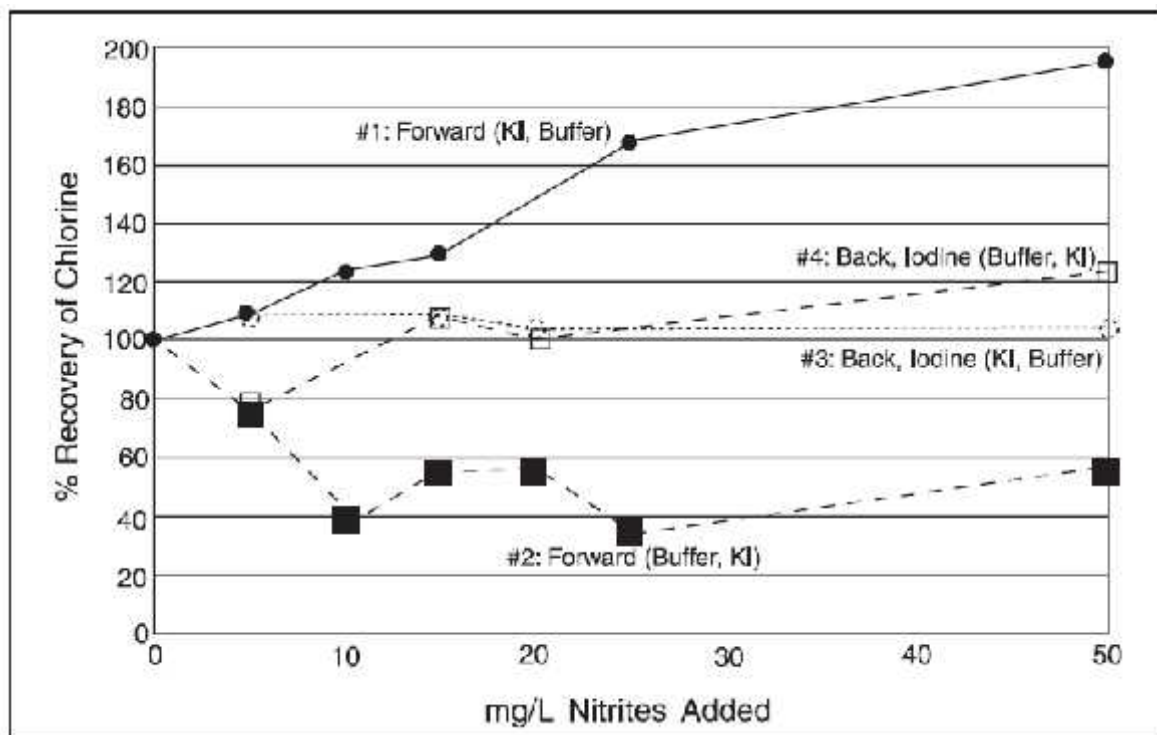
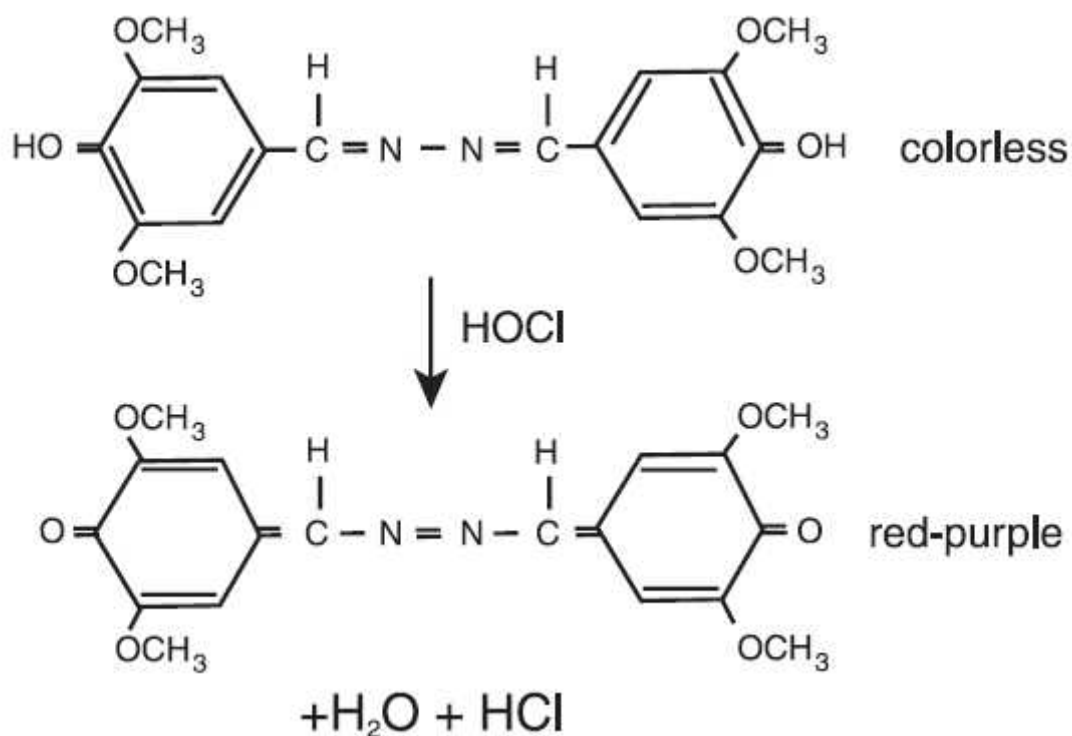


Figure 2.5: Nitrite interference in amperometric chlorine methods

A monochloramine standard was prepared in the range of 70 to 80 $\mu\text{g/L}(\text{Cl}_2)$. Small portions of a stock nitrite standard, equivalent to the addition of 0 to 50 mg/L nitrites, were added to 200 mL of the monochloramine standard. Analyses were performed in triplicate according to the sequences listed above. Mean percentage recoveries as a function of nitrite concentration are shown graphically in figure 2.5.

2.8 Syringaldazine FACTS sensor method

This method is based on the reaction of 3,5-dimethyl-4-hydroxybenzaldazine (syringaldazine) with free chlorine on a 1:1 basis:



The published method generally is known as the FAC sensor method (free available chlorine sensor testing with syringaldazine). The application range is reported as 0.1-10 mg/L Cl_2 . The test has been adapted to the determination of total chlorine as well as other oxidants [77].

The FACTS method has been reported to be specific for free chlorine, with little interference from manganese (+4) and monochloramine. A standard method procedure [78] for free chlorine determinations, it is not recognized by the ISO method.

Major disadvantages of the FACTS method are the insolubility of the indicator and its product, storage of the indicator solution, and a variable sensitivity to chlorine. The syringaldazine indicator is prepared in 2-propanol, in which it has limited solubility. It is necessary to gently heat and use ultrasonic agitation for several hours to dissolve syringaldazine in the 2-propanol. Also, the 2-propanol must be distilled to remove unidentified impurities which exert a chlorine demand.

Hach company research shows a FACTS indicator solution with consistent sensitivity to chlorine is difficult to produce, even with distillation of the 2-propanol. Standard methods

allows an alternate procedure to remove the chlorine demand by chlorinating the alcohol and dechlorinating by exposure to sunlight or ultraviolet (UV) light. This procedure is not recommended, due to the flammability of 2-propanol.

The FACTS procedure is fading of the oxidized (colored) species. This is due, in part, to the relative insolubility of the product when diluted by the aqueous sample. Chiswell and O'Halloran [79] reported the FACTS method is unsuitable for free chlorine testing due to the instability of the oxidized reaction product. Increasing the propanol concentration did not significantly improve the solubility of the oxidation product. Also, the product decomposes rapidly if the test pH falls out of the range of 6.5 to 6.8.

The standard methods procedure calls for a phosphate buffer to control the sample pH at 6.6. Hach company's research has shown that sample hardness at levels as low as 200 mg/L CaCO₃ will have an appreciable effect on the stability of the colored product. Precipitation of calcium phosphate destroys the buffer capacity, with a resulting test pH lower than 6.5. At this pH, color fading is appreciable and color measurements must be made at standardized intervals.

2.9 Potentiometric electrode sensor method

The electrode method is based on the potentiometric measurement of free iodine produced when iodide is added to an acidic sample containing an oxidant. The method is analogous to the iodometric titration method in that total oxidant is measured and speciation of disinfectants residuals is not possible. The electrode is based on the Nernst equation:

$$E = E_o + [2.303RT/2F] \log [I_2]/[I^-]$$

Where E = measured potential, E_o = standard potential, 2.3 RT/2F = Nernst constant, [I₂] = iodine concentration, [I⁻] = iodide concentration

The electrode method suffers from several interferences. Chloride ion can form the iodine-chloride complex (I₂Cl⁻) which is not sensed by the electrode. Organics in the water sample can react with the free iodine released during the procedure, yielding low readings.

Because the electrode will sense any oxidant capable of oxidizing iodide, species such as manganese, iodate, bromine, cupric and chloroxy will interfere.

Although it is claimed that a MDL of 5 µg/L (as Cl₂) total oxidant can be achieved [80], this involves tightly controlled conditions in the non-linear area of the electrode response. The procedure requires at least two minutes under constant stirring for a complete response. Considering the volatility of chlorine and iodine in natural waters, a practical level of detection using the electrode method is closer to 50 µg/L. Wilde [81] compared the electrode method to the forward amperometric method and the DPD colorimetric method on standards and cooling water samples for total residual chlorine at the Savannah River Site (SRS).

Table 2.3 the common methods used for analysis of free or total chlorine disinfectants in water

Method	Analysis Range (mg/L)	DL* (mg/L)	Application
DPD Colorimetric	0-5.0	0.005	Free and Total
ULR-DPD Colorimetric	0-0.50	0.002	total
DPD Titration	0-3.0	0.018	Free and Total
Iodometric	up to 4.0%	1.000	Total oxidants
FACTS	0-10.0	0.100	Free
Electrode	0-1.0	0.500	Total oxidants

2.10 Pool test kits methods

The first option for testing uses a liquid chemical OTO (othotolidine) that causes a colour change to yellow in the presence of total chlorine. It needs simply fill a tube with water, add 1- 5 drops of the solution, and look for the colour change. These kits are sold in many stores as a way to test the concentration of total chlorine in swimming pool water. This method does not measure free chlorine. Test kits to make basic measurements of free chlorine and pH from a sample of pool water, which are the most important items to

control in a swimming pool, are packaged with small dropper bottles of reagents. These reagents are typically OTO for chlorine and phenol red for pH. [82] The kits include vials for mixing a water sample with the test reagents, and color charts for reading the indicated levels. Besides chlorine and pH, which should be checked frequently, more sophisticated reagent kits provide tests for acid demand and base demand, total alkalinity (TA), calcium hardness, and cyanurate ("stabilizer") concentration. These additional tests tend to vary only over weeks or months in a well-maintained pool, and thus need not be checked as frequently as chlorine and pH.

2.11 Colour-wheel test kit methods

Colour wheel test kits use a powder or tablet chemical DPD (N, N diethyl-p-phenylene diamine) that causes a colour change to pink in the presence of chlorine. The colour wheels are simpler and less expensive than digital meters because to measure the intensity of the colour change, the field worker uses a colour wheel to visually match the colour to a numerical free or total chlorine reading. The test kit can be used to measure free chlorine and/or total chlorine, with a range of 0 – 3.5 mg/l, equivalent to 0 – 3.5 ppm (parts per million).

2.12 Digital colorimeters sensor methods

Digital colorimeters are the most accurate way to measure free chlorine and/or total chlorine residual in the field in developing countries. These colorimeters use the following method:

1. Addition of DPD tablets or powder into a vial of sample water that causes a colour change to pink; and,
2. Insertion of the vial into a meter that reads the intensity of the colour change by emitting a wavelength of light and automatically determining and displaying the colour intensity (the free and/or total chlorine residual) digitally. The range of the meter is 0 - 4 mg/l, equivalent to 0 - 4 ppm (parts per million).

2.13 Electronic ORP probes methods

Where the water is sanitized by means of oxidizers, some suppliers of electronic monitoring equipment recommend that the efficacy of the oxidizer be measured by the oxidation-reduction potential of the water, a factor measured in millivolts, where the minimum acceptable ORP level in public pools is 650 millivolts. This is supposed to ensure a 1-second kill rate for microorganisms introduced into the water. Unfortunately, a commonly used non-chlorine supplemental oxidizer, potassium monopersulfate KHSO_5 , can produce measured 650 mV levels even in the absence of all sanitizing residuals. ORP test cells are available as hand-held instruments, and as probes for mounting permanently in the pool circulation plumbing to control automatic chlorine feeders.

2.14 Standard amperometric direct chlorine sensor probes with electrical signal

Standard amperometric cells with two/three electrode chlorine probes are mainly use in process water or drinking water. These probes use an electrochemical amperometric principle with a dedicated liquid reagent behind a physical membrane. These probe measure free chlorine and are precise. [83] However, the reagent requires being controlled often, so it reduces the time without maintenance of the probe. Moreover, the presence of this membrane and the close volume for the reagent reduce the range of pressure and temperature. [84] This kind of probe needs to be use in special low pressure measuring chamber.

2.15 Effect of pH in chlorine sensor

In general, free chlorine sensors needed to be paired with some form of pH compensation. Compensation of the pH was necessary because only the hypochlorous acid (HOCl) form of free chlorine is reducible at the cathode of an amperometric device. As set forth above, free chlorine is effectively 100% HOCl , while above pH 10; free chlorine is effectively 100% hypochlorite ion (OCl^-). The relative concentrations of hypochlorite ion and hypochlorous acid varying with pH as Illustrated in Fig.2.6 [85]. Detection of pH is integral part of the chlorine determination. Current state of the art mostly reported that pH must be sensed before sensing chlorine for the accurate final output reading. However,

attempt has been made to control the pH to avoid the effect of varying pH on chlorine measurements. For example, buffers have been used in order to attempt to maintain the internal electrolyte solution at a selected pH. Further, William [86] has reported a passive pH adjustment for analytical systems. However, attempts to date involved complicated pH maintenance systems or independent pH compensation for the chlorine measurement [87-89].

