

LOW-COST EASY-TO-USE FREE CHLORINE SENSOR FOR MONITORING  
DRINKING WATER

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DRINKING WATER

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A Thesis Submitted to the School of Graduate Studies in Partial Fulfilment of the  
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# Lay Abstract

Low-cost sensors were developed to monitor free chlorine in drinking water for end users, especially in small and distant communities. Free chlorine keeps lethal microorganism pathogens from re-growing after disinfection. Re-growth is more likely to happen in these communities due to poor infrastructure and less usage-driven flow.

The contributions include:

- A low-cost sensing material for free chlorine based on pencil lead
- Determination of operating range of the sensor
- Study of sensing mechanisms
- Efficiency improvement and cost reduction
- Research articles, conference presentations, patent applications, and industrial collaboration based on above research

The resultant sensor is easy to use, robust in practical conditions and requires low maintenance, suitable for small and distant communities. Future work is the integration with sensing systems and the application of knowledge gained in this thesis for sensing applications in other fields.



# Abstract

In this thesis, low-cost free chlorine sensors for monitoring drinking water have been developed.

The starting material, pencil lead, was modified using an ammonium carbamate solution. The main emphasis for this technology is the low cost, scalable and environmental friendly process. The resultant materials were highly sensitive to free chlorine.

The second discovery was an advanced understanding of the unsteady state mass transfer during the sensing process, using the customly expanded Cottrell equation. This method could qualitatively indicate the absence of free chlorine, for applications where the removal of free chlorine is the goal. This method allowed better interpretation of transient data and simplified setup.

The third discovery was the use of pulsed amperometric detection to detect free chlorine at a much higher sensitivity, while reducing the complexity of the setup, further reducing the cost. This method was based on the previous findings plus understanding of the reaction kinetics.

The resultant sensors detected free chlorine with a detection of 0.0414 ppm, while the regulations require the free chlorine to be above 0.2 ppm. The response time was less than three seconds. The range of detection was up to around 20 ppm. The cost of materials for one sensor was less than ten dollars. The maintenance was minimal due to the lack of consumables. The operation could be as a meter or as a device in a large instrument. The target use of the sensors include small and distant communities, bottling industries, fruit and vegetable washing industries. The free chlorine sensing techniques can be readily expanded to biology, environment, and big data applications, based on the knowledge gained through the study.

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# List of Abbreviations

**CV** Cyclic voltammetry

**PAD** Pulsed amperometric detection

**RE** Reference electrode

**CE** Counter electrode

**WE** Working electrode

**DPD** *N,N*-diethyl-*p*-phenylenediamine

**LOD** Limit of detection

**ppm** Parts per million

**WHO** World Health Organization

# List of Symbols

$c$  Concentration in ppm

$i$  Current

$t$  Time

$n$  Number of electrons transferred

$F$  Faraday constant

$D$  Diffusion coefficient

$A$  Area

$V$  Voltage

$\tau$  Time constant

# Declaration of academic achievement

One research article as a first author was published:<sup>1</sup>

- Low-cost graphite-based free chlorine sensor.  
S. Pan, M. J. Deen, and R. Ghosh\*. *Analytical Chemistry* 87.21 (2015), pp. 10734-10737

My contributions were published in several research papers as a co-author:<sup>2-4</sup>

- Paper-based, hand-drawn free chlorine sensor with poly(3,4 – ethylenedioxythiophene):poly(styrenesulfonate).  
Y. Qin, S. Pan, M. M. Howlader, R. Ghosh, N.-X. Hu, and M. J. Deen\*. *Analytical chemistry* 88.21 (2016), pp. 1038410389.
- Open-Source Low-Cost Wireless Potentiometric Instrument for pH Determination Experiments.  
H. Jin\*, Y. Qin, S. Pan, A. U. Alam, S. Dong, R. Ghosh, and M. J. Deen. *J. Chem. Educ.*, 2018, 95 (2), pp 326330
- Integrated water quality monitoring system with pH, free chlorine, and temperature sensors.  
Y. Qin, A. U. Alam, S. Pan, M. M. Howlader, R. Ghosh, N.-X. Hu, H. Jin, S. Dong, C.-H. Chen, and M. J. Deen\*. *Sensors and Actuators B: Chemical* 255 (2018), pp. 781790.

Patent applications have been submitted in four countries:

- US20180224390A1,
- CA2994332A1,
- CN108351317A,
- IN201817004113A,
- United States Continuation-in-Part Patent Application Serial No.: 16/104,323.

The patents received interest from multiple companies in the industry and have been licensed by MILO to a number of companies.

Three additional research articles were written and ready to be submitted pending these patent applications.

# Chapter 1

## Introduction

### 1.1 Introduction

#### 1.1.1 Importance of drinking water

Water is a vital resource. Up to 70% of the human body is made of water, meaning there is 70 kg of water in a 100-kilogram person, who would normally ingest 4 kg of water per day.<sup>5</sup> One percent of loss of water, equal to one sixth of the daily ingestion, could cause discomfort such as thirst and reduced regulation of body temperature.<sup>5</sup> More water loss can lead to a decrease in cognitive ability,<sup>6</sup> reducing the quality of life. Prolonged dehydration could lead to life threatening diseases or complications.<sup>6</sup> Drinking water quality is an important measure for the quality of life.<sup>7</sup> Therefore, water is really important in everyday life and can be a matter of life and death.

Water is a limited resource. Only less than 3% of water on the planet is fresh water. Of the fresh water on the planet less than 1/10 is accessible for human consumption because the vast amount of drinking water is frozen in glacier and perennial snow. What is available for human consumption has to be recycled. Usually this recycled water contains pathogens which if left alone could cause life-threatening diseases.<sup>8-11</sup> While boiling can destroy most microorganisms, endotoxins expressed during the growth of microorganisms does not lose activity after more than 30 minutes of boiling.<sup>12</sup> For this reason, to help end users gain confidence, drinking water has to be disinfected before human consumption, even before transportation for human consumption.

#### 1.1.2 Importance of monitoring free chlorine in drinking water

##### Disinfection and preservation of the disinfection

Water disinfection involves either chlorination or advance oxidation combining UV and ozone.<sup>7,13,14</sup> In these methods, in the highly reactive chemical environment, the microorganisms are denatured, typically through lysis or inactivation due to oxidized cell membrane. There should be less than one colony-forming unit per 100 mL. Regardless of the

method of disinfection, there is a residue of disinfectant to inhibit pathogen regrowth.<sup>11</sup> In chlorinated water, the chlorine is usually reduced to 2 ppm whereas in the UV-ozone treated water, chlorine is added to such levels, as observed by the World Health Organization (WHO).<sup>7,13,14</sup> The residual chlorine in treated water is freely available for future reaction with active chemical compounds, hence the name free chlorine or free available chlorine.<sup>15</sup>

The advantage of free chlorine is the elimination of bacterial regrowth, greatly enhancing the safety of treated drinking water. The disadvantage is the side effects of free chlorine. Higher than 2 ppm, free chlorine will react with aminated compounds to form chloramines and other byproducts, which are harmful and unappealing. Lower than 2 ppm, there is an increasing risk of outbreak of pathogen due to regrowth. Much higher than 2 ppm, free chlorine has been known to cause cancer in some animal trials.<sup>7</sup> However, because the residual free chlorine is measured in water treatment plants, it is an unlikely case. Due to the chemical nature of free chlorine, it is necessary to monitor its concentration in water to ensure the free chlorine is in the right range for drinking water.

### **Ease of use in small and distant communities**

In small and distant communities, the public health is more related with water if the water is not up to treatment quality available in areas with more developed infrastructure. In small and distant communities, the infrastructure is poorer and skilled personnel is less available. Because of these infrastructure, the drinking water is more likely to be contaminated. The lack of personnel means that the problem will be identified with a delay in time. Plus, the low number of users means the water will flow less frequently in the pipeline. To compound the situation, small and distant communities are often far away from hospitals. Therefore easy-to-use free chlorine sensors are ideal to reveal the free chlorine condition in drinking water before consumption.

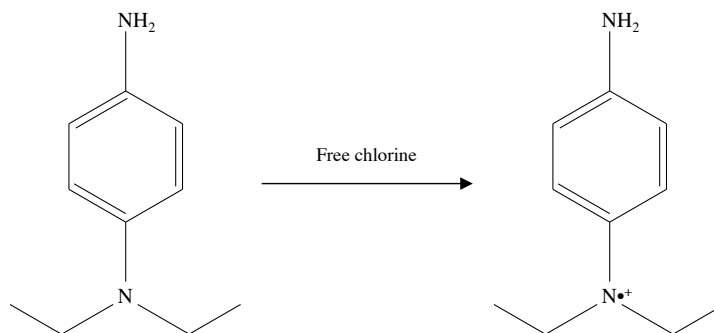
It is important to quantify the free chlorine in drinking water to know the disinfection and its preservation has been in place. If there is enough free chlorine, the chance of a microorganism to cause diseases is near zero. However, end users, especially in small and distant communities, do not have convenient technologies to know this important information of the drinking water. Ideal free chlorine sensors for such cases should be easy to use, require less consumables, have a low cost and demand minimal maintenance.

## **1.2 Current methods to measure free chlorine**

### **1.2.1 Commercial methods**

Currently in the industry free chlorine is measured either by colorimetry or by amperometry as the standard methods.<sup>7,13,14,16</sup> Both methods are accurate and suitable for use in an established industrial scenario to meet regulations. Specifics of their operation render them incompatible with low-cost and easy-to-use measurement of free chlorine.

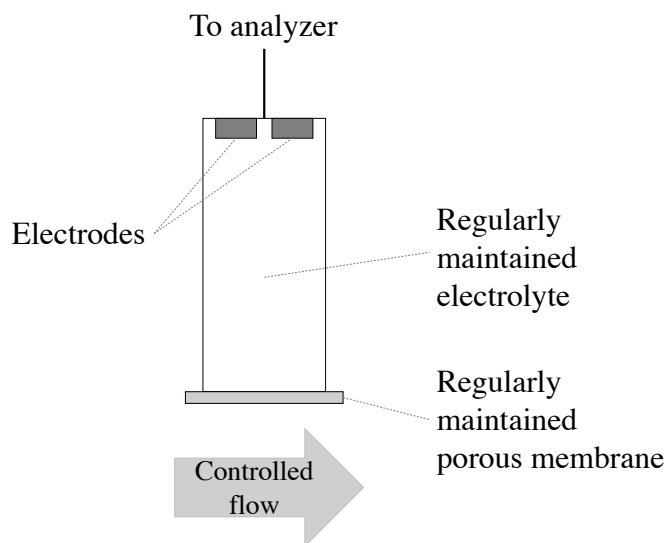
In the first method, colorimetry, a consumable chemical reacts with the water to give off a colour. This colour corresponds to the concentration of free chlorine and is measured by an optical instrument. *N,N*-diethyl-*p*-phenylenediamine (DPD) is widely used for colorimetry. Free chlorine oxidizes DPD to a pink-coloured compound as shown in Figure 1.1.<sup>15</sup>



**Figure 1.1:** *N,N*-diethyl-*p*-phenylenediamine (DPD), reacts with free chlorine to produce a colour for colorimetry. The colour intensity is correlated with free chlorine concentration.<sup>15,17</sup>

The advantages include: The whole system is portable, sometimes handheld. The whole system is less expensive than the in-line amperometric sensor. The disadvantages include: The DPD is a chemical consumable. According to Safety Data Sheets, DPD is toxic to aquatic life, its disposal requires professional services, which may not be easily available in small and distant communities. The operator needs to know the basics of colorimetry for accurate readings. The colorimetry measures one sample at a time; it is not suitable for in-line measurements unless automated by an elaborate fluid handling system.

In the second method, amperometry, the water is passed a sensing probe. The flow of water is controlled and monitored by a pump and a flow meter. In addition to sensing, the sensing probe is preconditioned with a consumable membrane and electrolyte. Due to the nature of its instrumentation, it is mostly used in water treatment plants.<sup>18</sup> Figure 1.2 shows a brief drawing of the sensing probe along with necessary supporting components identified. The advantages include: The amperometric instruments have high sensitivity and accuracy. They can be installed in-line. They can be remotely controlled as a part of an industrial process. The disadvantages include: Industrial amperometric free chlorine sensors are an elaborate system, comprising the probe, the analyzer, the flow control components and regularly maintained consumable parts, such as a protective membrane cap and the electrolytes inside. The cost and skill required to maintain the system are high. There have been constant research efforts for improvements of free chlorine sensing.



**Figure 1.2:** Schematic of an amperometric free chlorine probe, with necessary supporting components. Some parts are regularly maintained for the function of the sensor.

## 1.2.2 Recent research methods

In the literature the current study of free chlorine sensing sees two clear categories: Colour change in a solution or electrochemistry on a solid. In addition to these categories, there are a small number of innovative approaches, such as the use of the mechanical resonance frequency. This section finds insight from all cited references, attempts expose features relevant to the low-cost, easy to use free chlorine sensors for monitoring drinking water and highlights enabling features in bold font. The comparison is first listed in Table 1.2.

### Table of comparison of free chlorine sensors in literature

The references are categorized by feature. When designing a free chlorine sensor with a goal to meet, there are indispensable features to enable the final product for use in small and distant communities. Such features include reusability, no requirement of consumable chemical supplies, no toxic leachants, no skills required to operate, low-cost materials, etc. In addition to features for practical use, certain common features were the inspiration of this work, such as the reactivity of sulfur and nitrogen groups. Also listed are key features of sensor characteristics, such as limit of detection, range, etc. The features listed are relevant in applications of drinking water quality and public health, in both general and small communities.

One **category** involves the development of new chemicals that is sensitive to free chlorine. There are two main subcategories regarding the colour reaction: reversible and irreversible. The molecules in the *subcategory* of irreversible probe molecules can be used only once, creating chemical consumables during use. Their main use is *in vitro* cell imaging for very low concentrations hypochlorous acid or hypochlorites, where their localized colour



emission led to a well contrasted image<sup>19–41</sup> although some can also be used to sense free chlorine in water.<sup>42</sup> Many of these molecules offer high sensitivity.<sup>19,22,24,26–32,34–40,42</sup> However, many of these molecules consist of chemicals that are undesirable for use in drinking water, such as Zn, Cd, Cu, Ru, and aromatic rings.<sup>21,22,25,28,30–36,39,42</sup> A target molecule for drinking water sensing should ideally not contain any toxic substances, in both the fabrication and usage steps.

The *subcategory* of reversible colour-based chemicals for free chlorine sensing offers the ability of reuse of several times..<sup>43–53</sup> This aspect is considered an improvement compared to the irreversible chemicals. However, most of these chemical compounds require multi-step synthesis using costly starting materials or processes.<sup>54</sup> They are not suitable for the goals of this work. The ideal fabrication process should involve only benign reaction conditions, such as room temperature, atmospheric pressure, moisture or oxygen compatibility, and the best case of one-pot<sup>42</sup> or continuous reaction. Ruling out the use of transition metals, many of the molecules in this category employs sulfur- or nitrogen-containing groups, which are possible candidates for use with drinking water.

The other **category** involves the development of amperometric sensors.<sup>55–59</sup> These sensors did not require chemical consumables to operate. However most of them still require mixing or flow control and are not as accurate as the industrial method. The device used to measure free chlorine was the focus.

In addition to the main categories, there has been new processes, mechanisms and proofs of concept published, such as the change in current, resistance and relative change in resistance.<sup>2,60,61</sup> The sensor can be reusable in a case<sup>61</sup> and multi-use but disposable in other cases.<sup>2,60</sup> Overall, few systematic reports have regarded both the sensitive material and the measurement device at the same time.<sup>3</sup> However, while innovative, these mechanisms led to tedious process, required skilled users or required disposable parts.

Based on the literature review, the goal was set to develop a low-cost easy-to-use sensor for free chlorine. To use a low cost material, solid graphite and graphite present in pencil leads were picked for their delocalized bonds. To introduce a sensitivity to free chlorine, based on the structure of DPD (Figure 1.1), nitrogen containing groups, especially amine-sensitized ones were proposed. To develop an easy fabrication process, the electrochemical modification in benign aqueous solution was the candidate. For an accessible detection method, electrochemical detection was used. The motivation to meet the goal is explained in detail in the next section.

### 1.3 Motivation

An ideal free chlorine meter for end users should have the following features.

- Low cost
- Easy to fabricate
- Prepared without use of harmful substances

- Less consumables
- Low maintenance
- Resilient to concentration surges
- Minimal preconditioning required
- Easy to use

Faced with these goals, and based on the understanding of the state of art, a proof of concept sensing material was planned through the amination of graphite present in pencil lead electrochemically in a benign ammonium carbamate solution.<sup>1</sup> Although this proof of concept still lacked some of the features above, it would serve as the first step of cost reduction. Subsequent goals included investigations of the mechanisms involved in the sensing process, such as the mass transfer during the sensing, the reaction kinetics in combination of the mass transfer, the characteristic of the reference electrode, and the possible surge conditions of common ions and free chlorine spikes. The focus was to reduce the cost and increase the ease of use through the understanding of the sensing process. The thesis was then organized according to the steps in the effort to reducing cost and increasing usability.

## 1.4 Organization of thesis

In this thesis, after evaluating the necessity for low-cost easy-to-use free chlorine sensors, the focus of further cost reduction of a proof of concept pencil-based free chlorine sensor was followed through the understanding of mechanisms as listed in respective chapters. Table 1.3 summarizes the the specific features in each chapter to reduce cost and increase ease of use of the sensor.

In Chapter 2, aminated graphite was developed as the low-cost sensitive material. The measurement employs amperometry, with constant mixing and a reference electrode to offer a fast response time.

In Chapter 3, the detailed routine performance were checked with the most challenging drinking water samples. This ensures the sensor will not need replacement in case of surges of common interferences or free chlorine. The extended working range allows for use with fresh produce washing industry.

In Chapter 4, study of mass transfer mechanism allowed for measurement in static solutions, as well as removed the need for mixing for further lower cost. The sensor can now qualitatively indicate the absence of free chlorine, as a new application in chlorine removal applications, such as the bottling industry and point of use chlorine filters.

In Chapter 5, PAD is used for sensitive, fast, absence-identifying sensing of free chlorine without the requirement of mixing or use of a reference electrode. This update may require knowing the conductivity, depending on the level of fluctuation of salt concentration in the water, because the charging current component depends on the ionic strength of the test

solution. Conductivity meters have long been implemented for drinking water monitoring. Weighing the advantages and disadvantages, the use of PAD further lowered the cost.

In conclusion, low-cost easy-to-use free chlorine sensors have been developed. The main features include adequate performance for sensing free chlorine in drinking water, without the use of chemical consumables, interference from common ions, reference electrodes, flow control systems, regular maintenance or expert knowledge. The technical discoveries open new possibilities in neighbouring fields, such as biology, environment, etc. Future work was recommended as the modification planar graphite for alternative device design, low-cost implementation for PAD and Cottrell equation for sensing of new analytes, and integration of such implementations to sensing systems in all related research fields.

**Table 1.1:** Comparison to commercial free chlorine sensing

	Commercial colorimetry	Commercial amperometry	This work
Response time (s)	~120	120	< 3
Range (ppm)	0-8	Detectable to 20	19.2
Long term stability	N/A	6	> 12
Price (CAD)	~600	~3000	~20 (material)
Error	0.1 ppm	5%	0.0322 ppm
Sensing material	DPD (Chemical)	Gold mesh	Graphite modified with ammonium carbamate
Advantage	Water proof, rugged, on battery	In-line, high precision	Low-cost, low maintenance, quick, environmentally friendly, zero-free chlorine qualifiable, no chemical supplies needed
Disadvantage	Toxic to fish	Flow rate conditioning	Need conductivity value
Size	5 × 10 × 25 cm	60 × 60 × 20, plus similar sized accessories, mounted on industrial scaffolds	5 × 5 × 10 cm
Skills required	Knowledge of colorimetry	Industrial control	Similar to using thermometer

**Table 1.2:** Feature comparison in representative studies in literature

Feature to compare	Description of feature	Reference number
Active component	Sulfur groups	2, 21–24, 27, 38, 45, 46, 50
	Nitrogen groups	1, 15, 19, 31, 34, 36, 38, 39, 44, 46, 47, 49, 52, 60, 61
	Other mechanisms	25, 26, 28–30, 32, 33, 35, 37, 40–43, 48, 55–59, 62–66
Reversibility	Irreversible	2, 15, 19, 21–26, 28–42, 47–50, 62, 65, 66
	Reversible	1, 27, 43–46, 52, 55–61, 63, 64
Consumables	Not required	1, 55–61, 63, 64
	Required	2, 15, 19, 21–25, 27–50, 52, 62, 65, 66
Known toxic ingredients?	No	1, 40, 55, 58, 59, 63, 64
	Yes	2, 15, 19, 21–39, 41–50, 52, 56, 57, 60–62, 65, 66
Extensive synthesis?	No	2, 15, 28, 56–58, 60, 61, 63–66
	Yes	1, 19, 21–27, 29–50, 52, 55, 59, 62
Skilled training required?	No	None
	Yes	1, 2, 15, 19, 21–50, 52, 53–66
Suitable for bioimaging?	Yes	19, 21–23, 25–27, 31, 32, 34–37, 41, 44–48, 49, 52
	No	1, 2, 15, 24, 28–30, 33, 38–40, 42, 43, 50, 55–66
Limit of detection	Sufficient for 0.2 ppm	1, 15, 19, 21, 23–25, 27, 28, 34–36, 38, 39, 43–48, 52, 55–58, 60–65
	Insufficient	2, 22, 26, 29–33, 37, 40–42, 49, 50, 59, 66
Range	Wider than 0 – 2	2, 15, 19, 24, 26, 27, 29, 31–34, 37, 38, 45, 49, 56–61, 53, 64
	Insufficient	21–23, 25, 28, 30, 35, 36, 39–44, 46–48, 50, 52, 55, 62, 65, 66
Response time	Real time	1, 55–59, 63, 64
	Intermittent readings	2, 15, 19, 21–50, 52, 60–62, 65, 66
Physical sensor?	Yes	1, 2, 55–61, 64
	No	1, 15, 19, 21–50, 52, 62, 63, 65, 66

**Table 1.3:** Progress of cost reduction of the sensor in each chapter. Requirements: Yes or No.

Chapter	Consumables	Mixing	Reference electrode	Proprietary hardware
2	N	Y	Y	Y
3	N	Y	Y	Y
4	N	N	Y	Y
5	N	N	N	N

## Chapter 2

# Low-cost graphite-based free chlorine sensor \*

Pencil lead was used to fabricate a graphite-based electrode for sensing applications. Its surface was electrochemically modified using ammonium carbamate to make it suitable for sensing free chlorine in water samples. Chlorine is widely used as a disinfectant in the water industry, and the residual free chlorine concentration in water distributed to the consumers must be lower than that stipulated by regulatory bodies. The graphite-based amperometric sensor gave a selective and linear response to free chlorine in the relevant concentration range and no response to commonly interfering ions. It was evaluated further for storage stability, response time, and hysteresis. This sensor is being proposed as a low-cost device for determining free chlorine in water samples. Its ease-of-use, limitations, and feasibility for mass-production and application is discussed.

### 2.1 Introduction

Chlorine is widely used as a disinfectant in the water treatment industry for inactivation of pathogenic microorganisms such as *Cryptosporidium*<sup>8,9</sup> and *Escherichia coli O157:H7*.<sup>10</sup> Before chlorine-treated water can be sent from the treatment plant to the distribution system, it must meet certain standards for residual free chlorine concentration, which is typically below the 5 ppm range.<sup>8-10</sup> Free chlorine content in municipal water is currently measured using *N,N*-diethyl-*p*-phenylenediamine (DPD)-based colorimetry.<sup>15</sup> There have been some efforts toward developing alternative detection methods<sup>62</sup> and improving<sup>63</sup> or miniaturizing<sup>59</sup> existing devices and methods. With increasing public awareness of water quality and tighter public health regulations and practices, such as point-of-use sampling and analysis, a robust, reliable, low-cost, and portable free chlorine sensor would be highly desirable. This

\*Reprinted (adapted) with permission from (Si Pan, M Jamal Deen, and Raja Ghosh. Low-cost graphite-based free chlorine sensor. *Analytical Chemistry* 87.21 (2015), pp. 10734–10737). Copyright (2015) American Chemical Society.

is particularly relevant in small and remote communities, where highly trained personnel may not be available, and routine maintenance is less feasible.

Several promising materials for free chlorine sensing with linear response have recently been reported in the literature.<sup>52,55,57,58,61,64-66</sup> However, the sensing materials are either expensive (e.g., glassy carbon,<sup>57</sup> gold,<sup>58</sup> boron-doped diamond,<sup>64</sup> graphene,<sup>65</sup> carbon nanotubes,<sup>55,61</sup> ferrocene<sup>66</sup>) or potentially leach hazardous materials (e.g., benzethonium chloride,<sup>57</sup> aniline oligomers<sup>61</sup>). Moreover, in most cases, the upper range for sensing was 2.0 ppm,<sup>7,13,14,16</sup> and hysteresis during repeated measurements was not systematically studied. In a typical water-testing application, the concentration of free chlorine in the tested sample is likely to fluctuate and hysteresis, if present, would affect sensor performance. Equally important is the selectivity of the sensor, i.e., its ability to distinguish free chlorine from commonly interfering ions such as nitrate, sulfate, and (bi)carbonate ions, and reduced chlorine in the form of chloride ions.

Many free chlorine sensors utilize the reaction between it and amine groups on planar macrocyclic molecules.<sup>15,41,52</sup> Building on this, and the fact that graphite is conductive due to its delocalized  $\pi$  bonds parallel to the crystal planes,<sup>67</sup> we hypothesize that amine-modified graphite would be suitable for sensing free chlorine. More specifically, the 2p electron lone pair in an amine group would interact with the graphite through p- $\pi$  conjugation. As both graphite and glassy carbon have delocalized  $\pi$  bonds, we used amination to modify<sup>68-70</sup> graphite.