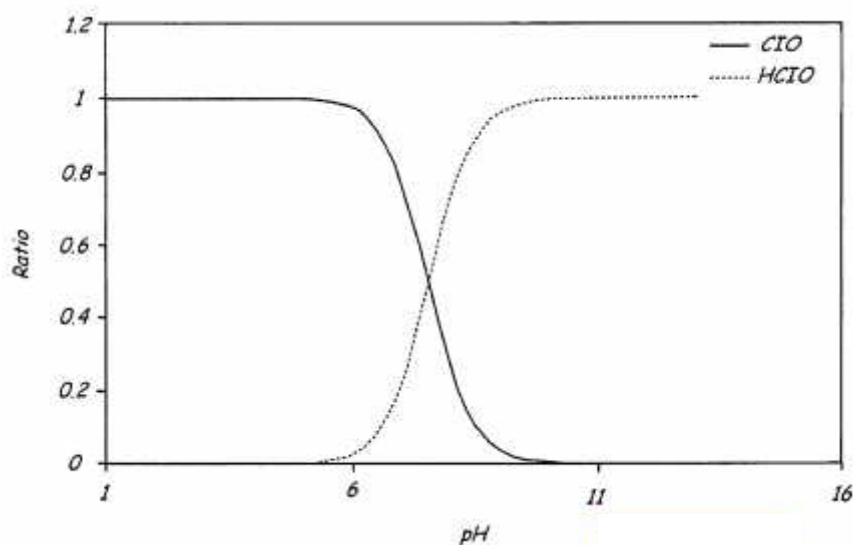


Figure 2.6: Chart of the ratio of free chlorine species as a function of the pH

2.16 Nano-micro technology sensor in FAC determination

Sonochemical method has been used to fabricate micro-electrode array reported by Myler et al. [90]. Sensors of this type were fabricated by first depositing an insulating polydiaminobenzene film on supporting gold electrodes. Sonication and subsequent ablation exposed discrete areas of the underlying conducting electrode, which collectively act as a microelectrode array. Polydiaminobenzene coated membranes were found to be capable of allowing the analytes and rejecting electrochemical interferences such as ascorbate in this case. Moreover, it shows high interfacial adhesion, mechanical strength and thermal stability, which is crucial for FAC sensor. Another group also used Sonochemically fabricated microelectrode by first depositing an insulating film on commercial screen printed electrodes, which was subsequently sonicated to form cavities (micro pores) of regular sizes in film. Few cases, chemical deposition of polysiloxane from

dichlorodimethylsilane was used to deposit a thin protective and diffusion mass transport controlling coating over the electrodes and applied for sensor applications in the presence of interferences [91]. An ultra-thin poly(*o*-phenylenediamine) film composite membrane has also been used as the outer covering barrier on gold sputter-coated porous polycarbonate membrane. Homogeneous poly(*o*-phenylenediamine) films of approximately 30 nm thickness acted as an effective diffusional barrier particularly for ascorbate [92].

To improve the sensitivity, few works have been done using immobilisation of carbon nanotube on the electrode surface. In addition to improving the sensitivity, CNT modified electrode reduce the applied potential and found to be stable in amperometric response [93, 94]. Monolayers of 3-mercaptopropionic acid (MPA) and 11-mercaptoundecanoic acid (MUA) self-assembled on a gold disk electrode showed micro-electrode behaviour, with pinholes acting as the microelectrodes [95].

Hemispherical diffusion of redox active solutes to a layer of independent molecule based nanoelectrode ensembles have been described by Creager et al. Analytical expressions are derived for the current–voltage relation corresponding to catalyzed electron transfer at an ensemble of redox-molecule-based nanoelectrode sites, and the expressions are used to interpret preliminary data for ultrasensitive electrochemical detection in flow streams via an electrochemical amplification process. This is thought to involve redox mediation by individual analyte molecules adsorbed onto monolayer-coated electrodes [96]. A one step approach to Pt nanopore ensembles has been developed using an amphiphilic block copolymer [polystyrene-block-poly (acrylic acid)] self-assembly. At lower scan rates, it remains the features of a single nanoelectrode, while at high scan rates the nanoelectrodes act independently. This is an important feature which can be followed for FAC sensor fabrication and other electroanalytical applications [97].

2.17 Standard analytical methods for chlorine sensor

The U.S. EPA has approved several methods, based on colorimetric (DPD), amperometric, iodometric, and syringaldazine methods, for the determination of free, total, and combined

chlorine in drinking water (Table 2.4). The DPD colorimetric method for residual chlorine is the most widely used to determine free and total chlorine. The amperometric titration technique requires a higher degree of skill and care than the colorimetric method. The iodometric method is less sensitive than the amperometric method but is suitable for measuring total chlorine concentrations higher than 1 mg/L. The syringaldazine method is a colorimetric/spectrophotometric method specific for the analysis of free chlorine. Other methods include Standard Method 4500-Cl B proposed by the American Public Health Association, where the minimum detectable concentration is approximately 0.04 mg/L.

For this method, acid titration (pH 4) is preferred, because some forms of combined chlorine do not react at normal drinking water pH conditions (APHA et al., 2005). In addition, methods approved by the International Organization for Standardization (ISO, 2006) for the determination of free chlorine and total chlorine include ISO 7393-1 (1985) (titrimetric), ISO 7393-2 (1985) (colorimetric), and ISO 7393-3 (1990) (iodometric titration)

Table 2.4: EPA-approved analytical methods for chlorine sensor [98]

Methodology	Method	Chlorine residual measured (MDC)	Comments
DPD colorimetric	SM 4500-Cl G	Free, combined, total (0.010 mg/L)	Interferences: oxidized manganese; high organic content
	EPA 330.5	Total (0.2–4 mg/L)	
DPD ferrous	SM 4500-Cl F	Free, combined, total (0.018 mg/L)	Interferences: oxidized manganese and copper; combined chlorine of > 0.5 mg/L can give high [Cl]
	EPA 330.4	Total (NA)	
Amperometric	SM 4500-Cl D	Free, combined, total (NA)	Interferences: chloramines can give high [Cl]; very low temperature requires long titration time; presence of copper and silver can cause electrode to malfunction; manganese, iron, and nitrite can be minimized by acidification
Iodometric electrode	SM 4500-Cl I	Total (> 1 mg/L)	Interferences: manganese and other oxidants
	EPA 330.3	Total (>0. 1 mg/L)	
Syringaldazine (FACTS)	SM 4500-Cl H	Free (0.1 mg/L)	Interferences: None reported

FACTS, Free available chlorine test, MDC, Minimum detectable concentration, NA, Not available

Therefore, chlorine should be determined immediately after sampling (APHA et al., 2005); for samples collected in the distribution system, it is preferable to conduct the analysis in the field using a field test kit (Harp, 2002). Field test kits are based on the DPD colorimetric method for measuring free or total chlorine in water. The use of automatic colorimeters eliminates the human error associated with colour matching. The visual comparators for free and total chlorine include colour cube (range 0.1–2.5 mg/L) and colour disc (0–3.5 mg/L). Pocket colorimetry kits may allow the determination of free chlorine (0.02–2.0 mg/L) or total chlorine (0–4.5 mg/L), whereas spectrophotometers may allow chlorine analysis in the range 0.1–10 mg/L, depending on the model. A digital titrator based on the DPD-FAS (ferrous ammonium sulphate) method can also be used for field determination of chlorine in the concentration range 0.01–3.0 mg/L. When using the DPD colorimetric test, it is important to ensure that field staffs are well trained to do both free and total chlorine measurements. This ensures that false positive results are not inadvertently reported if there is a monochloramine residual present (Pon, 2008). A monochloramine residual is due to the presence of ammonia in either the supply (naturally occurring) or the distribution system (naturally occurring or use of chloramine). Special analysers are often used to control the feed rate of chlorine and monitor chlorine residuals online. The analysers use amperometric titration, colorimetric, or oxidation–reduction potential probe methods. Free and combined forms of chlorine may be present simultaneously in chlorinated water. Chloramines are the combined forms resulting from the reaction of chlorine with naturally occurring ammonia or ammonia added as part of the water treatment strategy. Total chlorine is the combination of free and combined chlorine.

2.18 Challenges and future trend

FAC sensor is one of the important sensors with a high environmental impact which will facilitate sourcing pure water, however, its improvement associates few challenges. Majority FAC sensors are pH sensitive, therefore, need to control the pH of the sample during the measurement. Few strategies are currently being used to control pH or to correct pH in the sample solution, such as chemical corrections or using pH probe. Ultimately it makes the FAC sensor fabrication more complicated and expensive.

The signal measured by current FAC probes on the market varies with flow rate as the electrodes are macroscopic in size. Micro or nano cylindrical or disc size electrode may reduce the effect of flow rate due to their spherical and semi-spherical diffusion orientation.

Response time of the current FAC sensor need to be improved, as current available FAC sensors has a large variation of response time start from 60 s. Current ATi membrane probes show response time of 60s, whereas Emerson probes show 4/5 mins. In addition to response time, controlling temperature of the sample is also an issue. The reaction rate varies with the change in temperature; therefore, detection of free available chlorine using the sensor technology can be changed with the change in temperature. Appropriate algorithm must be designed to account temperature corrections. Frequency of calibration of the FAC sensor found to be another issue where current commercial sensors require weekly calibration.

CHAPTER III**Experimental Section**

Electrode fabrication and the electrochemical behavior of fabricated electrode to monitor free available chlorine (FAC) have been described in this thesis. In this chapter, detail procedure as well as instrumentation on electrode fabrication and its application to monitor FAC is described.

3.1 Chemicals

All chemicals and solvents are used in the synthetic and analytical works were of analytical grade obtained from E. Merck, Germany, British Drug House (BDH) of England and Sigma-Aldrich, India. The used chemicals were- Sodium thiosulfate, Disodium hydrogen phosphate (Na_2HPO_4), Sodium dihydrogen phosphate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$), Sodium nitrate (NaNO_3) Sodium sulfate (Na_2SO_4) Sodium bicarbonate (NaHCO_3), Disodium carbonate (Na_2CO_3) and Sodium chloride (NaCl) were purchased from Sigma-Aldrich, India. Sodium hypochlorite (NaOCl) was obtained from MERCK, Germany. Ammonium carbamate, Potassium iodide and Starch were obtained from British Drug House (BDH), England. 99.997% dry nitrogen (BOC, Bangladesh) was used for purging purpose. For cleaning and all other purposes distilled water was used. All chemicals were used as supplied except purification of the solvent.

3.2 Equipments

Voltammetric and amperometric measurements were performed with a potentiostat / galvanostat (model: μStat 8400, Drop Sens, Spain), which were be applied to the desired potential to the electrochemical cell (i.e. between a working electrode and a reference electrode), and a current-to-voltage converter which measures the resulting current and the data acquisition system produces the resulting voltammogram. The pencil lead (HB, 2B, 6B, 0.7×100 mm) was purchased from local market. The Ag/AgCl reference electrode and the platinum wire counter electrode were purchased from CH Instruments, Inc. (Austin, TX). The reference electrode was

filled with 1 M KCl solution. Pencil graphite electrode employed as a working electrode with Ag/AgCl and Pt wire as reference and counter electrodes, respectively and other instruments were used (i) an AGE (Glassgo, India) magnetic stirrer with a Teflon coated magnetic bar. (ii) a pH meter (ORION 2 STAR made by Thermo Electron Corporation) was employed for maintaining the pH of the solutions. Preparation of the solutions was done by ordinary laboratory glassware. (iii) An electronic balance (Model: HR-200, Japan) was used to weigh required amount of compounds. Scanning Electrone Microscopy-EDX (manufacture by Jeol, USA) was used for the electrode surface characterization.

3.3 Preparation of pencil graphite electrodes (PGEs)

Various grade (i.e. HB, 2B, 6B) pencil graphite was used as the electrode materials. To compare the results glassy carbon electrode has also been used in this study. All the electrodes were tested in 1 mM ferricyanide solution to understand the electrochemistry of PGE. A cutter was used to make the PGE from the pencil graphite. The lead was then rinsed with distilled water to remove any traces of adhesive. This exposed surface served as the point of attachment of the PGE to the potentiostat.