The fabrication of free chlorine-sensing material based on electrochemical amination of graphite in commercial 2B pencil lead is discussed. The use of pencil lead as an inexpensive graphite sensor has been reported in the literature.<sup>71,72</sup> In the current study, free chlorine concentration was determined by chronoamperometry. In addition, linearity, hysteresis, response time, repeatability, storage stability, specificity, and application of free chlorine sensing were assessed.

## 2.2 Experimental

### 2.2.1 Materials

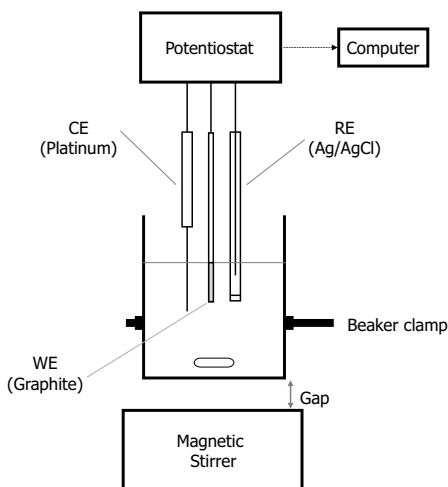
Most chemicals used in this study were purchased from Sigma-Aldrich and used as received. Those obtained from other suppliers are specifically identified. The Ag/AgCl reference electrode (CHI111) and the platinum wire counter electrode (CHI115) were purchased from CH Instruments, Inc. (Austin, TX). The reference electrode was filled with 1 M KCl (P217-500, Fisher Scientific, ON, Canada) solution. The pencil lead (TrueColor, 2B, 0.7 × 100 mm) was purchased from TrueColor Co., Ltd. (Kunshan, Jiangsu, China).

### 2.2.2 Setup

A three-electrode setup using an EmStat2 instrument (PalmSens BV, Utrecht, The Netherlands) was used to carry out both the graphite modification and free-chlorine detection



experiments. The electrolytes were held in a 10 mL beaker and stirred magnetically at 600 rpm. The beaker was clamped to maintain a gap with the magnetic stirrer. Figure 2.1 shows the schematic of this setup.



**Figure 2.1:** Schematic of three-electrode setup used to fabricate sensors and sense free chlorine.

### 2.2.3 Sensor Fabrication

Pencil lead was cleaned using lab tissue and rinsed with deionized water. Specifically, the pencil lead was wrapped by lab tissue and pulled out. The trace of pencil was examined. When the trace was barely visible, the pencil lead was considered polished. The electrochemical modification<sup>68</sup> of the graphite surface was carried out at 1.0 V versus Ag/AgCl reference electrode using an initial electrolyte solution consisting of 0.1 M sodium phosphate buffer (pH 7.0), to which 0.1 M ammonium carbamate (29283425G) solution was added until the pH changed to 8.9.

### 2.2.4 Free Chlorine Sensing

Free chlorine was sensed by chronoamperometry<sup>71</sup> at 0.1 V versus the Ag/AgCl reference electrode. The experiments were started with 10 mL of 100 mM sodium phosphate buffer (pH 7.0) in the beaker. Different volumes of sodium hypochlorite (425044250 ML) 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). The free chlorine concentration in the sodium hypochlorite stock solution was quantified by iodometry using

sodium thiosulfate (SX0815-1, EMD, Mississauga, ON, Canada), potassium iodide (74210-140, Anachemia, Montreal, QC, Canada), and starch. The interference by different species was tested using  $\text{NaNO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ , and  $\text{NaCl}$  (S7653-1KG) stock solutions. Free chlorine containing tap water was tested with the method discussed in this paper as well as with a commercial Pocket Colorimeter II (Hach Company, Loveland, CO) for comparison.

## 2.3 Results and discussion

### 2.3.1 Electrode Modification

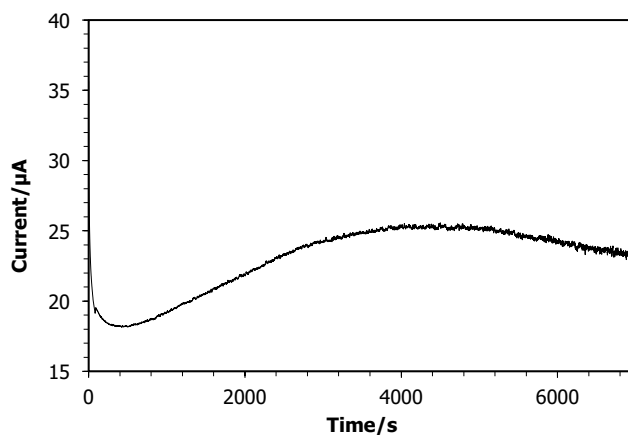
Figure 2.2 shows the current-time profile obtained during electrochemical modification of the graphite surface. It has been reported that the primary amine group in carbamate forms a radical due to electrochemical oxidation and subsequently attaches to the edges of graphene.<sup>68-70</sup> The current decreased first due to the depletion of carbamate close to the working electrode surface, then increased due to the activation of the working electrode surface, and finally decreased due to the decrease of available active sites on the working electrode. This trend agreed with an earlier report on a similar modification.<sup>68</sup> The feature of a successful reaction is the decrease of current followed by the increase. The current is expected to further if the reaction is carried on further. The modification could be carried out using a simple setup and did not involve any harsh reaction conditions. Moreover, the method is amenable to mass production. The technique could easily be adapted to modify other related materials, such as carbon nanotubes and graphene based on the availability of delocalized  $\pi$  bonds.

The most direct independent verification of modification was the change of hydrophilicity of the surface of the pencil lead. Before the modification, the pencil lead appears hydrophobic. There is little water wetting the surface of it, both before and after the lab tissue polishing. However, after the modification, the pencil lead is well wetted up to the point submerged in the modification electrolyte. This change of apparent hydrophilicity indicated change of chemistry on the surface of the pencil lead. Because the aminated group is more polar thus more hydrophilic than the nascent graphite surface, this observation suggested amination of the graphite surface.

Other indirect verification effort was attempted. However, due to the physical structure of the probe in question such as the cylindrical geometry, the small diameter, the intense dark colour, spectroscopic methods were infeasible. Separate modification of graphite powders in an aqueous slurry yielded two distinct fractions of product: Floating particles and sunken particles, suggesting two distinct chemistry existed after the modification process. The attempt to use the wetted particles as an electrode for free chlorine sensing was unsuccessful.

Modification of pencil leads of diameters 0.5, 1.3 and 6.0 mm yielded similarly linearly responsive electrodes for free chlorine sensing in the preliminary explorations. They were not systematically studied. Unmodified pencil leads of any source produced transient,

uncorrelatable response under constant stirring in buffered solutions, and were considered control experiments.



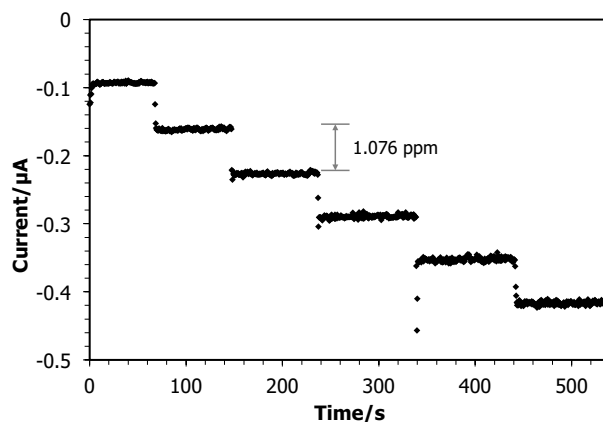
**Figure 2.2:** Current–time profile obtained during electrochemical modification of the surface of pencil lead.

### 2.3.2 Free Chlorine Sensing

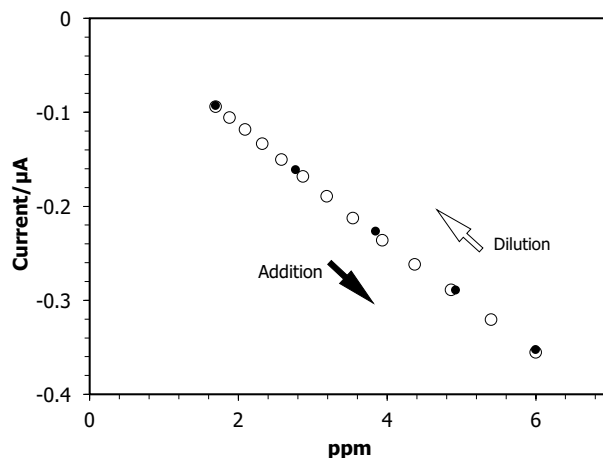
Figure 2.3 shows the chronoamperometric response to increasing free chlorine concentration by 1.076 ppm per step. The increase in the cathodic current in each of the steps was comparable, and the net change in current correlated linearly with the quantity of free chlorine added. The sensitivity to free chlorine in this measurement was  $0.303 \mu\text{A ppm}^{-1} \text{cm}^{-2}$ . The response was repeatable, and the sensitivity did not change with a change in the electrode area. The response time for 90% change ( $t_{90\%}$ ) in signal was less than three seconds. We hypothesize that the electrode reacts cathodically with HClO, whose reduction potential is around +1.63 V. The voltage of chronoamperometry was well outside the voltage range for dissolved oxygen.<sup>73,74</sup> Therefore, sample deaeration was not required. The noise levels in these experiments (maximum fluctuation equivalent to 0.13 ppm) were lower than the reported values (0.69 and 1.33 ppm, respectively) in the literature.<sup>55,57</sup>

### 2.3.3 Hysteresis

Figure 2.4 shows the change in current in response to the addition or removal of free chlorine from the sample being tested. These results indicate very low hysteresis; the maximum hysteresis throughout the tested concentration range was 0.04 ppm at 6 ppm. In contrast to the literature without hysteresis study,<sup>55,57</sup> these results indicate the real utility of repeatable readings in cases where free chlorine may increase or decrease.



**Figure 2.3:** Current–time profile obtained from experiment carried out to determine the effect of free chlorine addition with 1.076 ppm of free chlorine added in each step. The starting concentration was 1.076 ppm.

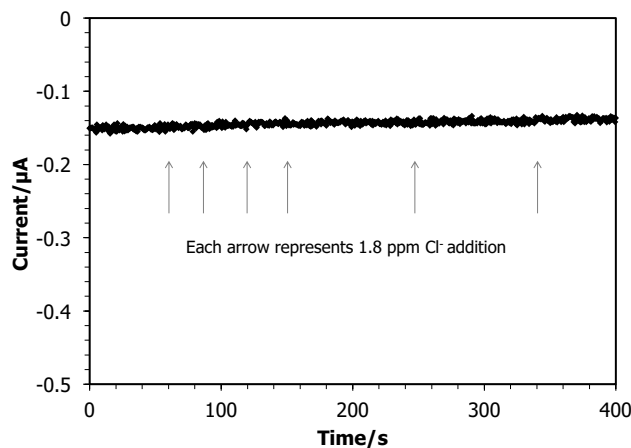


**Figure 2.4:** Change in current in response to the addition or removal of free chlorine in an experiment carried out to evaluate hysteresis of the sensing material. Solid points were additions and hollow dilutions. Each data point represents one measurement.

### 2.3.4 Interference

Figure 2.5 shows the signal response to additions of 1.8 ppm chloride at random time points into a simulated tap water sample. The experiment tested whether the sensing responds to the reduced form of the chlorine element. There was no sensible signal change resulted

from each addition. The reduced chlorine did not contribute to the signal. The plateau regions in Figure 2.3 were indeed not a measure of the total chlorine elements in the solution.



**Figure 2.5:** Control experiments by adding  $\text{Cl}^-$  several times during a measurement to show the insensitivity to repeated additions of reduced chloride as around 2 ppm.

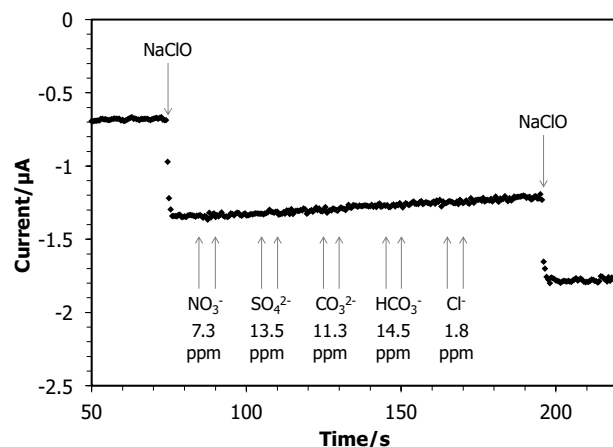
Figure 2.6 summarizes the effects of potential interfering species,<sup>7,13,14</sup> which were added sequentially, each as a set of two 10  $\mu\text{L}$  solution pulses (7.3 ppm sodium nitrate at 85 and 90 s, 13.5 ppm sodium sulfate at 105 and 110 s, 11.3 ppm sodium carbonate at 125 and 130 s, 14.5 ppm sodium bicarbonate at 145 and 150 s, and 1.8 ppm sodium chloride at 165 and 170 s) to a 10 mL 0.1 M sodium phosphate (pH 7.0) buffered solution containing around 2 ppm free chlorine. At 193 s, the addition of NaClO (containing about 2 ppm free chlorine) caused an identical signal increase as the previous NaClO pulse addition at 73 s.