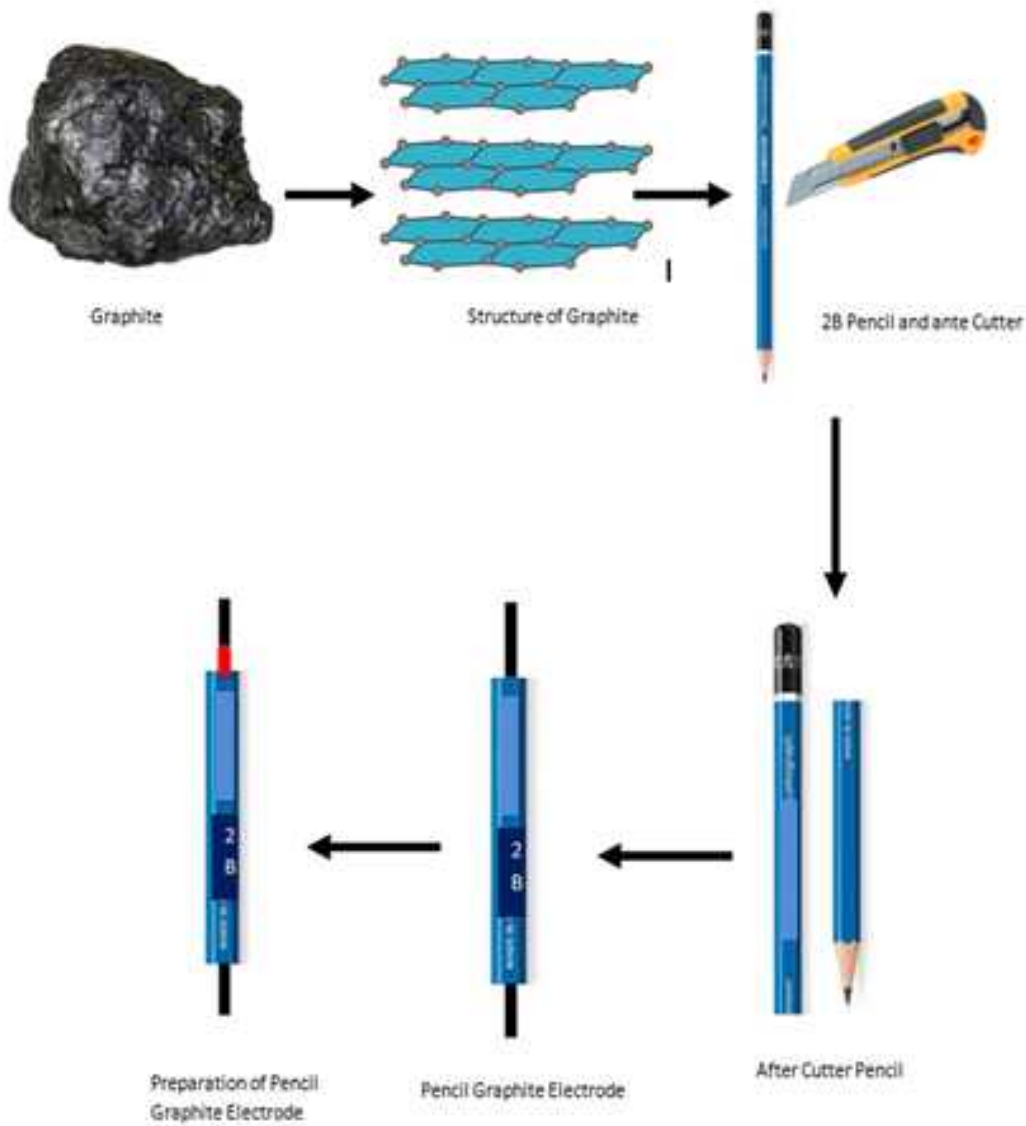


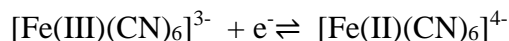
Figure 3.1: Schematic diagram of pencil graphite electrodes

3.4 Pencil graphite electrodes polishing

This electrode preparation includes the polishing and conditioning of the electrode. Prior to the analysis of each solution, end section of the PGE was removed using a razor blade, and the exposed PGE tip polished on 150-grit sandpaper until a substantial amount of graphite was removed. PGEs were then polished on this surface by softly pressing the electrode against the polishing surface in the end for 5-10 minutes. The PGEs was then rinsed with anhydrous ethanol, followed by distilled water, before being immediately tested. Before each run in the same solution, the PGE was re-polished. Before being use the PGEs successively rinsed with distilled water. At this point the electrode surface would look like a shiny black mirror.

3.5 Standardization of the system

The whole electrochemical setup was tested using a standard experiment. In the standard experiment we have studied the following redox couple at a glassy carbon (GC) electrode.



The reaction above was studied electrochemically by pumping electrons into the system from a GC electrode and by measuring the change in the flow of current during the reaction. This is done most conveniently by scanning the potential of the electrode at a constant rate.

In general, the peak current of diffusion controlled reversible or quasi-reversible electro - chemical reaction follows Randles–Sevcik equation;

$$I_p = 0.4463nF \sqrt{\frac{nFD}{RT}} AC\sqrt{v}$$

Where i_p : the peak current, n : the number of electrons, F : Faraday constant, T : the temperature in Kelvin, R : the gas constant, A : the surface area of the working electrode, D : the diffusion coefficient of the electroactive species, C : the bulk concentration of the electroactive species and v : the scan rate of voltammograms.

3.6 Sensor fabrication

Pencil lead was cleaned using lab tissue and rinsed with distilled water. The electrochemical reaction of the pencil graphite electrode surface was carried out at various potential to optimize the effective potential for FAC sensing. In this system Ag/AgCl as reference electrode is used with an initial electrolyte solution of 0.1 M sodium phosphate buffer (pH 7.0), working electrode is a PGEs, and Pt wire as counter electrode.

The working electrode is an electrode where the redox reactions of the substances take place. The reference electrode provides the current required to sustain in electrolysis at the working electrode so that its behavior remains essentially constant with the passage of small current. The counter electrode in the three-electrode system is made of an inert metal.

3.7 Free Chlorine Sensing

Free chlorine was sensed by chronoamperometry at 1.5 V versus the Ag/AgCl reference electrode. The experiments were started with 20 mL of 100 mM sodium phosphate buffer (pH 7.0) in the beaker. Different volumes of sodium hypochlorite stock solution were added to the beaker to simulate an increase in free chlorine concentration. Decrease in free chlorine was simulated by removing 1 mL of liquid from the beaker and replacing it with 1 mL of 100 mM sodium phosphate buffer (pH 7.0).

Cyclic voltammograms were performed over the definite potential range vs. Ag/AgCl in a cell containing 20.0 mL of 0.1 M PBS solution. The cell was assembled and filled with 20.0 mL of supporting electrolyte solution. The surface of the electrodes is completely immersed. The solution has been kept quiet for 10 seconds. To determine the potential window, scanning is initially carried out with the supporting electrolyte solution to obtain the background voltammogram. The voltammogram containing the analyte in supporting electrolyte is taken under two different modes, at i) various scan rates and ii) various concentrations.

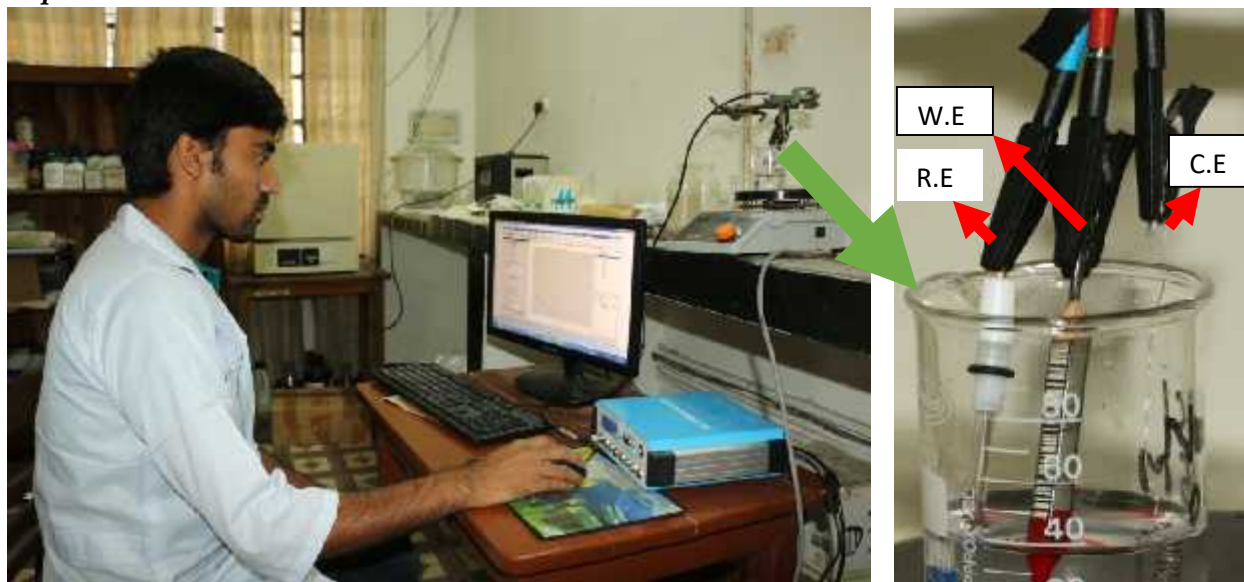


Fig 3.2: Electrochemical experimental setup.

For amperometric experiments, the voltage was switched directly from open circuit to the appropriate applied potential. The experimental setup is shown in Fig. 3.2. Solutions were agitated with a stirrer at a fixed speed for both PBS solution and cell media studies. This was in order to facilitate diffusion and improve the homogeneity of the solution.

Initially, studies were carried out with the sensor in 0.1 M solutions containing phosphate buffer solution in order to determine whether the performance was suitable for the subsequent monitoring of cells. Amperometry, over prolonged times in cell culture was performed by applying a potential to the electrode immersed in a 20 ml volume of cell culture medium. The resulting real time current responses were recorded over a period of time.

3.8 Interference studies

A three electrode system was employed where pencil graphite electrodes were employed as a working electrode with Ag/AgCl and Pt wire as reference and counter electrodes, respectively. 1mM sodium hypochlorite (NaOCl) was added and current response measured at room temperature. $E_{app} = 1.5V$ vs. Ag/AgCl in the presence of 0.1M PBS solution. 1.17×10^{-4} mM sodium nitrate, 1.40×10^{-4} mM sodium sulfate, 1.88×10^{-4} mM sodium carbonate, 2.37×10^{-4} mM

Experimental

Chapter III

sodium bicarbonate, 5.07×10^{-5} mM sodium chloride were added in solution. Again sodium hypochlorite NaOCl was added in 0.1M PBS solution [132].

3.9 Stability studies

Electrode stability was evaluated using amperometry at potential 1.5 V vs. Ag/AgCl by addition of 1mM sodium hypochlorite (NaOCl) at room temperature (298K). In between measurements the electrode was stored at room temperature [132].

CHAPTER IV

Results and Discussions

4.1 Electrochemical setup standardization

Cyclic voltammograms (CVs) of ferricyanide at pencil graphite electrode were performed at concentration of 2mM of ferricyanide 0.1 M KNO_3 as supporting electrolyte, each solution was scanned at different scan rate equal to 20, 40, 60, 80, 100, 120, 140, 160 mV/s. The resultant CV curves and the electrochemical parameters are shown respectively in figure 4.1 and Table 4.1.

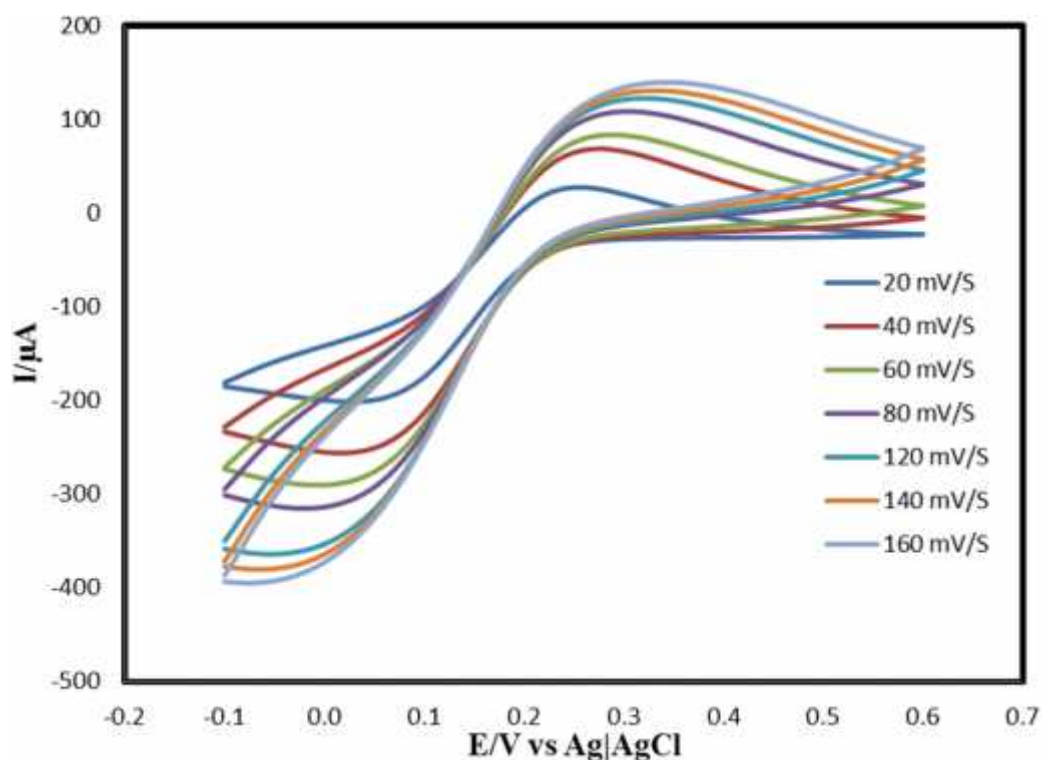


Figure 4.1: Cyclic voltammograms of ferricyanide at pencil graphite electrode were performed at concentration of 2mM of ferricyanide 0.1 M KNO_3 as supporting electrolyte, different scan rate 20, 40, 60, 80, 100, 120, 140, 160mV/s.

Table 4.1: Electrochemical parameters obtained from voltammograms of figure 4.1

V_s^{-1}	$v^{1/2}$	E_{pa} V (+)	E_{pc} V (+)	i_{pa} μA (+)	i_{pc} μA (-)	i_{pa}/i_{pc}
0.02	0.141421	0.26	0.06	61.370	-62.417	0.96
0.04	0.200000	0.24	0.07	86.834	-86.834	1.00
0.06	0.244949	0.26	0.03	98.208	-78.368	1.25
0.08	0.282843	0.25	0.01	109.075	-100.791	1.08
0.10	0.316228	0.29	0.02	124.330	-126.00	0.98
0.12	0.34641	0.29	0.02	130.875	-135.959	0.96
0.14	0.374166	0.31	0.01	131.250	-139.25	0.94
0.16	0.400000	0.31	0.01	144.417	-150.333	0.96

= scan rate; $v^{1/2}$ = SQRT of scan rate; E_{pa} = anodic peak potential; E_{pc} = cathodic peak potential; i_{pa} = anodic peak current; i_{pc} = cathodic peak current.

In general, the peak current of diffusion controlled reversible or quasi-reversible electro-chemical reaction follows Randles–Sevcik equation

$$I_p = 0.4463nF \sqrt{\frac{nFD}{RT}} AC\sqrt{v} \quad \text{-----} \quad (1)$$

Where i_p : the peak current, n : the number of electrons, F : Faraday constant, T : the temperature in Kelvin, R : the gas constant, A : the surface area of the working electrode, D : the diffusion coefficient of the electroactive species, C : the bulk concentration of the electroactive species and v : the scan rate of voltammograms.

Thus, if we know the value of diffusion coefficient of ferricyanide at 298K the surface areas for ferricyanide are calculated from the slope of the plot of i_p versus \sqrt{v} (Fig. 4.2).

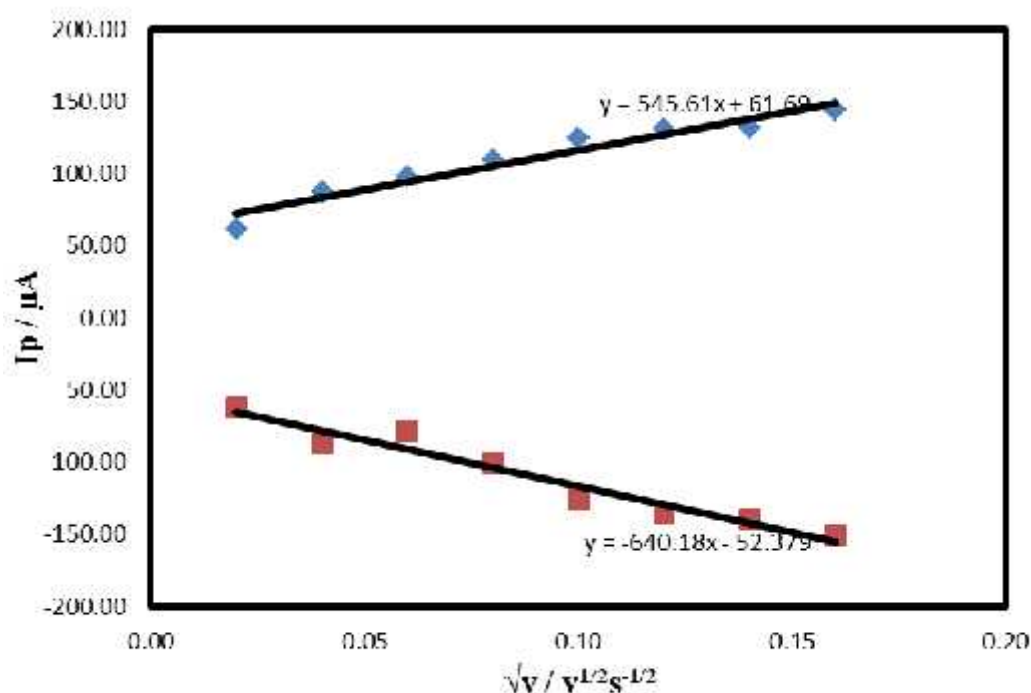


Figure 4.2: The anodic and the cathodic peak heights as function of the square root of the scanning rate for pencil graphite electrode.

From equation (1) we get,

$$\text{Slope} = 0.4463nF \sqrt{\frac{nFD}{RT}} AC$$

$$A = \frac{\text{Slope}}{0.4463nF \sqrt{\frac{nFD}{RT}} C}$$

From the curve (Fig 4.2) the value of slope is $\sim 545.6 \times 10^{-6}$ and the standard value of diffusion coefficient for ferricyanide in PGE is $6 \times 10^{-9} \text{ cm}^2/\text{s}$. where concentration $C = 2 \times 10^{-4} \text{ mol}/\text{cm}^3$ so we get,

$$A = \frac{545.6 \times 10^{-6}}{0.4463 \times 1 \times 96500 \sqrt{\frac{1 \times 96500 \times 6 \times 10^{-9}}{8.314 \times 298}} \times 2 \times 10^{-4}}$$

$$A = 0.004 \text{ cm}^2$$

From the theoretical value the surface area of PGE electrode i.e. used for experiment is 0.004 cm^2 . We show that the experimental value of surface area is very close to theoretical value. This calculated result has been used in further studies.

4.2 Preparation of pencil graphite electrodes

2B pencils were used as the base material for the developed PGEs. 2B PGEs were chosen as previous research because graphite to possess electron transfer rates more similar to GC than any other graphite hardness when tested with the redox benchmark reagents of ferricyanide. The eraser was detached and the wood casing removed using a knife until the pencil could be easily passed through a 5 mm in diameter hole.

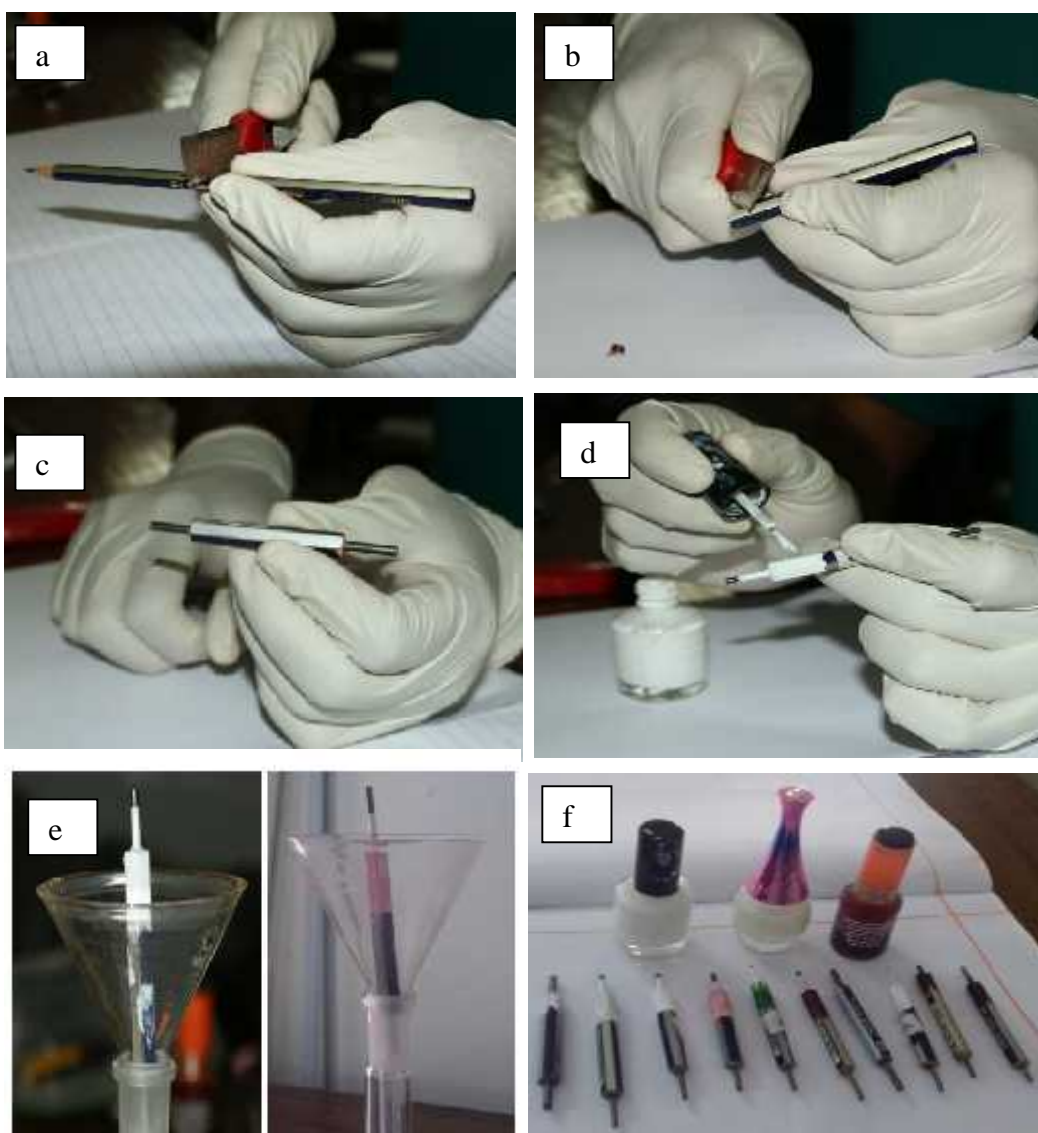


Figure 4.3: (a-f) fabrication of pencil graphite electrodes

Figure 4.3 (a) Collected PGEs from local market (b) Cutting the PGEs with ante-cutter. (c) Preparation of PGEs (d) Polished PGEs with nail-polish (e) Dried of PGEs after nail-polish (f) Prepared all PGEs with nail-polish.

Finally, the wood from the top about 1.5 cm of the pencil was carefully removed using a small razor blade, until the pencil lead was fully exposed. The lead was then rinsed successively with distilled water to remove any traces of adhesive. This exposed surface served as the point of attachment of the PGEs to the potentiostat.

4.3. Characterization of pencil graphite electrodes

The physical properties of pencil graphite electrodes that are described the look or feel of a substance. Electrode was made from locally available and cheap pencil graphite instead of conventional costly platinum, gold or glassy carbon electrodes.

Chemical properties that are relate to the ability of a substance to react with other substances or to transform from one substance to another. The chemical properties of a substance relate to its chemical composition and the way the atoms in the molecules are chemically bonded together. A pencil can write on certain objects, namely paper the rubber on the eraser will melt the metal near the eraser will conduct heat pencil lead is usually Amorphous graphite and graphite's chemical properties include conduct electricity.

As the expose length increased, electro active area and total capacitance ($C_T = C_{DL} + C_f$) also increased. Using the correlated increase in C_T and in electro active area (A_e), the following equation was derived considering the surface area of pencil graphite electrode.

$$\text{Surface area of pencil graphite} = \pi r^2 + 2 \pi r h$$

Although π is approximately 3.14, in this activity we will use $\pi = 3.14$ for calculations.

Overall evaluation of the PGEs

In addition to possessing increased sensitivity, the developed PGEs sensors demonstrated several structural and logistical advantages over both GCEs and PGEs (Table 4.2).

Table 4.2: Qualitative comparison of GCE and PGEs [99,100,101]

Electrodes	Approximate cost per electrode	Total scans possible with each electrode	Total polishing/Preparation time per scan
GCE	\$ 190	indefinite	15-60 min
PGE	\$ 0.15	40-50	30s-1.5 min

Though exact preparative methods for GCEs vary slightly, in most cases GCEs must be polished prior to each scan, using a procedure which typically requires three successive treatments with alumina polish. The total time required for this rigorous process can vary from 15 to 60 min, depending upon the particular sequence used. This time requirement quickly accumulates when attempting to run multiple scans in each test solution, such that polishing becomes a key constraint on the maximum rate at which analysis can be carried out. In contrast, the total preparative time for PGEs between scans varies from approximately 30 s (when polishing on sandpaper between analyses in the same solutions) to 1.5 min (when removing the tip between analyses in different solutions), and each PGEs can be used for approximately 40–50 scans (which could only be used for 2–3 scans).

PGEs were checked regularly in ferricyanide for any alterations in signal occurring as a result of the decrease in length over the course of testing. However, no significant peak shift was observed, indicating that the PGEs can be used along their entire length.

Furthermore, because of the simple polishing requirements of PGEs relative to GCEs, the use of PGEs for analytical analysis can save more than 15 min per scan, leading to more

rapid analysis. Thus, despite the initial time investment required for their preparation, in the long term, the use of PGEs leads to a significant time savings.

The developed PGEs also demonstrated a very significant reduction in cost relative to the commercial GCEs. GC (\$10 per canister) was able to cost approximately 50 PGEs for a cost of \$0.15 each. This represents a dramatic savings over the \$190+ generally needed to purchase a commercial GCE. Even assuming a total average of only 25 scans per pencil (to account for defective pencils and any breakage which might occur) approximately 5000 PGEs could be prepared for the cost of a single GCE, equating to over 15,000 scans[102,103,104].

4.4 SEM images of working electrodes

The pencil graphite electrodes is used as working electrode and has been made from 2B wood pencil collected from the local market. Figure 4.4 shows the surface morphologies of bare PGEs. Greyish-black color corresponds to graphite on the surface. Surface is not smooth as well. It is also seen from the picture that a lot of grooves present at surface morphology of the PGEs. It indicates that the graphite rod of the pencil is not pure crystalline. A lot of defects and few foreign materials may be present there.

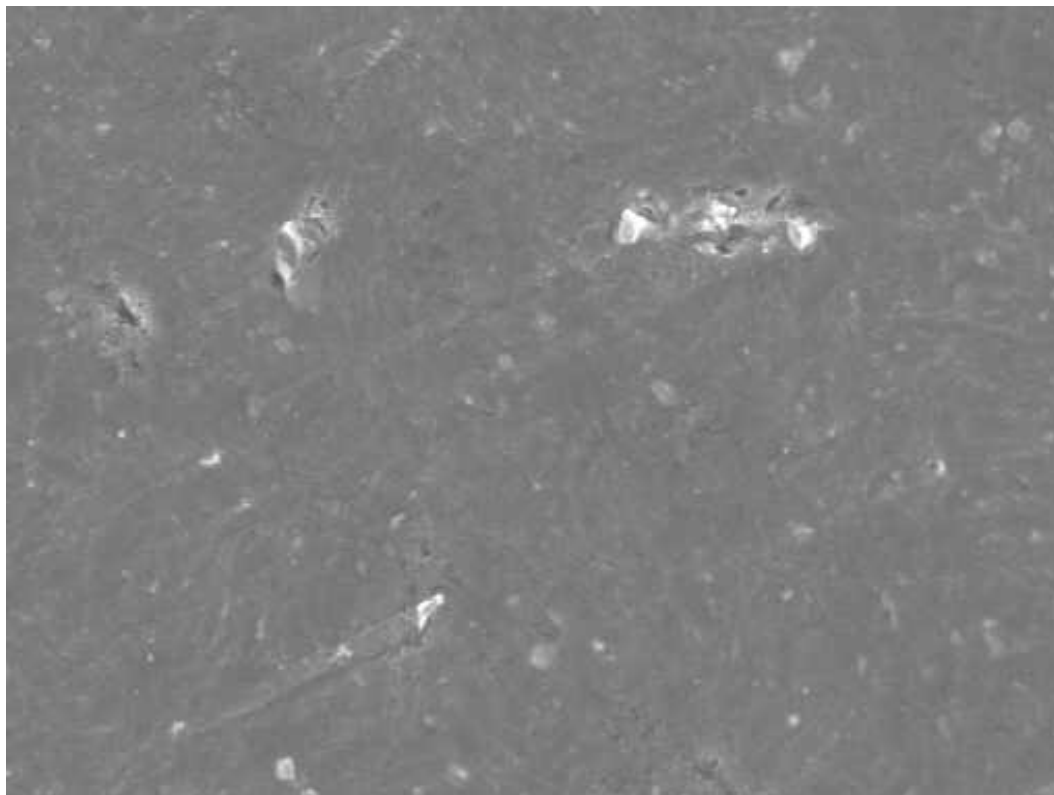


Figure 4.4: SEM image of bare PGEs [135]

4.5 EDX of bare PGEs

Figure 4.5 shows the EDX results of bare surface of PGEs. It is seen from the graph that PGEs surface are impure as guessed by SEM. Instead it is composed of 70% carbon, 10.3% silicon, 3.68% Iron, 3.06% oxygen, 5.50% calcium, 3.49% aluminum and trace amount of magnesium and calcium gluing agent etc. usually co-exist with graphite. In bare glassy carbon electrode, there are 100% carbon and no impurities. So it is concluded that PGEs is mainly carbon composite.