### 2.3.5 Application

Figure 2.7 shows that the measured free chlorine concentrations of five tap water samples were very close to those obtained using commercial DPD colorimetry (Pocket Colorimeter II). This correlation suggests that tap water samples could directly be tested without buffering.

### 2.3.6 Feasibility of Reuse

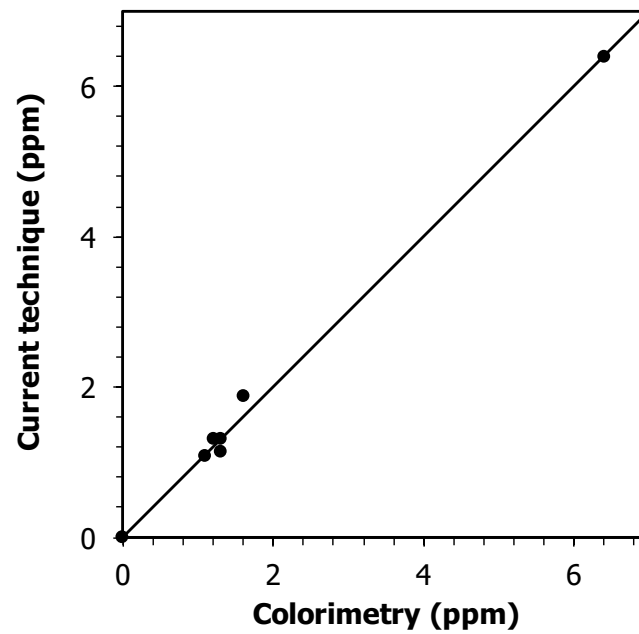
It is desirable that a sensor be suitable for repeated use in a highly reproducible manner. One of the electrodes used in the experiments described in this chapter was stored in deionized water for a period of 7 weeks without any deterioration in performance during repeated use following storage.



**Figure 2.6:** Insensitivity to commonly interfering ions as denoted in the figure and intact response to an identical amount of free chlorine after these ions introduction. Each arrow was one addition by 10  $\mu\text{L}$  of the respective solution to 10 mL of buffered solution.

## 2.4 Conclusions

A pencil lead-based graphite sensor was fabricated to detect and quantify free chlorine in water samples. The response was linear and selective for free chlorine. Potential interfering species, such as nitrate, sulfate, carbonate, bicarbonate, and chloride, showed no response. The sensitivity to free chlorine was  $0.302$  (SD:  $0.013$ )  $\mu\text{A ppm}^{-1} \text{cm}^{-2}$ . The response time ( $t_{90\%}$ ) was less than 3 s. In the tested range of 0-6 ppm, the hysteresis was very low. The feasibility of directly testing tap water samples was demonstrated.



**Figure 2.7:** Free chlorine measurement with five tap water samples using the current technique and DPD colorimetry. An additional buffered 6.4 ppm free chlorine-containing sample was measured as a positive control.

## Chapter 3

# Free chlorine sensing with modified graphite electrode: Resolution and selectivity

The current chapter concerns the improvement of the sensor discussed in chapter 2. Using a modified process, the sensitivity of the sensor probe could be improved, its range extended and selectivity improved. One particular sensor was tested repeatedly to check for the repeatability of the signal, especially in low ranges. The sensor was subjected to high concentration of free chlorine to test whether it could survive a free chlorine surge. The sensor was also tested using solutions containing high concentration of common interference ions. The sensors were tested for reproducibility.

### 3.1 Introduction

Water quality is an important metric of the quality of human life. Chlorine is widely used for killing harmful bacteria to make water safe for human consumption. The World Health Organization recommends a free chlorine residue range of 0.2 to 2.0 ppm<sup>13</sup> in municipal drinking water to suppress lethal bacteria such as *E. coli*,<sup>10</sup> and to inactivate parasites such as *Cryptosporidium*.<sup>9</sup> Therefore, the availability of inexpensive free chlorine detection devices is vitally important for guaranteeing drinking water safety.<sup>11</sup>

There have been numerous publications on free chlorine sensing materials<sup>55,57,64,65</sup> with promising outcomes and free chlorine sensing approaches with systematic attempts<sup>2,3,75</sup> in recent years. We have previously discussed the fabrication of pencil lead (i.e. graphite) based inexpensive but effective free chlorine sensor for free chlorine monitoring in drinking water.<sup>1</sup> Its sensitivity and selectivity under commonly anticipated conditions was assessed using real tap water as well as lab-prepared simulated solutions.<sup>1</sup> However, the performance of the sensor in the “out of the normal range” of conditions was not systematically tested. A robust sensor should also be able to handle such special conditions. For instance, spikes in salt concentration and indeed free chlorine concentration in drinking water pipeline are



real possibilities.

In this chapter, it is described and discussed how the sensitivity of the pencil lead based sensor could be increased by altering the voltage used for electro-coating the sensor surface. We then analyze sensitivity, noise, and range and limit of detection of the new improved sensor. After confirming sensing repeatability, we systematically investigate selectivity by testing the effects of interfering agents at high concentrations. We also discuss the limitations of this improved sensor.

## **3.2 Experimental details**

### **3.2.1 Materials**

Unless specifically mentioned, chemicals were purchased from Sigma-Aldrich, St. Louis, MO, USA and used as received. The reference electrode (Ag/AgCl type, CHI111) and the counter electrode (CHI115) were purchased from CH Instruments, Inc., Austin, TX, USA. The stationery pencil lead used to fabricate the sensor was purchased from TrueColor, Kunshan, Jiangsu, China). The name of chemicals used in the text indicate their type. Detailed description of chemicals were presented in Chapter A Section A.1.1.

### **3.2.2 Fabrication**

The sensor fabrication procedure was a modified version of that described in our earlier paper.<sup>1</sup> Briefly, a three-electrode system (EmStat 3, PalmSens, the Netherlands) was used to apply 1.1 V (with respect to the reference electrode) to the pencil lead immersed in reaction mixture prepared by adding 0.1 M ammonium carbamate solution to 0.1 M sodium phosphate (pH 7.0) buffer. This electrochemical modification was carried out for 7200 seconds, at a stirring speed of 600 rpm in a 10-mL beaker. The reaction temperature was maintained at 24 degrees Celsius.

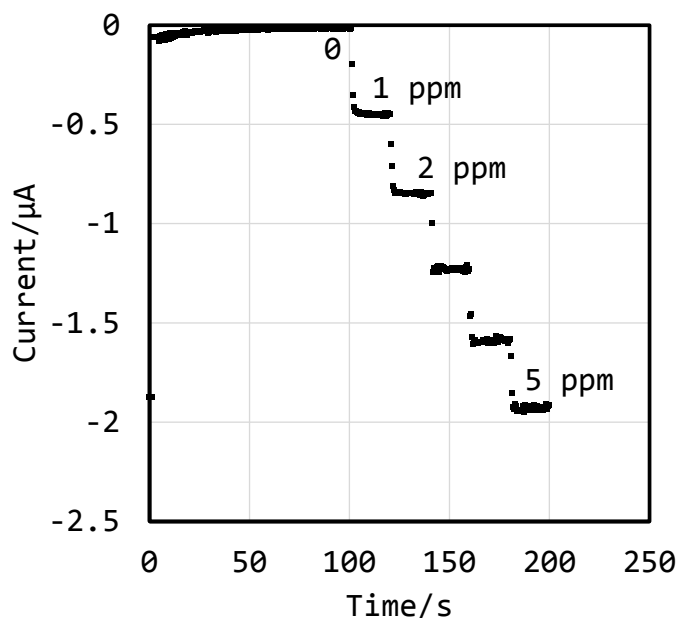
### **3.2.3 Sensing**

The sensing experiments were carried out using 0.1 V applied voltage and the test solutions was prepared in 0.1 M phosphate buffer (pH 7.0). Different free chlorine concentration samples were obtained by adding different measured volumes of stock hypochlorite solution. The volume change in this procedure was negligible. All amperometric data was obtained at a rate of two samples per second and processed as described elsewhere.<sup>1</sup>

## 3.3 Results and Discussion

### 3.3.1 Improved sensitivity

Figure 3.1 shows a typical amperometric response for free chlorine measurement in the 0-5 ppm range. The correlation between current and concentration was linear. The apparent sensitivity was  $-33.5 \text{ nA ppm}^{-1} \text{ mm}^{-2}$ . The sensitivity normalized by the area was around ten times that of the original sensor.<sup>1</sup> The response time was less than 2 seconds. The standard deviation in each free chlorine concentration value was around 0.6% of the signal, i.e. 0.016 ppm. The worst case was 9.3 nA which corresponded to 0.024 ppm for the 5 ppm measurement. Compared to results published in our previous paper,<sup>1</sup> the sensitivity was better, the value being smaller by a factor of five. Also, the standard deviation was half of that previously reported.<sup>1</sup> Further, the current range was now increased to the microampere range. This increase made the upgraded sensor compatible with low-cost electronics.

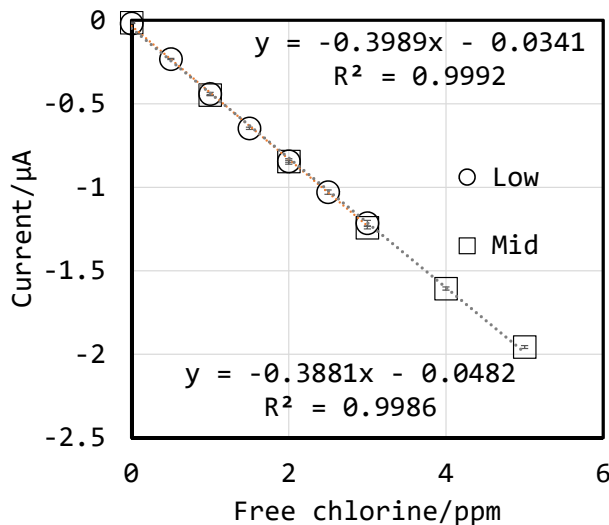


**Figure 3.1:** A typical sensor output for the 0-5 ppm free chlorine range. Each step represents an increment in 1 ppm concentration. The sensitivity was  $-33.5 \text{ nA ppm}^{-1} \text{ mm}^{-2}$ . The response time ( $t_{90\%}$ ) was less than 2 seconds.

### 3.3.2 Repeatability in low and mid ranges

Figure 3.2 shows the calibrations in the 0-6 ppm (mid) and 0-3 (low) free chlorine concentration ranges. The two individual correlations overlapped perfectly as can be seen in the figure. The errors based on multiple runs for each experimental concentration was small.

For the mid-range, the limit of detection (i.e. 3 standard deviations / slope) was 0.0096 ppm. The coefficients of variance of the signal average for each concentration were around 0.9% for free chlorine containing samples and 20.0% for chlorine-free samples. Table 3.1 summarizes the sensitivity values for six different sensors operated under identical conditions. The sensitivity values were very close to each other with the standard deviation being 0.0005 and the coefficient of variance being 1.66%. The limit of detection, accounting for variations among the 6 different sensors was 0.0510 ppm. This meant that 0.2 ppm free chlorine concentration could be measured very reliably. This represents a major improvement over our previously reported sensor, which had a limit of detection of 0.13 ppm,<sup>1</sup> which was close to the 0.2 ppm critical lower limit.



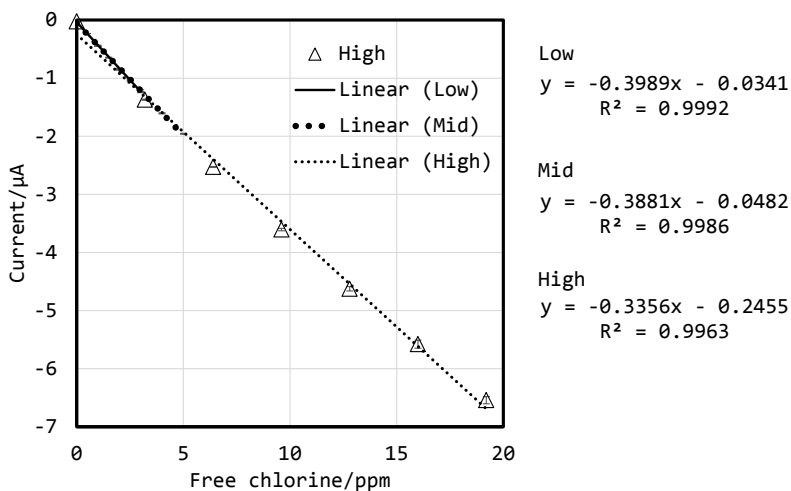
**Figure 3.2:** The correlation of signal and concentration in three repeated runs under two different ranges of calibration, i.e. low and mid. The calibration curves overlapped, indicating 5 ppm is within the linear dynamic range of the sensor.

### 3.3.3 Repeatability and deviation in high ranges

Figure 3.3 shows the correlation between sensor signal and free chlorine concentration in the high range of calibration, i.e. up to 19.2 ppm. Although the correlation was linear, the regression coefficient was lower than those of the low and mid ranges. Also, the sensitivity was 15.9% lower as shown by the deviation between the calibration curves. This effect indicated the 19.2 ppm range, while still practically linear, was near the limit of the dynamic range of the sensor. The main motivation behind testing the sensor for this range was to guarantee that the sensor had surge immunity. In addition, there are several applications where measurement of high free chlorine concentration is important. One such application is the testing of fruit and vegetable washings<sup>76</sup> in which free chlorine concentration is expected to be around 10 ppm.

**Table 3.1:** Sensitivity values of different sensors and their variation

Number	Sensitivity ( $\mu\text{A ppm}^{-1} \text{mm}^{-2}$ )	$R^2$
1	-0.03413	0.9983
2	-0.03411	0.9986
3	-0.03553	0.9991
4	-0.03544	0.9993
5	-0.03522	0.9994
6	-0.03505	0.9992
Average	-0.03491	-
Standard Deviation	0.0005	
COV (%)	1.66	

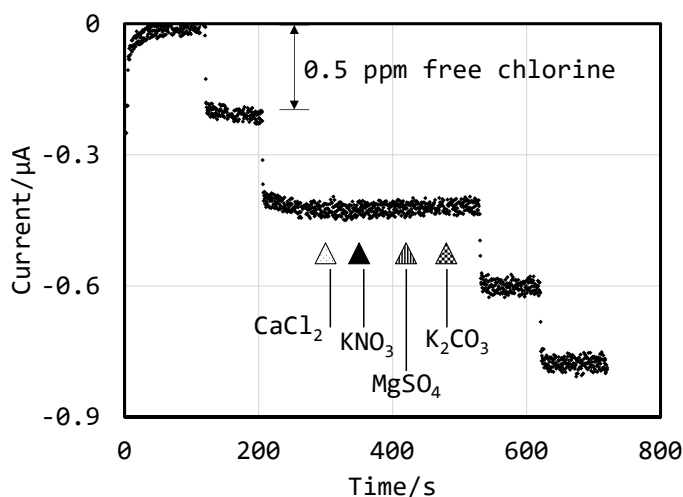


**Figure 3.3:** Calibration curve for the high range of calibration along with those for the low and mid ranges. The deviation indicates the high range reaching the linearly dynamic range of this free chlorine sensor.

### 3.3.4 Interference by high concentrations of common ions

Free chlorine concentration measurement could potentially be affected by interfering agents such as salts e.g. carbonates, phosphates and chlorides. Municipal drinking water could contain up to 200 ppm phosphate and sodium ions. The desired concentration range for these species is 150 ppm.<sup>77</sup> Figure 3.4 shows the effects of the introduction of some of these common interfering species (i.e. calcium chloride, potassium nitrate, magnesium sulfate and potassium carbonate)<sup>7,13,14</sup> on free chlorine measurement using our sensor. The concentration of calcium chloride used in these experiments was 180 ppm while for the others, the corresponding concentration was  $1.0 \times 10^3$  ppm. Drinking water defined as very hard water by WHO<sup>78</sup> contains a maximum calcium concentration of 180 ppm. The higher concentration used for the other interfering species was to ensure that the sensor was not

effected by concentration surges. The experiment was initiated by two sequential additions of free chlorine (0.5 ppm concentration increase resulting from each), followed by the addition of calcium chloride, potassium nitrate, magnesium sulfate and potassium carbonate, followed by two more sequential additions of free chlorine (0.5 ppm concentration increase resulting from each). The results obtained showed that not only did the interfering agent have no effect on the sensor signal, their presence also had no impact on the efficiency and precision of subsequent free chlorine measurements. The deviation caused by high concentration of calcium ion suggested the sensor is more prone to inorganic fouling, as suggested by the hydrophilicity change in Chapter 2. In contrast, the commercial amperometric sensor, which utilizes a hydrophobic porous membrane, would be more prone to biofilm fouling.<sup>79,80</sup>



**Figure 3.4:** Test for interference by common interfering agents (concentration of calcium ions = 180 ppm ( $\text{CaCl}_2$  at 499 ppm), concentration of all other interfering agents =  $1 \times 10^3$  ppm).

### 3.4 Conclusions

The improved free chlorine sensor described in this chapter showed superior performance compared to the sensor described in our previous publication. The high sensitivity, low noise and high repeatability resulted in a limit of detection values of 0.0510 ppm. This meant that reliable monitoring for 0.2 ppm level free chlorine concentration, typically required for bacteriostatic effect would be feasible using the new sensors. The sensor could handle free chlorine concentration surge and its performance was not affected by high concentrations of common interfering species. In addition, the sensor was suitable for other applications such as testing of fruit and vegetable wash liquids

## Chapter 4

# Free chlorine sensing method with improved limit of detection

A simplified sensing protocol and increased the limit of detection (LOD) of a previously reported low-cost, graphite-based free chlorine sensor were achieved by removing the mixing component. In a static solution, without any stirring, the transient signal was recorded. This signal was analyzed using the Cottrell equation, based on the typical usage. The slope of the Cottrell equation correlated well with the concentration as commonly used in the literature. Moreover, the intercepts were used to distinguish the absence of free chlorine with a higher distinction, which supersedes the accuracy of the use of LOD. The mechanism giving rise to these observations are discussed.

### 4.1 Introduction

Chlorine is widely used to make water bacteria free and thereby render it safe for drinking. The World Health Organization guideline for free chlorine residue in municipal drinking water is 0.2 to 2.0 ppm.<sup>13</sup> In this concentration range, it kills lethal bacteria such as *E. coli*,<sup>10</sup> and inactivate parasites such as *Cryptosporidium*.<sup>9</sup> The ability to monitor free chlorine from point of application to point of use is key to ensuring drinking water safety.<sup>11</sup> Therefore, availability of low-cost free chlorine measuring instruments is critically important for achieving the above objective.

Currently, free chlorine is measured using expensive amperometric sensors (such as FCL, Emerson Process Management, Hamilton, Canada). These can only be operated by trained personnel, and require replenishment of electrolyte, and frequent replacement of the membrane cap. Therefore, these are unsuitable for testing water in small and remote communities, where availability of trained operators, technical support and access to consumables could all be limiting. There are several recent publications on low-cost free chlorine sensors.<sup>1-3,55-57,61,64,65,75</sup>

In a recent paper, we described the fabrication of an inexpensive graphite-based free chlorine sensor,<sup>1</sup> by electrochemical treatment of pencil lead with ammonium carbamate.

The resultant sensor was suitable for measuring free chlorine in the relevant range, i.e. 0.2 to 2.0 ppm and showed linear correlation up to 6 ppm, with a <3 s response time, for a constantly mixed sample. While this sensor addressed our primary goals, i.e. development of a sensitive and low-cost device, certain issues such as the ease of use remain. More specifically, the requirement for constant and precise mixing of the sample during testing could be a limiting factor. In this chapter, it is attempted to simplify the testing protocol by eliminating the mixing requirement. We do so by analyzing transient current data obtained from unmixed or static sample solutions. The data is processed using the Cottrell equation,<sup>81</sup> taking into consideration the geometry of the sensor.

## 4.2 Experimental details

### 4.2.1 Materials

Unless specifically mentioned, chemicals were purchased from Sigma-Aldrich, St. Louis, MO, USA and used as received. The reference electrode (Ag/AgCl type, CHI111) and the counter electrode (CHI115) were purchased from CH Instruments, Inc., Austin, TX, USA. The stationery pencil lead used to fabricate the sensor was purchased from TrueColor, Kunshan, Jiangsu, China). The name of chemicals used in the text indicate their type. Detailed description of chemicals were presented in Chapter A Section A.1.1.

### 4.2.2 Fabrication

The fabrication was the same as that in the previous chapter. Briefly, the modification was carried out at 1.1 V vs the reference electrode. We found out that there were a few bubbles of gas evolution on the working electrode, much less compared to the oxygen evolution in water, so we hypothesized the reaction can be sped up by applying a higher activation energy, i.e. a higher voltage. The higher intermediate production will result in a denser modification with the same timeframe.<sup>68</sup>

### 4.2.3 Sensing

In the sensing, while the instrument settings were identical to those reported in our previous paper<sup>1</sup> the sample was not stirred. After immersing the electrodes in the test solution for one minute, the instrument was turned on.

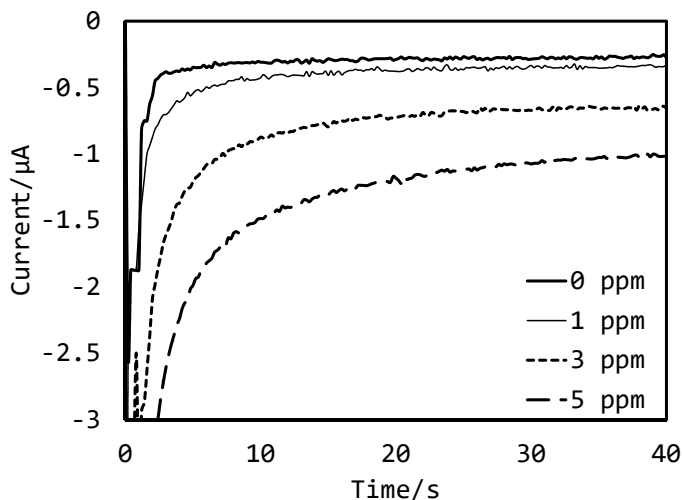
## 4.3 Results and discussions

### 4.3.1 Transient response to free chlorine in static solutions

Figure 4.1 shows the transient responses raw data obtained with different test solutions. We processed the above data using the Cottrell equation,<sup>81</sup>

$$i = nFAD^{0.5}c(\pi t)^{-0.5} \quad (4.1)$$

In the above equation,  $n$  is the number of electrons transferred,  $F$  is the Faraday constant,  $96485 \text{ A s mol}^{-1}$ ,  $A$  is the area of the electrode,  $D$  is the diffusion coefficient,  $c$  is the bulk concentration of the analyte, and  $t$  is the time. The reaction was assumed to be much faster than transport, i.e. diffusion.



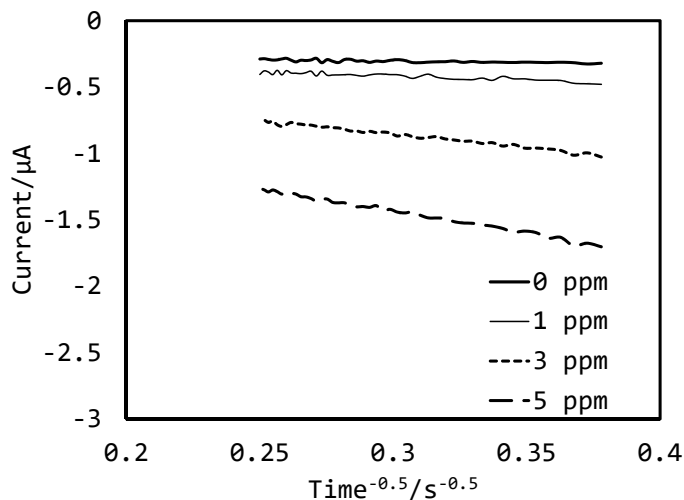
**Figure 4.1:** Transient current profile of measurements of free chlorine concentration in 0, 1, 3 and 5 ppm. The current magnitude decreased with time. The rate of decrease also decreased. The spacing of the 0-ppm profile was irregular with respect to the rest curves. This figure prompted the further investigation for information from these profiles.

Figure 4.2 shows the current data obtained between 7-16 s plotted against  $t^{-0.5}$ , consistent with the Cottrell equation. The time slice selected is the typical range for faradaic dominant systems.<sup>82-84</sup> The resulting straight lines obtained at the different free chlorine concentrations are typical of those obtained during unsteady state diffusion-based mass transfer.<sup>82,85</sup> The slope of the straight lines increased with free chlorine concentration.

### 4.3.2 Expanded Cottrell equation for geometric factors

Figure 4.3 shows plots of slope and intercept data obtained from four repeated experiments as functions of free chlorine concentrations. These results suggest that both slope and





**Figure 4.2:** Replotted data from Figure 4.1 as a function of  $t^{-0.5}$  as present in the Cottrell equation. Conforming with published results for diffusion-controlled mass transfer, the profiles were straight lines in the relevant time window.<sup>81,82,84</sup> The slopes increased with the free chlorine concentration, while for 0 ppm, it was nearly a flat line. The irregular 0-ppm profile spacing is inherited from Figure 4.1 and is further illustrated in Figure 4.3.

intercept correlated linearly with concentration, and could therefore be used as tools for concentration measurement. The respective values of  $b$  and  $k$  are  $-0.1057 \mu\text{A ppm}^{-1}$  and  $-0.5902 \mu\text{A s}^{-0.5} \text{ppm}^{-1}$ .