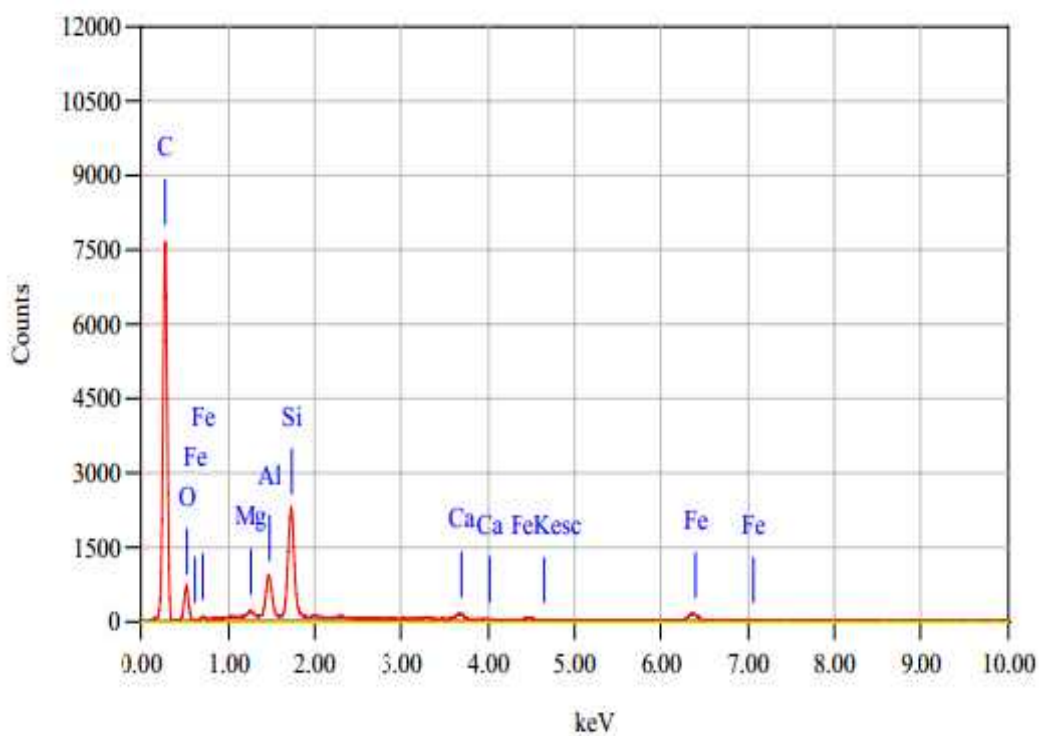


Figure 4.5: EDX of bare pencil graphite electrodes [135].

Table 4.3: Percentage of composite metal in pencil graphite electrodes

Element	KeV	Mass %	Counts	Error %	Atom%
C	0.277	79.39	42944	0.00	89.61
O	0.525	3.06	4350	0.03	2.59
Mg	1.253	0.40	786	0.39	0.22
Al	1.486	3.49	6562	0.05	1.77
Si	1.739	10.03	18574	0.02	4.84
Ca	3.690	5.50	1133	0.38	0.32
Fe	6.398	3.68	1617	0.27	0.65
Total		100.00			

4.6 Optimization of pH

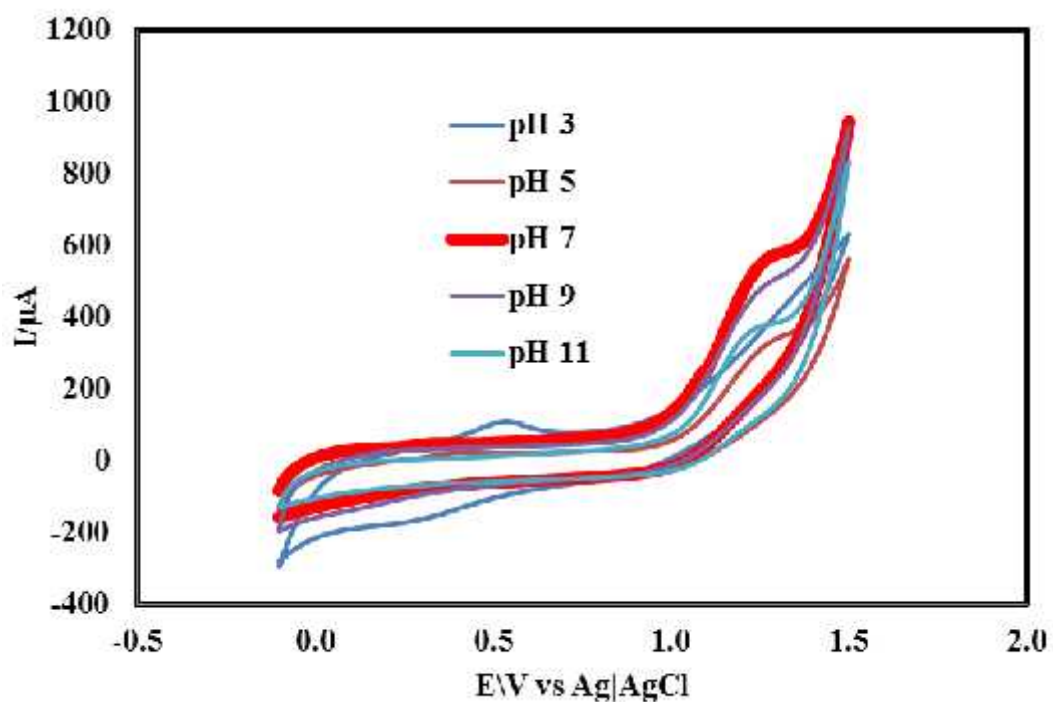


Figure 4.6: CVs of the 0.1 M PBS scan rates at different pH in NaOCl of PGEs (scan rate: 0.05 V/s).

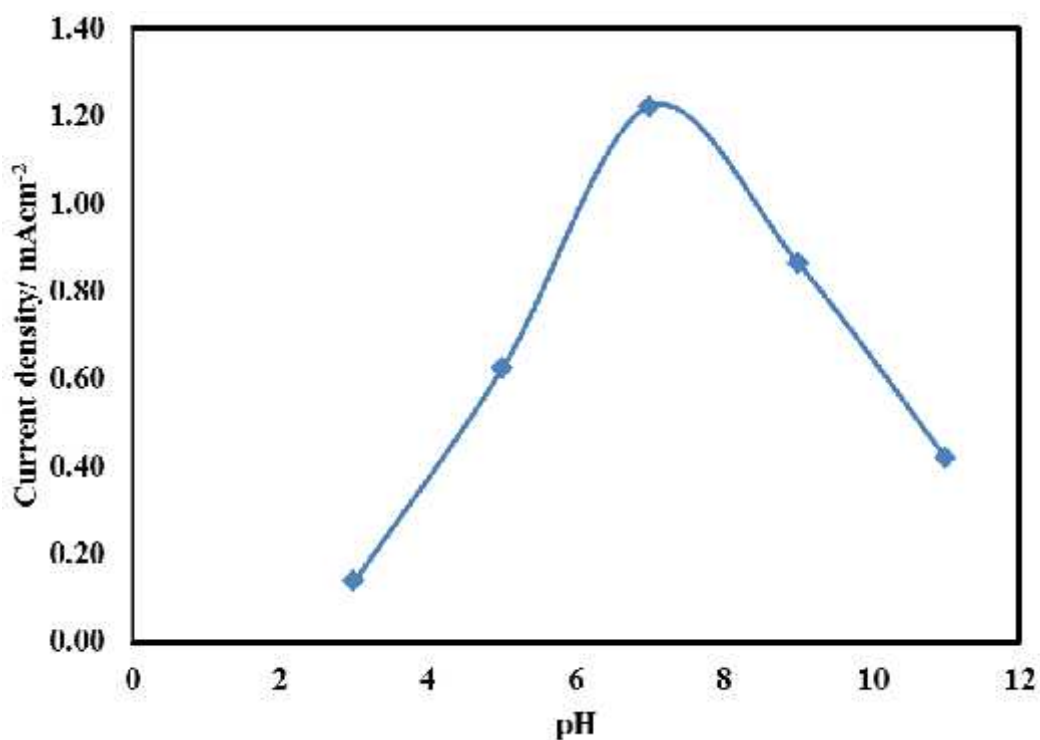


Figure 4.7: Plot of pick current vs. pH of NaOCl in different pH (3, 5, 7, 9 and 11) at scan rate of 0.05 V/s.

The effect of pH on the CVs of 10 mM NaOCl using PGE as working electrode was studied, where pH range was 3 to 11 (Fig.4.6). Where pH 7 found to have shown maximum current signal compare to the other pH values.

4.7 Electrochemical characterization of bare GC electrodes

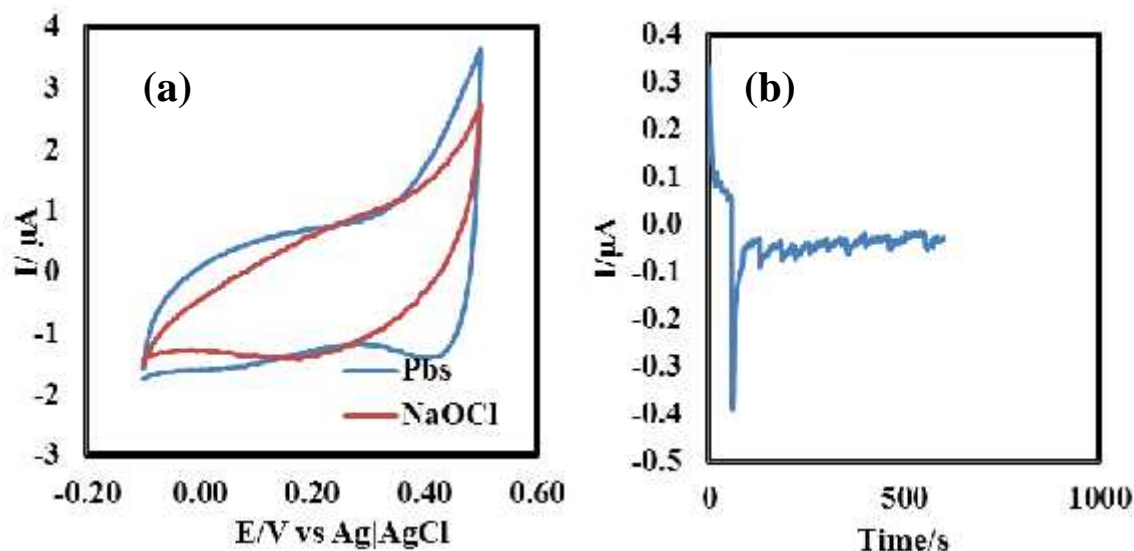


Figure 4.8: (a) CV of bare GC electrodes in $E_{app}=0.45\text{V}$ 0.1 M pH 7 PBS (b) Current-time profile obtained from experiment carried out to determine the effect of free available chlorine addition in 0.1 M pH 7 PBS with 1mM of free chlorine added in each step at $E_{app}=0.45\text{V}$

GCE electrodes also were used for the free available chlorine detection as preliminary study; however, it shows there is no signal both in CV and in amperometry for the standard addition of NaOCl solution (Fig. 4.8).

4.8 Electrochemical behavior of PGEs

Electrochemical modification of PGEs using ammonium oxalate

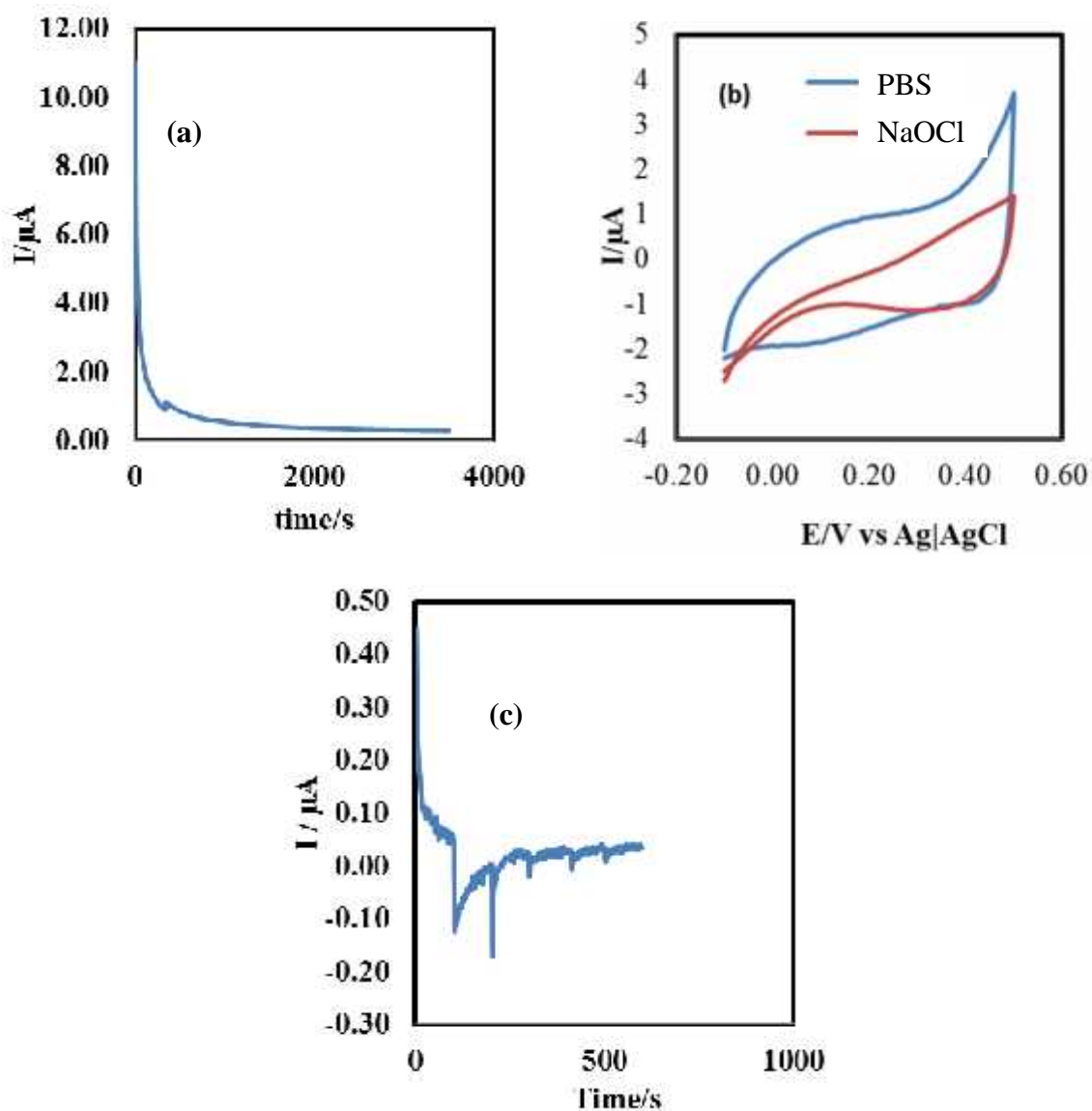


Figure 4.9: (a) Current-time plot during modification of PGE using ammonium oxalate with E_{app} : 0.50V (b) CV of buffer and NaOCl solution using ammonium oxalate modified PGEs with E_{app} : 0.50V (scan rate: 0.05 V/s). (c) Current-time profile obtained during electrochemical sensing of free available chlorine; (1mM standard addition in 0.1 M pH 7 PBS buffer) with E_{app} : 0.50V

PGEs have been modified with ammonium oxalate for sensing FAC. Chronoamperometry has been used (Fig. 4.9a) for the modification. Fig. 4.9 (b) shows the CV of NaOCl and PBS using modified electrodes, where there is no change in current observed for the

NaOCl addition. Also there is no amperometric signal can be seen using the modified electrode (Fig. 4.9c).

Cyclic voltammetry is the most widely used technique as it provides considerable information on the thermodynamics of oxidation processes. Cyclic voltammograms were recorded for 10 mM NaOCl at PGEs at 0.1M PBS pH 7.0 using.

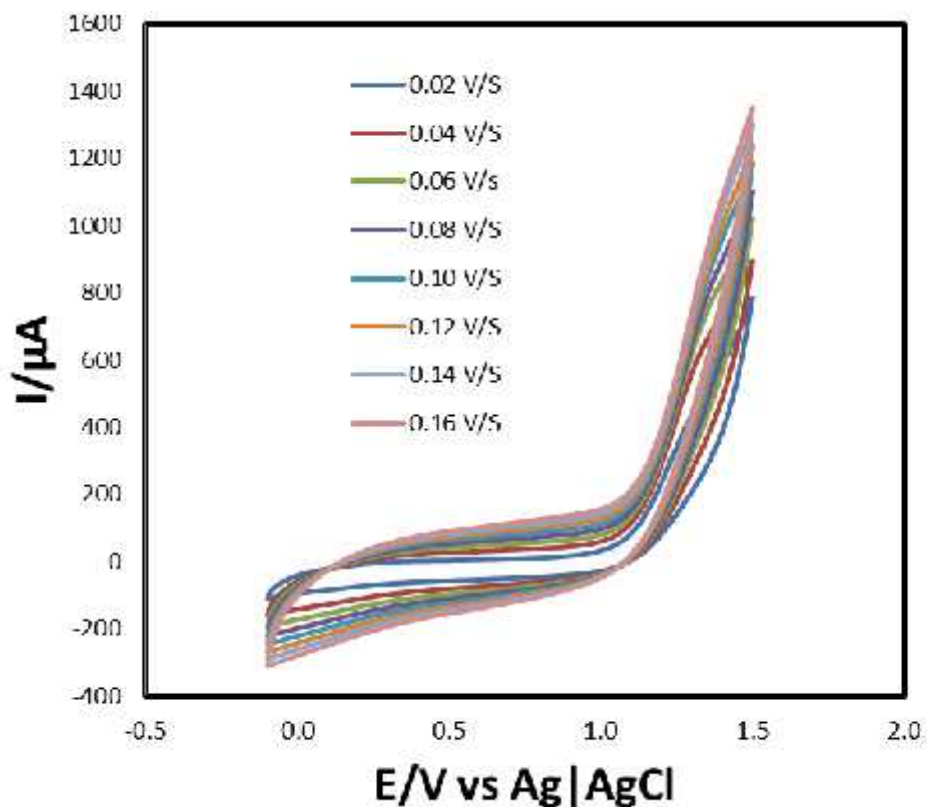


Figure 4.10: CVs of the 0.1 M PBS at different scan rates in NaOCl of PGEs at $E_{app}=1.5V$ (scan rate: 0.05 V/s).

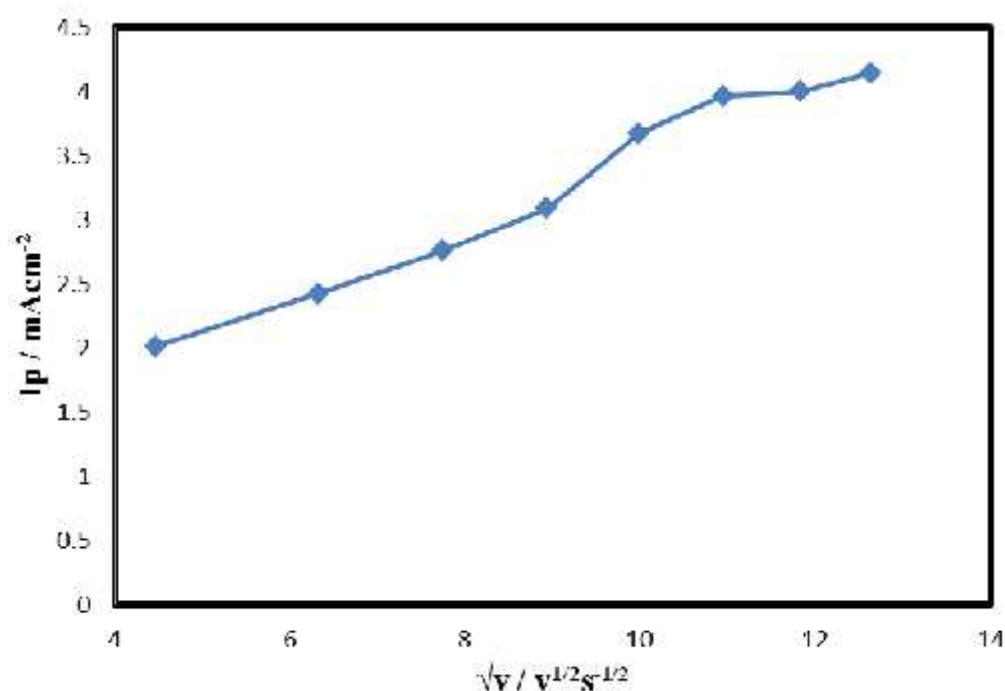


Fig. 4.11: Variation of peak current with SQRT of scan rate pencil graphite electrode at $E_{app}=1.5V$

It is also seen that the peak current increases with scan rate in figure 4.11. The voltammogram takes longer to record as the scan rate is decreased. Therefore, the size of the diffusion layer above the electrode surface becomes different depending upon the voltage scan rate used. In a slow voltage scan the diffusion layer grows much further from the electrode in comparison to a fast scan. Consequently, the flux to the electrode surface is considerably smaller at slow scan rates than it is at faster rates. As the current is proportional to the flux towards the electrode the magnitude of the current becomes lower at slow scan rates and higher at high scan rates [105].

Figure 4.11 reveals that with increasing scan rate, the peak potential separation increases because the cathodic peak shifts towards negative and that of anodic towards positive. Here the cause is the effect of IR drop. Current passage through either a galvanic or an electrolytic cell requires a driving force or a potential to overcome the resistance of the ions to move towards the anode or the cathode. The force is generally referred to as the ohmic potential or the IR drop [106]. This fact occurs because for positive (cathodic) current, the actual working electrode potential is less negative than the applied

(measured) potential, while for negative (anodic) current, the shift is in the positive direction. It also shows that the increase of peak currents with $v^{1/2}$ indicates that the process is impurely diffusion controlled in figure 4.11[107]. It is also observed that the peak current of both anodic and cathodic peaks are increased with increasing $v^{1/2}$ [105].

4.9 Concentration effects of PGEs towards FAC

It can be noted that fabricated electrochemical free chlorine sensors are not as well developed as other sensors. The major challenge is the lack of reversible sensing materials for HOCl or OCl⁻. A promising electrochemical sensing material should either react with free chlorine in a reversible manner or selectively transport HOCl or OCl⁻ to the target substrate. The chemical reagents used in electro chemical techniques (such as amperometry) can react with free chlorine, but the process is irreversible. While ion-selective transport membrane exists for many ions, very few were found for HOCl or OCl⁻ due to their oxidizing nature. Therefore, developing advanced materials for free chlorine sensing is urgently needed.

In order to address the analytical applicability of the PGEs, we investigated the electro-catalytic activity of these electrodes towards chlorine. Fig.4.12 presents the CV responses of PGEs in 0.1M PBS without (a) and with NaOCl of 10 mM (b). Upon the addition of NaOCl, an increase of the anodic concentration effect current density can be observed for PGEs.

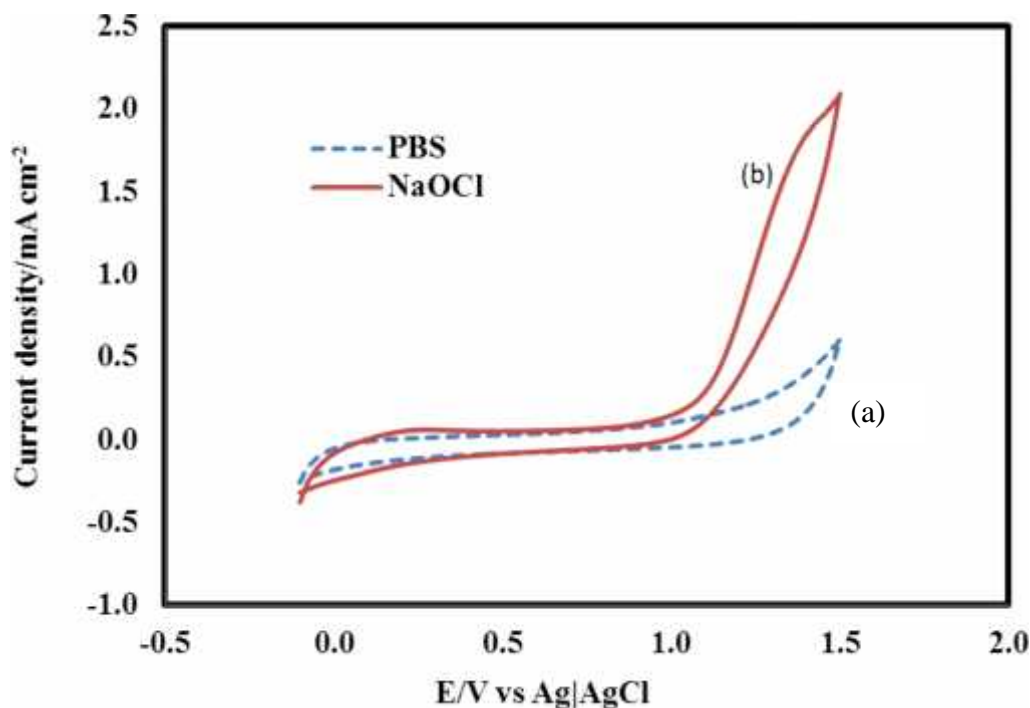


Figure 4.12: CV curves in PGEs electrodes (a) in the absence of NaOCl and (b) in the presence of 10 mM NaOCl in 0.1M phosphate buffer solution containing at $E_{app}=1.5V$ (scan rate: 0.05 V/s).

It also can be seen that with the addition of NaOCl, the anodic peak shifts to the higher potential, which maybe attributing to the diffusion limitation of NaOCl at the electrode surface. This indicates that PGE scan catalyze oxidation of NaOCl in 0.1M PBS pH 7 solution. This specifies that PGEs exhibit excellent electro-catalytic activity towards the oxidation of NaOCl without using any modified electrode.

PGEs are composite materials, the composite materials are carbon, calcium, magnesium, silicon, iron and potassium are presented in PGEs. The limitation in sensing material forces the utilization of amperometric electrodes for electrochemical sensing of free chlorine in figure 4.13. The composite materials are sensing the current. Normally, cyclic voltammetry measurement has to be done first to determine the optimized voltage bias for amperometric measurement. Moreover, dissolved oxygen is electro-active in the usual voltage range between +0.08 to +1.5V for cyclic voltammetry sensing of free chlorine. The interference from dissolved oxygen increases the sensing accuracy. Finally, the

requirement of a potentiostat for an amperometric sensor increases the complexity as well as the cost of the sensor [108,109,110].

It also can be observed that catalytic peak potential for pencil graphite electrodes shifted 1.5V potential for 10 mM NaOCl addition. Pencil composite are acts as catalyst substance.

4.10 Free chlorine sensing

In order to obtain a better understanding of the sensitivity of the chlorine sensor the current response change with concentrations was investigated. Figure 4.13 shows the amperometric response to increasing free chlorine concentration by 1mM per step. The increase in the anodic current in each of the steps was comparable and the net change in current correlated linearly with the quantity of free chlorine added. The sensitivity to free chlorine in this measurement was $50\mu\text{AmM}^{-1}\text{cm}^{-2}$. The response was repeatable and the sensitivity did not change with a change in the electrode area. The response time for 90% change in signal was less than three seconds. We hypothesize that the electrode reacts anodically with HOCl, whose oxidation potential is around +1.50V. The voltage of chronoamperometry was well outside the voltage range for dissolved oxygen [111]. Therefore, sample deaeration was not required. The limit of detection in these experiments was found to be $46\mu\text{M}$ that are lower compare to the reported values 79 and $133\mu\text{M}$ [112,113].