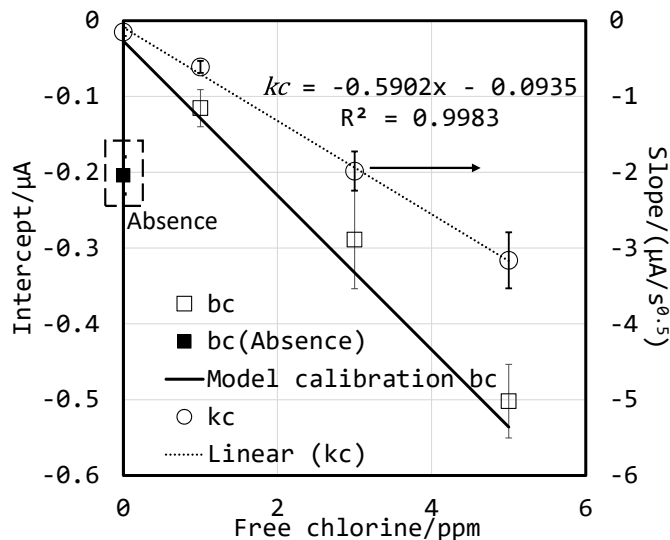
The classic Cottrell equation considers unsteady state diffusion at a semi-infinite plane.<sup>82</sup> For any other geometry, an expansion term<sup>82,85</sup> is added, e.g. specifically for a sphere, the expanded Cottrell equation is:

$$i = nFAD^{0.5}c(\pi t)^{-0.5} + nFADcr^{-1} \quad (4.2)$$

where  $r$  is the radius. The ratio of the slope and intercept for a sphere equals  $r/\sqrt{\pi D}$ , a term independent of  $C$ , or  $t$ . For a cylinder, obtaining an analytical solution is difficult and hence a numerical approximation involving Bessel functions<sup>85,86</sup> is used. This makes it incompatible with low-cost electronics.

### 4.3.3 Need for expanded Cottrell equation due to geometry

An alternative based on a semi-infinite plane consideration could be used for systems where the diffusion length scale is much smaller compared to the diameter of the cylinder.<sup>82</sup> However, in our system, the diffusion layer surrounding the electrode would be approximately  $200 \mu\text{m}$ <sup>87</sup> while the diameter of the working electrode is  $700 \mu\text{m}$ . Therefore, when using a planar approximation<sup>82,88</sup> for our system, an expansion term for the transient current has to



**Figure 4.3:** Plots of intercepts and slopes of four repeated experiments. The circles agreed with the typical usage of Cottrell equation, whereas the intercept of 0 ppm was an outlier. This effect qualitatively indicated the absence of free chlorine. In conventional methods, the smallest measurable concentration is the LOD.

be included:

$$i = kct^{-0.5} + bc \quad (4.3)$$

To establish whether this correlation could be used for calibration, a new set of experiments were carried out and the data obtained was replotted according to Equation 4.3. The respective average values for intercepts ( $bc$ ) and slopes ( $kc$ ) thus obtained were plotted as shown in Figure 4.3. While the slope and intercepts of the free chlorine-samples fit the model, chlorine-free samples did not. In the absence of free chlorine, a charging current response<sup>82-84</sup> at the solution interface could be expected, whereas in the presence of free chlorine, the Cottrell equation-based response would be expected. The qualitative indication bypasses the attempt to measure values smaller than the limit of detection. Therefore, the sensor is not only suitable for measuring free chlorine concentration but also very useful for certifying chlorine-free samples, as required with chlorine filters and in the bottling industry.

## 4.4 Conclusion

The expanded Cottrell equation has been developed, the mechanisms discussed with published theoretical works, the effect illustrated experimentally in this work, and significance of this work discussed. Future research will focus on the effect of electrode size, the dependence of a reference electrode, temperature dependence and new applications that may result from the understanding of the mass transfer process.

## Chapter 5

# Free chlorine sensing using Pulsed Amperometric Detection (PAD)

Pulsed Amperometric Detection (PAD) was used to sense free chlorine without using a reference electrode, due to the pulsed sensing mechanism. A linear correlation with free chlorine concentration was observed. The limit of detection, range and calibration curve were evaluated as suitable for practical free chlorine sensing. Furthermore, the sample without free chlorine was distinguishable well from the calibration curve. The benefits of such a sensing technique include reduced cost, reduced maintenance, simpler layout while maintaining sensitivity. The disadvantage is the baseline correction requiring the conductivity of the solution being tested.

### 5.1 Introduction

Free chlorine is kept at around 2 ppm in drinking water to inhibit the bacterial regrowth. If the free chlorine is less than 2 ppm, there is a risk of lethal outbreak of microorganisms such as *E. coli*. and *Cryptosporidium*.<sup>8-10</sup> If it is higher than 2 ppm, long-term health risks such as bladder cancer are associated with excess ingestion of free chlorine.<sup>14</sup> Therefore, free chlorine is an important characteristic to monitor in drinking water.

Current methods of detection of free chlorine of the colorimetric kind would require a chemical supply, thus is less favourable compared to the amperometric methods developed so far in this thesis. Current methods of the amperometric kind would all require a maintained solution of either the electrolyte in the commercial amperometric sensors or the use of a reference electrode in the methods from the literature. New designs of free chlorine sensing have been published in the recent literature, including new materials,<sup>1,2,55,57,61,64,65</sup> new device designs<sup>2,58-60</sup> and innovative protocols.<sup>2,3,56</sup> While these amperometric methods provide good performance, the use of the reference electrode would now be the biggest drawback. The reference electrode is used to maintain a stable potential using a high concentration electrolyte solution within the reference electrode. One example of this solution is 3 M KCl. Over time, the concentration of the KCl will decrease due to diffusion into

the test solution, so the KCl solution needs to be replaced regularly. To improve the efficacy of the low-cost free chlorine sensing system, a method using PAD without the use of a reference electrode is presented in this chapter.

Specifically, during PAD a pulsed voltage was applied for a short period of time, while measuring the current at the end of each pulse.<sup>89,90</sup> The potentials of the electrodes in PAD were not maintained by a reference electrode. The raw signals were processed. Then, a calibration curve was presented. Subsequently, the mechanism involved was discussed. Lastly discussed were the implications of PAD on aspects such as the reduction of cost and the miniaturization of devices.

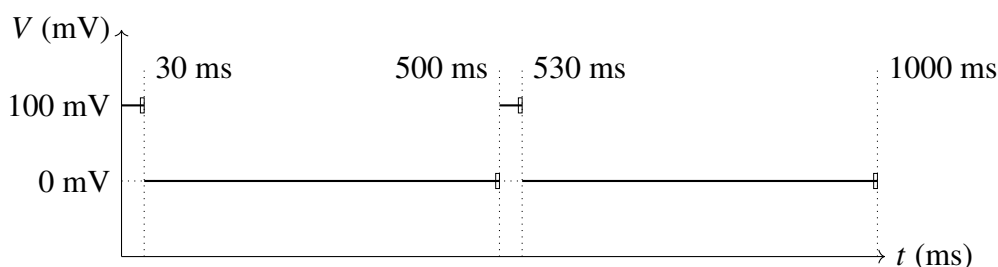
## 5.2 Experimental Details

### 5.2.1 Materials

Unless otherwise noted, all chemicals were purchased from then Sigma-Aldrich and used without further treatment. The modified electrode as in Chapter 2 was used as the working electrode. The counter-reference electrode was an unmodified pencil lead after lab tissue polishing. The testing solution was 0.1 M pH 7.0 sodium phosphate buffer with free chlorine from zero to five ppm. The name of chemicals used in the text indicate their type. Detailed description of chemicals were presented in Chapter 2 Section A.1.1.

### 5.2.2 PAD measurements

EmStat 3 (PalmSens, the Netherlands) is set in PAD mode with the following parameters,  $t_{\text{interval}} = 0.5$  s,  $t_{\text{pulse}} = 0.03$  s,  $E_{\text{pulse}} = 0.1$  V,  $E_{\text{dc}} = 0.0$  V,  $t = 15$  s.



**Figure 5.1:** Artificial stimulation signal for pulsed amperometry. The voltage  $V_1 = 0.1$  V is applied for  $\Delta t_1 = 30$  ms and  $V_2 = 0.1$  V for  $\Delta t_2 = 470$  ms, respectively. Usually, the signal is measured at the ends of both periods of  $\Delta t_1$  and  $\Delta t_2$ , marked using rectangles.

The PAD is shown in Figure 5.1. One certain voltage is applied between the working electrode and counter electrode for m amount of time, followed by another certain voltage applied for n amount of time. At the end of each period, the current is measured. Usually these periods are in milliseconds to seconds, and the shorter period is denoted as the

pulse branch and the longer direct-current branch. The currents are called  $i_{\text{pulse}}$ , and  $i_{\text{dc}}$  respectively. Additionally,  $i_{\text{pulse}} - i_{\text{dc}}$  is called  $i_{\text{diff}}$ .

**Table 5.1:** Nomenclature of a simple PAD

	Branch 1	Branch 2
Time period	Short	Long
Time applied (ms)	30	470
Voltage applied (mV)	100	0
Referred to as	Pulsed	Direct-current
Current	$i_{\text{pulse}}$	$i_{\text{dc}}$

The  $i_{\text{pulse}}$  was reported as the raw signal. The two electrodes were let equilibrate for 45 seconds after 30 seconds of magnetic stirring. The measured range of free chlorine was 0-5 ppm to cover the practical usage range. The average of the last five points in the raw data of each measurement was taken as the reading of a measurement. Measurement of free chlorine was repeated five times at each concentration.

### 5.2.3 PAD data processing

The last five readings in each PAD measurement was averaged as the reading for one measurement. A sample of this signal is shown as Figure 5.2. The means from five measurements were averaged and the mean of the means was used for calibration of instrument response to free chlorine at each concentration. The error bars were calculated standard uncertainty based on the t distribution. The effective degrees of freedom for a concentration were calculated using Welch-Satterthwaite formula (Equation 5.1) of approximation of uncertainty due to the small sizes of sample.<sup>91</sup>

$$\nu_{\text{eff}} = s_{\text{overall}}^4 \left( \frac{s_1^4}{\nu_1} + \frac{s_2^4}{\nu_2} + \frac{s_3^4}{\nu_3} + \frac{s_4^4}{\nu_4} + \frac{s_5^4}{\nu_5} \right)^{-1} \quad (5.1)$$

where  $\nu_i$  is the degrees of freedom in each measurement,  $\nu_{\text{eff}}$  the effective degrees of freedom of the overall measurement and  $s_i$  the sample uncertainty. Then the error bars were then drawn using coverage factors from the t distribution table at a confidence interval of 95% based on the effective degrees of freedom for the measurement of each concentration.

$$U = k_{\text{overall}} s_{\text{overall}} \quad (5.2)$$

where  $U$  is the uncertainty of overall measurements of a concentration at 99% confidence,  $k_{\text{overall}}$  the overall coverage factor at 99% confidence and  $s_{\text{overall}}$  the standard uncertainty of overall measurements of a concentration. The variance of samples as calculated below

$$s_x^2 = \frac{1}{N - \rho} \sum_{i=1}^N (x_i - m)^2 \quad (5.3)$$

where  $x_i$  is the data point,  $N$  the number of data points in a measurement,  $\rho(= 1)$  the number of parameters to determine and  $m$  the mean of measurement.

### 5.2.4 Charging current data fitting

The charging currents in each branch were fitted using a two exponent function<sup>83,92-95</sup> as below:

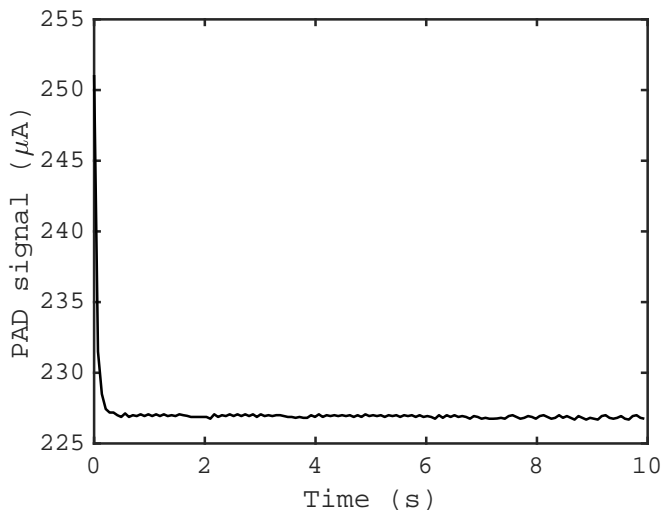
$$i_c = i_1 e^{-\frac{t}{\tau_1}} + i_2 e^{-\frac{t}{\tau_2}} \quad (5.4)$$

where  $i_1$  and  $i_2$  are the coefficients while  $\tau_1$  and  $\tau_2$  are time constants. The initial few data point was discarded based on the rising edge phenomenon.<sup>84,96</sup> The terminal data points were also discarded on the basis that the noise level was much higher than the change towards the end of the measurement.