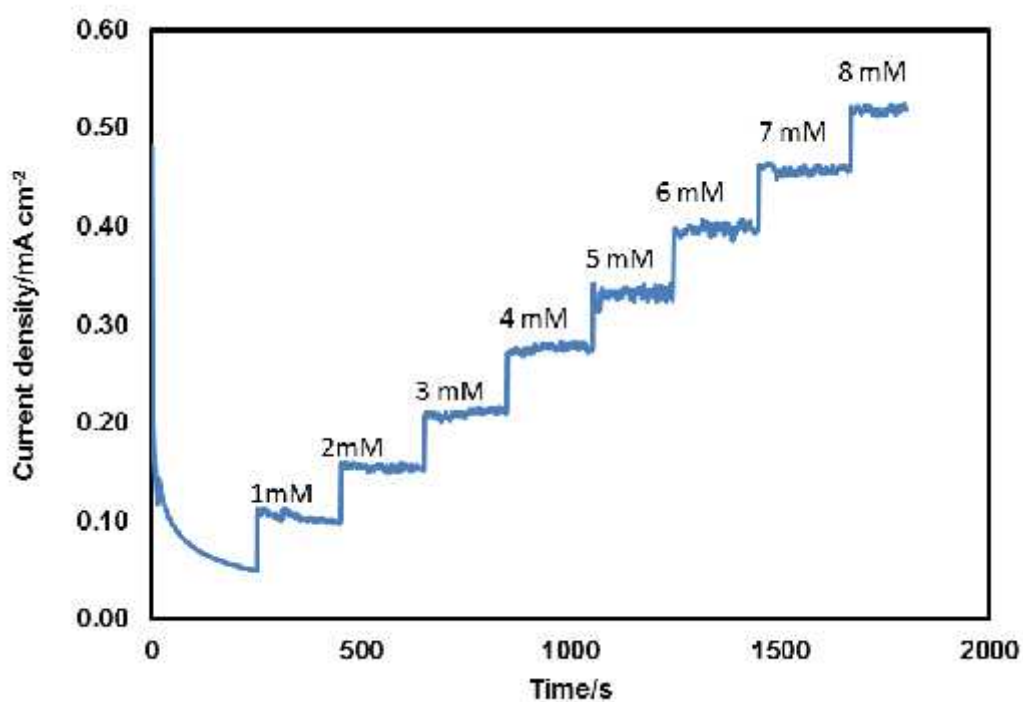


Figure 4.13: Typical amperometric current response of the PGEs upon the successive injection of NaOCl with concentrations from 1mM to 8 mM into a stirred at $E_{app}=1.5V$ 0.1 M PBS pH 7.

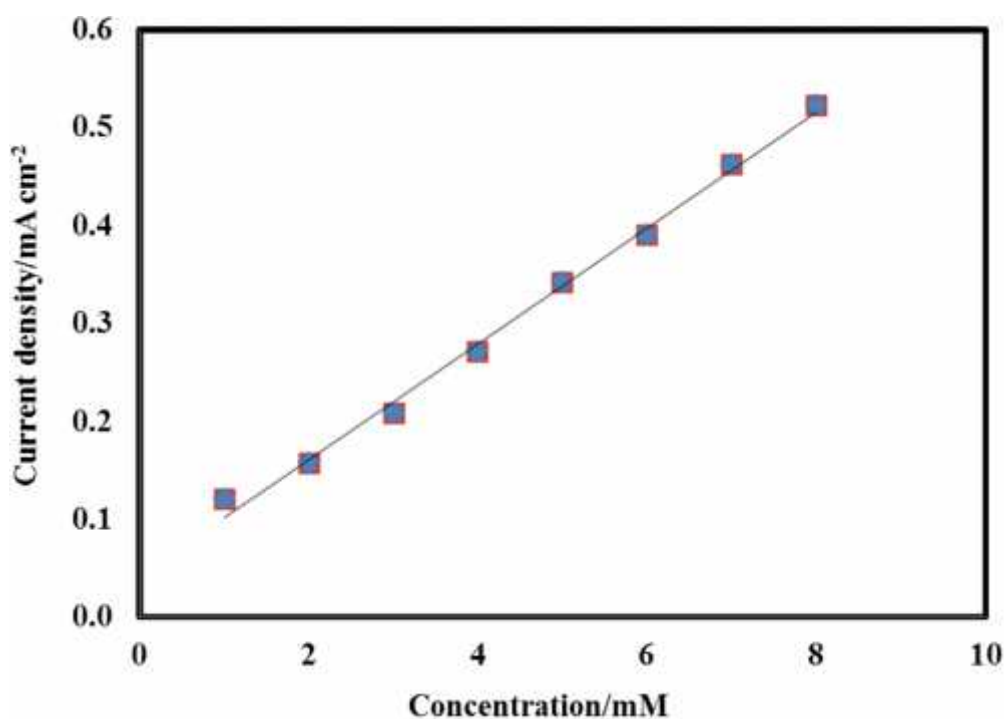


Figure 4.14: The plot of concentration effect current density versus the corresponding concentrations of NaOCl in PGEs.

From linear calibration graph, sensitivity has been calculated using the current density value obtained at each concentration shows in figure 4.14. It is seen that PGEs is linear for chlorine detection up to 8mM, with a sensitivity $50\mu\text{AmM}^{-1}\text{cm}^{-2}$ and standard deviation $18.41625\mu\text{AmM}^{-1}\text{cm}^{-2}$ which is more sensitive than other chlorine sensor [116,117,132]. The chlorine sensitivity for pencil graphite electrodes is significantly higher than the majority of the reported literature [114,115].

The pencil graphite electrodes were also used for detection of chlorine with a relatively wide concentrations ranging up to 8mM, with a limit of detection of 46 μM at a signal-to-noise ratio of 3 shows in figure 4.13.

The performance of previously reported sensor platform for chlorine detection where majority of them involved complicated processing steps, which are not efficient to improve the sensitivity, response time and overall reliability of the system compare to the other chlorine sensor.

In order to investigate the sensing application of NaOCl at pencil graphite electrodes the current response is measured for chlorine into stirred 0.1 M PBS solution pH 7.

Fig. 4.15 shows a typical amperometric response of the pencil graphite electrodes upon the successive addition of a certain concentration of NaOCl into stirred 0.1 M PBS pH 7 solution. At the applied potential of 1.5 V, the anodic current of the sensor increased dramatically and achieved 90% of the steady-state current within 3s, revealing a fast amperometric response behavior.

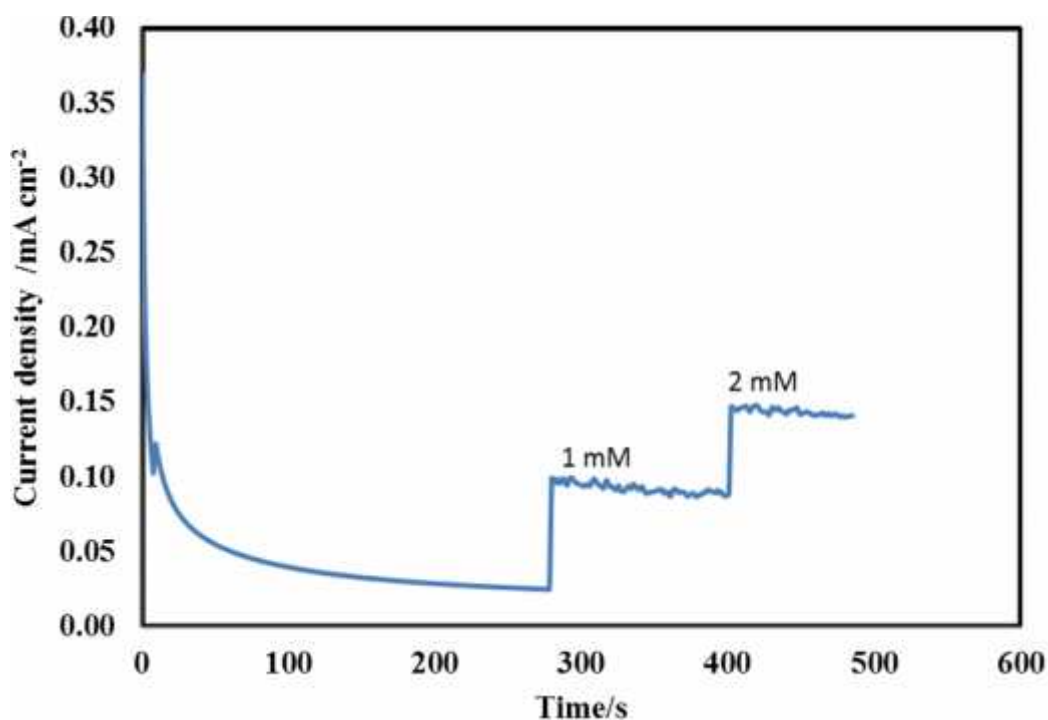


Fig. 4.15: Typical amperometric current response of the PGEs upon the successive addition of NaOCl into stirred 0.1 M PBS solution.

Sensitivity has been calculated using the current density value obtained at each concentration. Sensitivity of chlorine obtained was $50\mu\text{AmM}^{-1}\text{cm}^{-2}$ for pencil graphite electrodes.

It shows that PGEs is linear for chlorine detection 2mM with sensitivity $\sim 0.15\text{mA}/\text{cm}^{-2}$. Once the above challenges are properly addressed, the concern for free chlorine sensors would become more accuracy to those other sensors. Such concerns include the improvement of reliability and the reduction of fabrication costs.

4.11 Interference

We have examined the amperometric responses of the pencil graphite electrodes at an applied potential of +1.5 V in 0.1 M PBS pH 7 solution with continuous additions of 1mM NaOCl at containing scan rate 0.05 V/s and other supplied samples.

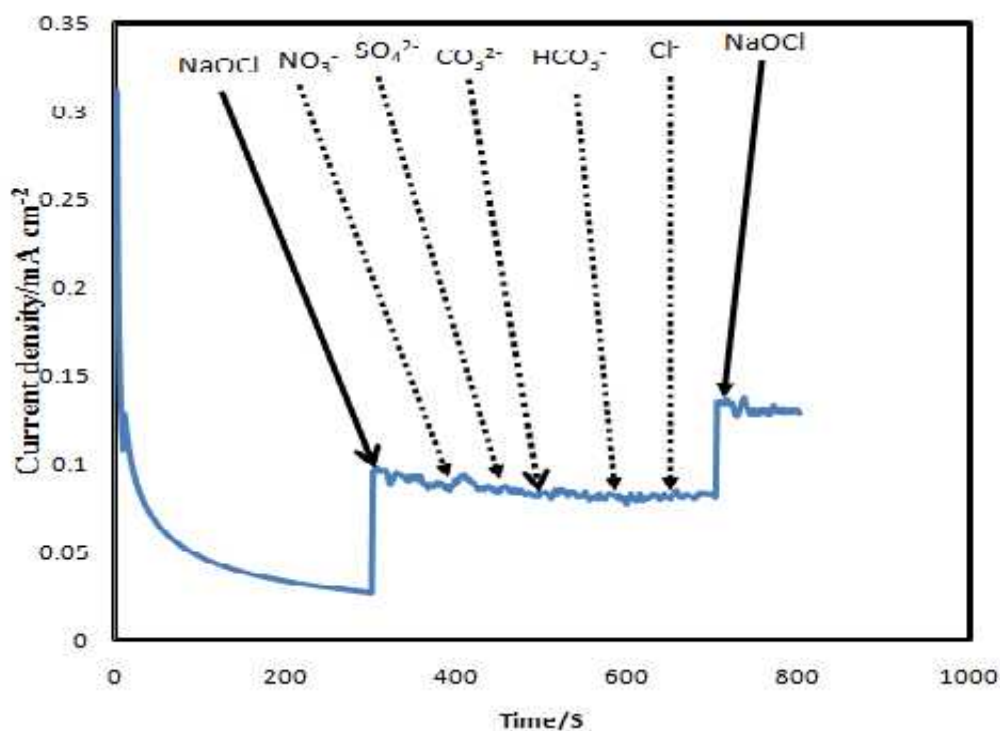


Figure 4.16: Interference test of the sensor in 0.1 M PBS at 1.5V with NaOCl and other interferents including 1.17×10^{-4} , 1.40×10^{-4} , 1.88×10^{-4} , 2.37×10^{-4} and 5.07×10^{-5} mM nitrate ion, sulfate ion, carbonate ion, bicarbonate ion and chloride ion respectively [132].

Figure 4.16 summarizes the effects of potential interfering species, which were added sequentially, (1.17×10^{-4} mM sodium nitrate at 425 and 430s, 1.40×10^{-4} mM sodium sulfate at 475 and 480s, 1.88×10^{-4} mM sodium carbonate at 525 and 530s, 2.37×10^{-4} mM sodium bicarbonate at 600 and 605s, and 5.07×10^{-5} mM sodium chloride at 650 and 655s) to a 20 mL 0.1 M sodium phosphate (pH 7.0) buffered solution containing 1mM free chlorine. At 750 s, the addition of NaOCl caused an identical signal increase as the previous NaClO pulse addition at 750s. The current response is better result than other literature [118,119,120,121,122]. Potential interfering species, such as nitrate, sulfate, carbonate, bicarbonate, and chloride, showed no response.

4.12 Stability of the bare pencil graphite electrodes

The stability of the PGEs was determined over a period of two week, with analysis carried out every day, 5 assays each day with 1.0 mM sodium hypochlorite addition (Fig 4.17 &

Fig 4.18). In between the testing, the electrode was stored in air at ambient conditions. Electrode was found to retain high activity after two week.

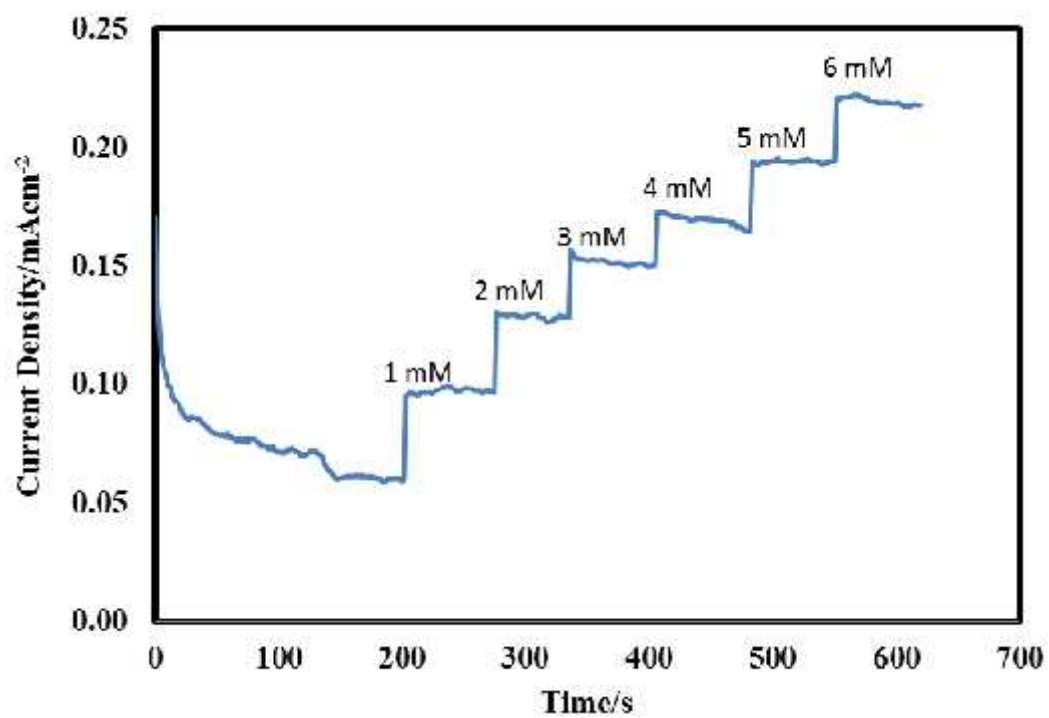


Figure 4.17: Stability of the PGEs over a period of two week.

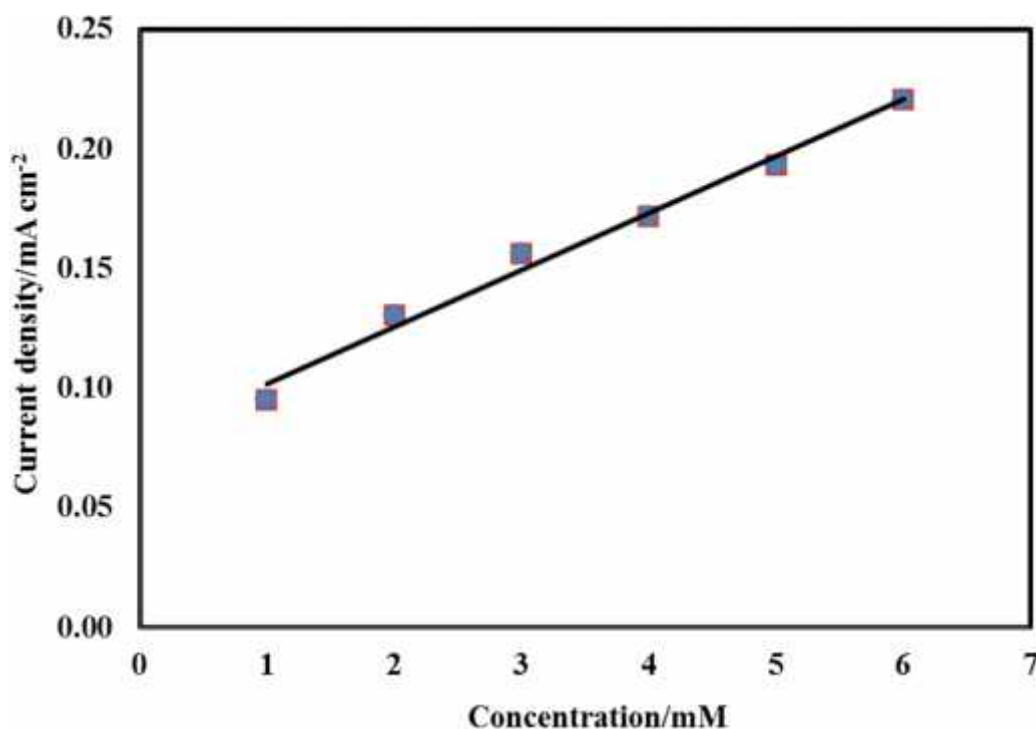


Figure 4.18: Concentration dependent current response of the in pH 7 PBS over a PGEs period of two week.

From figure 4.19, it exposes that the stability of PGEs 97.93% after 15 days of its initial activity. On the other hand stability of pencil graphite electrodes decreased unchanged after 14 days of its initial activity and after 15 days it was slightly change.

This is due to the fact of the crystalline which shows a high surface to volume ratio due to their small size. Because of their high surface-to-volume ratio and tunable electron transport properties due to quantum confinement effect, their electrical properties are strongly influenced by minor perturbations.

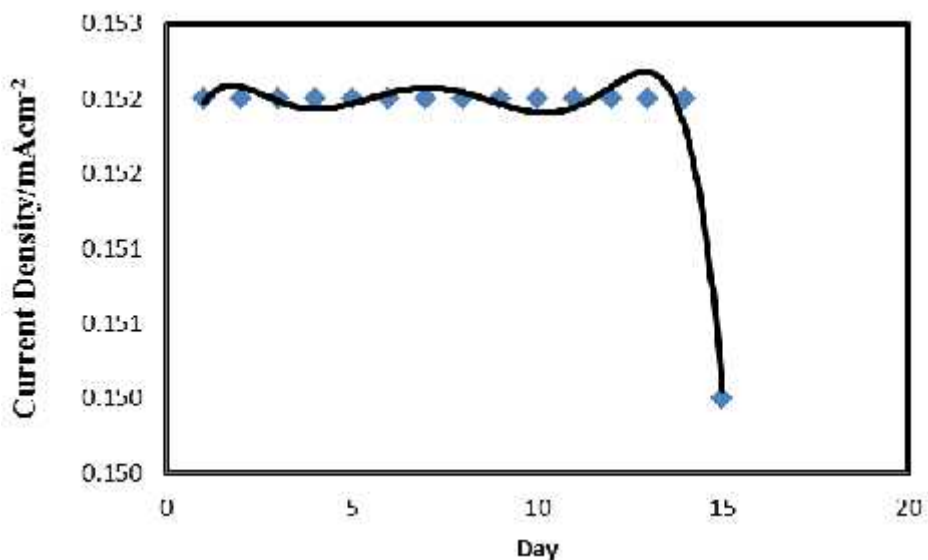


Figure 4.19: Stability of the PGEs over a period of two weeks.

4.13 Feasibility of reuse

It is desirable that a sensor be suitable for repeated use in a highly reproducible manner. One of the electrodes used in the experiments described above was stored in distilled water for a period of 7 weeks without any deterioration in performance.

The reproducibility for five pencil graphite electrodes was carried out comparing the oxidation peak current of 10mM NaOCl in a solution of PBS (pH=7). It indicates the good reproducibility of PGEs. Only a slightly change of the oxidation peak current of 10 mM NaOCl was observed in figure 4.20 & 4.21.

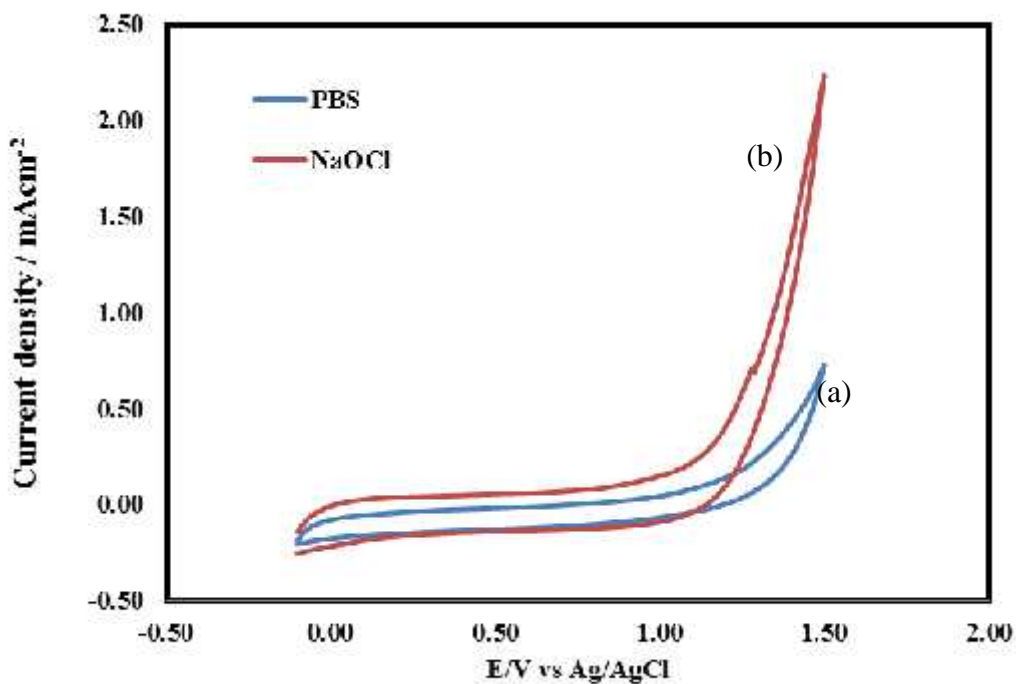


Figure 4.20: The re-verification CV of PGEs. CV curves in PGEs electrodes (a) in the absence of NaOCl and (b) in the presence of 10 mM NaOCl in 0.1M phosphate buffer solution containing (scan rate: 0.05 V/s).

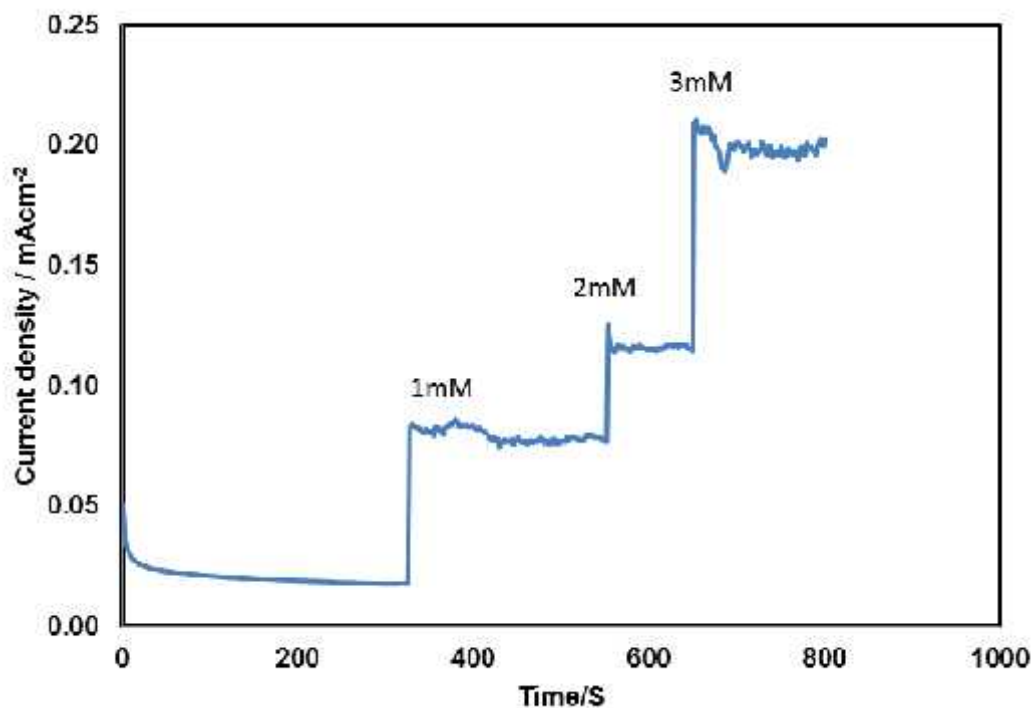


Figure 4.21: The re-verification amperometry of PGEs

4.14 Summary for fabricated electrochemical free chlorine sensor

The literature on electrochemical free chlorine sensors is limited. Within the limited scope, the amperometric sensors have been identified as the widely used structure for the electrochemical detection of free chlorine. The comparison between conventional electrochemical free chlorine sensor and fabricated ones is given in Table 4.4. A list of fabricated electrochemical free chlorine sensors are provided in Table 4.4 with their electrode sensing materials, key performance parameters, and corresponding fabrication processes. The comparison shows that more works were focused on the optimization of working electrodes than the development of active sensing materials.

Although fabricated free chlorine sensors can be developed for cost effective applications, their sensitivity varies widely and they are less accurate and reliable than the conventional sensors. This indicates that the fabricated electrochemical free chlorine sensor is a challenging area of research that requires further intensive investigations.

Table 4.4: Summary of electrochemical FAC sensor

Electrochemical technique	Electrode / Sensing material	Detection range[mM]	Sensitivity	Response time [s]	Stability	Ref.
Amperometry	Au	1.5-8	69.20 $\mu\text{AmM}^{-1}\text{cm}^{-2}$	20	7 days	123
	Au	2-5	14.20 $\mu\text{AmM}^{-1}\text{cm}^{-2}$	120	10 days	124
	Pt	4-400	–	–	–	125
	Pt	1.5	8.00 $\mu\text{AmM}^{-1}\text{cm}^{-2}$	–	5h	126
	PGEs	0-6	0.302 $\mu\text{Appm}^{-1}\text{cm}^{-2}$	3	-	132
	PGEs	1-8	50.00 $\mu\text{AmM}^{-1}\text{cm}^{-2}$	3	14 days	This work

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