## 5.3 Results and discussions

### 5.3.1 Analysis of PAD data

Figure 5.2 shows a raw signal of PAD with an initial step decrease and a stable plateau. The response time was less than 1 s. The response is explained in terms of the pulsed reaction and diffusion, and the charging current.



**Figure 5.2:** A sample PAD signal during the measurement, showing an initial steep decrease followed by a relatively long period of stable signal. The response time is less than 0.5 s.

The stable signal is the result of the dynamics of the PAD. The system is assumed to have reached equilibrium after a short period of time since a short pulse is applied followed

by a long period of relaxation of 10 times longer. The disturbance is thus temporary. The expected signal is expected to be stable based on the following qualitative discussions. The rate of reaction depends concentration, i.e. a higher rate of consumption of free chlorine is associated with a higher local concentration. The rate of diffusion depends on the difference in concentration.<sup>85,86</sup> The further away the system is from the equilibrium: a) the less decrease in concentration due to reaction and b) the more driving force in diffusion to increase the concentration. Eventually these rates of opposite effects allow the system to attain a new dynamic equilibrium as represented by the plateau of the later portion in the raw signal of PAD.

The initial decrease was attributed to the charging current.<sup>82-84</sup> The stable plateau was attributed to a new dynamic balance due to pulsed reaction and constant back diffusion. The charging current is reversible, and is a function of time.<sup>83,94</sup> The stable reaction current was dependent on time and initial concentration as explained by the following equation:

$$i_{\text{PAD}} = i_{\text{c}}(t) + i_{\text{r}}(t, c) \quad (5.5)$$

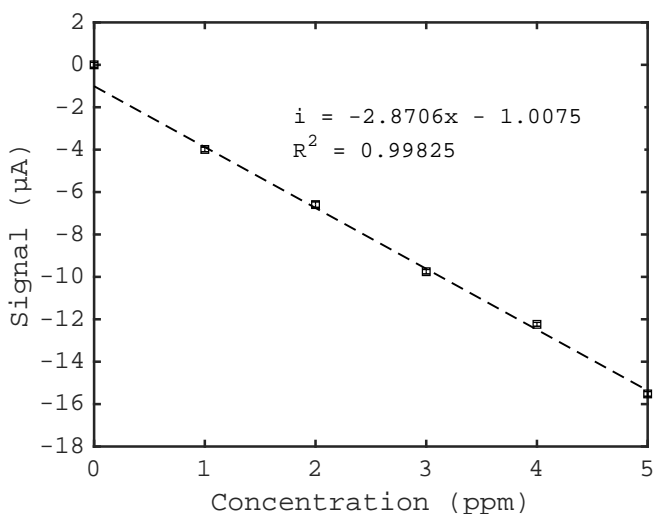
where  $i_{\text{PAD}}$  is the current of PAD measurements,  $i_{\text{c}}$  the charging current and  $i_{\text{r}}$  the reaction current. Thus at a given time point, the signal is a function of concentration only, as demonstrated in the calibration curve in the next section.

### 5.3.2 Sensing of free chlorine using PAD

Figure 5.3 shows a calibration of concentration vs signal difference against a baseline value. The reading in each raw PAD data is the mean of the stable points and the errors have been propagated. The results are a sum of five measurements. The sensitivity was  $-2.8706 \mu\text{A ppm}^{-1}$ . The limit of detection was 0.0414 ppm. A shift away from the calibration curve at zero ppm is observed. It is attributed to the change of surface capacitance by the presence of free chlorine. Previously published results<sup>1,55,57</sup> indicated the presence of free chlorine caused the current to shift to more negative values. This feature can be used to distinguish the absence of free chlorine reliably in a simpler way compared to that used in Chapter 4.

### 5.3.3 The charging current

Figure 5.5 shows the fit of a function of two exponents of charging time constants to the charging current. The fitted function agreed with the experimental result closely on a double log plot. The two time constants are attributed to two capacitances, the Stern layer capacitance and the diffuse layer capacitance, arising from an immersed electrode in aqueous solutions with positively and negatively charged ions.<sup>83,92-95</sup> The capacitance of the Stern layer is due to the compact adsorbed layer marked by the Outer Helmholtz Plane as shown in the diagram in Figure 5.4.<sup>83,92-95</sup> The capacitance of the diffuse layer is due to the movement of ions in the non-uniform distribution of charge near the interface.<sup>83,94,95</sup> Ions in different concentration would shield the electrode differently. The time constant



**Figure 5.3:** PAD calibration curves obtained at 0-5 ppm using five repeated measurements. The error bars signify 99% confidence interval. The zero free chlorine measurement falls off the calibration curve on the opposite direction of the signals, indicating the absence of free chlorine can be qualitatively indicated.

will vary according to the capacitance and resistance. It is possible to model the correlation according to the literature studies.<sup>83,92-95</sup> For this work, the published mechanism supports the reversible charging current to reach a dynamic balance during repeated pulses.

### 5.3.4 Advantages and disadvantages

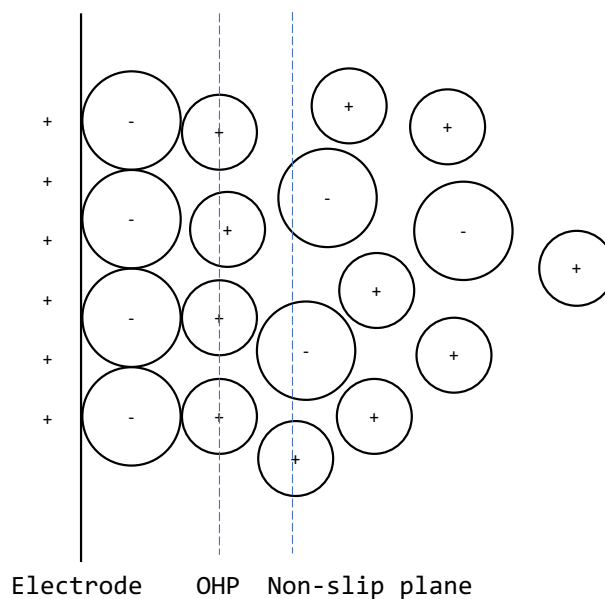
The advantages of PAD include: 1) no consumable chemicals, 2) no regular replacement of the probe solution, 3) no reference electrode used and 4) the ability to detect the absence of free chlorine. The disadvantages include: a) The conductivity of the solution may be required. b) Despite a simple reading, the underlying mechanism is more complex. However, the benefits outweigh the drawback after consideration.

In context of drinking water monitoring, conductivity, which can be used to calculate ionic strength, has long been implemented widely. Using modern technology, it is feasible to integrate multiple measurement units in one device.<sup>3</sup> The maintenance of a conductivity meter does not involve periodic replacement of a working solution as is the case of a reference electrode. Both the cost and size can be reduced towards low-cost device for free chlorine monitoring in drinking water using PAD.

## 5.4 Conclusions

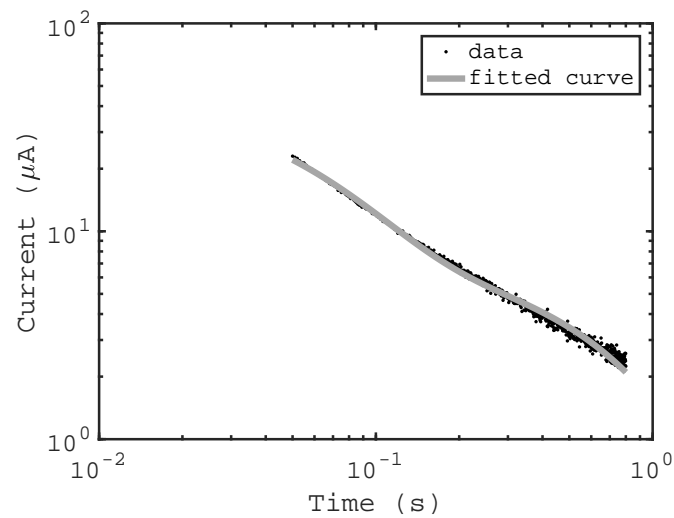
The PAD was successfully used to measure free chlorine concentration with high sensitivity, including the absence of free chlorine. Without using a reference electrode the cost was





**Figure 5.4:** Diagram of the Outer Helmholtz Plane and the Non-Slip Plane of a electrical double layer of the electrode submerged in a solution containing ions. The double layer, to the left of the Non-Slip Plane and the diffuse layer to the right each gives rise to a capacitance.

further reduced and so may be the size. The possibility to integrate PAD in a drinking water quality monitoring system was demonstrated. A conductivity measurement, which may be required depending on water quality, may already be present in such systems. The benefit of not requiring a reference electrode outweighed the extra step to use the sensor. So far, the free chlorine sensor for drinking water quality monitoring can be very low cost: without requirements of consumable chemicals, controlled mixing, reference electrode or commercial hardware as encountered during the development of the sensor. Future work is recommended for the full integration based on the requirements in specific usage cases.



**Figure 5.5:** Sample two-time constant fitting of charging current on a double log scale to expose deviations. The two time constants indicate there are more than the electrical double layer capacitance involved in pulsed stimulation at around 2 Hz.<sup>92-94</sup>

# Chapter 6

## Conclusions and future work

### 6.1 Conclusions

Low-cost easy-to-use free chlorine sensors have been developed. The target usage was the monitoring of water in small and distant communities. After the initial proof of concept, the sensors were refined. The involved mechanisms are investigated. New applications were introduced when possible during the investigation. In addition to research articles, patents have been pursued out of the consideration of novelty of some of the sensor formats. Some promising prospects were recommended based on the understanding gained from this work. The details are summarized by chapter as follows.

In Chapter 1, the drive for this project was analyzed. Modern drinking water is disinfected to prevent diseases, and free chlorine is added to maintain the disinfection. To build confidence in drinking water, the effectiveness of free chlorine needs to be accessible to end users, using low-cost and easy-to-use sensors. The focus of this thesis was determined to be low cost.

In Chapters 2 and 3, a working proof of concept was developed, tested and upgraded for better robustness. The first step to low cost and ease of use was the modification of pencil lead with ammonium carbamate to form a sensing material that did not require consumable chemicals to operate. Then the sensitivity, resistance to increased amounts of interferences, and free chlorine surges were established through repeated rigor tests. At this point, it still requires constant mixing during use.

In Chapter 4, then by studying the mass transport process, the sensor was upgraded to one without the need of constant stirring. Along the way, one new implication from experimental results allowed for the determination of absence of free chlorine. This new function provides a new opportunity for the sensor in free chlorine removal applications, such as in chlorine filters and in the bottling industry. At this point, the sensor still requires a reference electrode.

In Chapter 5, based on the previous findings, and further understanding of the interfacial phenomena, the sensor was upgraded to the pulsed mode using PAD. In this mode, the sensor does not require a reference electrode nor stirring. Moreover, it is still possible

to detect the absence of free chlorine. One caveat emptor here is the dependence of the baseline on conductivity, for which the meter has long been widely implemented. In most cases, the maintenance is easier for a conductivity meter than for a reference electrode. By far, the pulsed sensing scheme is the most useful and advanced state of my research. In the following sections, research contributions and future work are listed.

## 6.2 Research contributions

Table 1.3 lists the major contributions to sensor design features on simplicity, while the major research findings in chapter are as follows. In Chapter 2, there is no requirement of consumable chemicals or regular maintenance of the sensing probe or the use of harsh chemicals or reaction conditions. In Chapter 3, the extensively tested sensor can also work in produce washing industry. In Chapter 4, the requirement of mixing is removed through the study of mass transfer. In Chapter 5, the requirement of reference electrode is removed by using PAD based on the study of reaction-diffusion and interfacial phenomena. Future work on alternative sensing materials using a graphite slab, the low-cost implementable PAD device, low-cost implementation for calculations of Cottrell equation, integration of the sensors in sensing systems. It is also suggested some of the techniques can be used on environmental and health-related research topics.

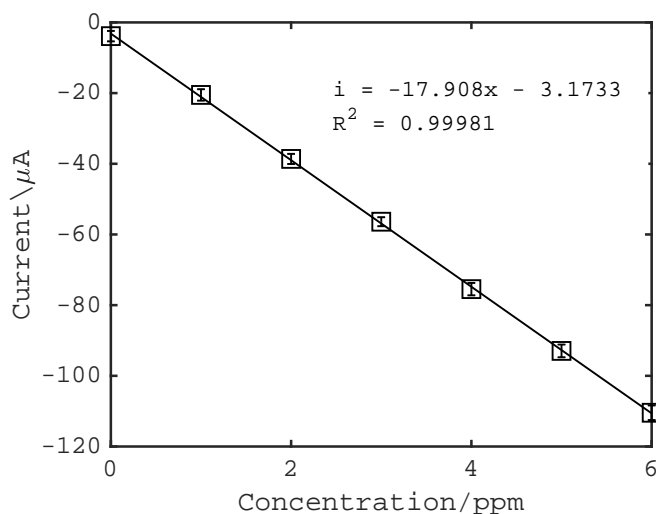
## 6.3 Future work

### 6.3.1 Alternative format for free chlorine sensing materials

Preliminary research on the modification of planar graphite raw material has been successful. The planar graphite was cut into long cuboids and functionalized the same way as in Chapter 2. The resultant response was in agreement with published results in literature.<sup>1</sup> A picture of the modified electrode is supplied as Figure A.3 in Appendix A. The results of the modifications are shown as Figure 6.1. This observation indicates new possibilities of fabrication of working electrodes in planar format for free chlorine sensing. Planar format may allow easier integration with a sensing system, where all sensing electrodes are fabricated on one common planar substrate.<sup>3</sup> Moreover, fabrication of flow cells<sup>56</sup> for tools of analysis may require specific geometry of the working electrode. Using the current modification method, a solution can be passed to a prefabricated device to carry out the modification process.

### 6.3.2 Low-cost implementation of PAD and calculations for Cottrell equation

Preliminary research shows the possibility to implement standalone PAD and Cottrell equation by programming common microcontrollers. This finding allows for miniaturization



**Figure 6.1:** Response to free chlorine using graphite cuboid materials, indicating the wide adaptability of the modification technique in this work. It is possible to modify prefabricated devices containing delocalized  $\pi$  bonds into free chlorine sensing devices.

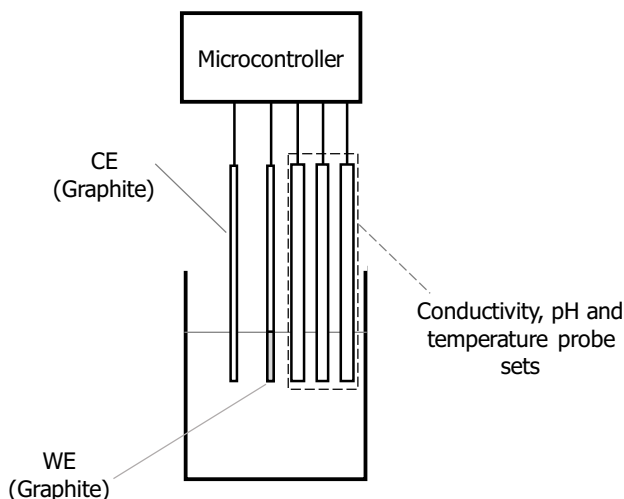
and integration. When only PAD is needed for a dedicated device, such as free chlorine sensing, a microcontroller is capable of generating the voltage pulses as shown in Figure 5.1 in Chapter 5. A custom transimpedance amplifier suitably adjusted for the target current range would convert the raw current signal to voltage. A low-cost, on-chip analog to digital converter can read the voltage, calculate for the reading and communicate the results to the user. In the case of the standalone meter, the results would be displayed on a screen. In the case of an integrated sensor system, the results would be communicated digitally to other devices for further processing. In addition to free chlorine, there are other chemicals undergoing reaction to monitor, such as the glucose concentration in bioreactor effluents.<sup>97</sup> Recent publications on low-cost analytical devices created new interest in the research community.<sup>84,98,99</sup> Task-specific implemented sensors can offer accommodation to constraints of applications, flexibility or reduced cost. The details of integration of these sensors are discussed in the next subsection.

### 6.3.3 Device integration into sensing systems

It has been shown that the current sensing probe can be integrated into a system for water quality monitoring.<sup>3</sup> Because of the open design, additional functionalities can be added for better user experience, such as wireless capability.<sup>4</sup> It is also possible to systematically develop sensing systems for complex analysis.<sup>100</sup>

Because sensing of free chlorine requires pH, temperature and optionally conductivity if using PAD, the ideal layout of the standalone sensor is shown as Figure 6.2.

Single function sensors, if designed to be openly accessible, can form a system of sen-



**Figure 6.2:** Future work: Diagram a complete free chlorine sensing instrument, including free chlorine, and required measurements of pH, temperature and conductivity. The operation, data processing, and communication would all be handled by the microcontroller.

sors to augment each other. For example, in testing free chlorine, information of pH and temperature are required. These requirements are because the pH influences the equilibrium in the reaction of free chlorine, thus influencing the amount of free chlorine of the same addition of sodium hypochlorite stock solution. Temperature influences the reading of pH, and the reaction rate, although to a less degree of the latter. In real applications, the water to measure could range from pH 4.5 to 9.0 as the widest possible range for drinking water applications. The temperature could vary between negative and up to 35 degrees Celsius. Temperature and pH must be taken into account for accurate free chlorine measurement. An example, widely available are the pH correction in commercial free chlorine measurements and the automatic temperature compensation in commercial pH measurements.

The correlation between measurements are governed by their respective chemical formulae, calculation for which may be carried out using a microcontroller. The microcontroller can further operate mechanisms, such as heating, addition of sodium hypochlorite, increasing or decrease the pH using sodium hydroxide or hydrochloric acid solutions, etc. Such sensing and actuating systems would be capable of performing closed-loop operations, for example, maintaining the local free chlorine concentration of a personalized water source in restricted environment, such as in outdoors activities with no reliable source to fresh municipal drinking water. The experience of integration of sensor systems will enable a researcher to adapt the general knowledge for purposes related to other topics of public health.

### 6.3.4 Other sensings in public health

#### *In vivo* transient sensing

Controlled mixing is not feasible in most cases of *in vivo* applications, where the electrodes may be swallowed or pierced into the patient's body. For example, sensors implanted into brain<sup>101</sup> to monitor brain activities may face complex response from the immune system of the body, and the implantable sensor for glucose<sup>102</sup> monitoring will encounter complex, real-time reactions related with glucose metabolism. Some of these electrodes may be microelectrodes<sup>103,104</sup> where mass transfer may be of interest. Using the knowledge from the use of Cottrell equation, as well as PAD, there are possible opportunities to use microelectrodes for *in situ*, *in vivo* to improve the sensing of biological analytes,<sup>105</sup> such as common metabolites, glucose, oxygen, pH and ionic strength as well as electricity, which are related with life processes and may cause disease if out of balance. The integrated sensors may allow for complex sensor arrays for studying complex biological processes.

#### Sensing in environmental settings

Water, soil or air samples may contain molecules of interest in very low concentration that usually requires enrichment before testing.<sup>106,107</sup> PAD may be useful because its high sensitivity has been proven in Chapter 5. The terminal stable reading of a PAD is close to the equilibrium concentration, as compared to orders of magnitude higher reduction in transient technologies. For example, a simple method of collection volatile organic compounds in air indoors may require collecting the sample using water to avoid contamination of air sample, and for the ease of residential use. This enrichment may not enrich the analyte to a very high concentration, where PAD will be generally useful.

It is also possible to discover complex of compounds without *a priori* knowledge about their respective properties. Using an customizable array of sensors, operating in PAD mode, or transient mode or controlled mixing mode, an exploratory preliminary test can generate comprehensive information for later processing. The suitable data processing includes artificial intelligence and data mining. The ability to build sensor arrays on demand would allow the otherwise well developed information technologies to have a sense on the physical variables, possible predict adverse changes in climate and air quality.

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# Appendix A

## Supporting Information

This appendix describes how to make, use and store a pencil lead-based electrode for free chlorine sensing. The fabrication is described in a step-by-step fashion in order to facilitate the reproduction of the sensor. The operations are described using commands of the general form action plus object.

### A.1 Fabrication of pencil lead-based sensor for free chlorine

#### A.1.1 Materials

The chemicals needed are listed in Table A.1. Unless otherwise noted, all chemicals were bought from Sigma-Aldrich (MilliporeSigma since 2015), and used without purification.

#### A.1.2 Methods

##### **Prepare the solution for the modification of the electrode from graphite in pencil lead**

- 1) Measure 2.5369 g of sodium phosphate monobasic
- 2) Measure 4.0949 g of sodium phosphate dibasic
- 3) Put the measure salts in a 500 mL beaker
- 4) Put a magnetic stirring bar in the beaker
- 5) Put the beaker over a magnetic stirrer
- 6) Set the magnetic stirrer on 200 rpm
- 7) Wait until the salt dissolves

**Table A.1:** Materials and chemicals used in the experiments

Name	Item number	Company
Pencil lead	2B, 0.7 × 100 mm	TrueColor, Jiangsu, China
Counter electrode	CHI115	CH Instruments, Austin, TX, USA
Reference electrode (Ag/AgCl)	CHI111	CH Instruments, Austin, TX, USA
pH meter	PHB-600R	OMEGA Engineering Inc., Standford, CT, USA
Disodium phosphate	(S6876-1KG)	Sigma-Aldrich, St. Louis, MO, USA
Monosodium phosphate	(S0751-1KG)	Sigma-Aldrich, St. Louis, MO, USA
Sodium hypochlorite solution	(425044-250ML)	Sigma-Aldrich, St. Louis, MO, USA
Sodium hydroxide	(S5881-500G)	Sigma-Aldrich, St. Louis, MO, USA
Ammonium carbamate	(292834-25G)	Sigma-Aldrich, St. Louis, MO, USA
Potassium chloride	(P127-500)	Fischer Scientific, ON, Canada
Sodium chloride	(S7653-1KG)	Sigma-Aldrich, St. Louis, MO, USA
Sodium thiosulfate	(SX0815-1)	EMD, Mississauga, ON, Canada
Potassium iodide	74210-140	Anachemia, Montreal, QC, Canada

8) Set up a vacuum filtration system by:

- (a) Put a 0.45  $\mu\text{m}$  pore size hydrophilic membrane on the filtre head
- (b) Tighten with two fingers
- (c) Make sure the container is clean, because the liquid will be used later
- (d) Mount the filtre head on the vacuum container

9) Start the vacuum pump

10) Wait for half an hour to let the dissolved gas evaporate

11) Carefully decant the degassed and filtered buffer to a air tight container, such as a bottle

- 12) Wash the filtration system clean
- 13) The resultant buffer will have a pH slightly less than 7.0; adjust the pH to 7.0 using a calibrated pH meter,

**Calibrate the pH meter, PHB-600R (OMEGA Engineering Inc., Stamford, CT, USA)**

- 1) Fill a clean wash bottle with deionized water
- 2) Set pH meter into calibration mode
- 3) Take the probe out of the storage solution by unscrewing the cap
- 4) Carefully wash the probe with a wash bottle
- 5) Put the probe in the standard solution of pH 7.0
- 6) Wait two minutes
- 7) Pressure calibrate button to store the calibration information for pH 7.0
- 8) Take the probe out of the standard solution of pH 7.0
- 9) Carefully wash the probe with a wash bottle
- 10) Put the probe in the standard solution of pH 10.0
- 11) Wait three minutes
- 12) Pressure calibrate button to store the calibration information for pH 10.0
- 13) Take the probe out of the standard solution of pH 10.0
- 14) Carefully wash the probe with a wash bottle
- 15) Put the probe in the standard solution of pH 4.0
- 16) Wait two minutes
- 17) Pressure calibrate button to store the calibration information for pH 4.0
- 18) Take the probe out of the standard solution of pH 4.0
- 19) Carefully wash the probe with a wash bottle
- 20) Leave the pH meter in the pH buffer to adjust

**Adjust the pH of the buffer**

- 1) Stir the pH buffer on a magnetic stirrer
- 2) Add one drop of 0.5 M NaOH solution
- 3) Wait one minute
- 4) Repeat until the pH is 7.0
- 5) Store the NaOH solution in an air tight condition or discard according to safety regulations

**Make the 0.5 M NaOH solution**

- 1) Measure 4g NaOH quickly from the bottle
- 2) Close the bottle tightly each time after taking NaOH from the bottle
- 3) Add water to the 19 mL volume mark
- 4) Mix the solution well
- 5) Complete to 20 mL once all solids dissolve
- 6) Store in an air tight container
- 7) Put the sodium hydroxide bottle back to the chemical storage cabinet

**Make the 0.1 M ammonium carbamate solution**

- 1) Measure 0.7807 g ammonium carbamate
- 2) Put the ammonium carbamate in a 100 mL beaker
- 3) Measure 100 mL water
- 4) Add the water to the beaker
- 5) Put a magnetic stirring bar in the beaker
- 6) Put the beaker over a magnetic stirrer
- 7) Set the magnetic stirrer to 200 rpm
- 8) Wait for the salt to dissolve
- 9) Decant the solution in an air right container
- 10) Clean the balance and spatula

**make the mixture of pH 8.9 ammonium carbamate solution**

- 1) Take a clean beaker of 25 mL
- 2) Add 12 mL ammonium carbamate solution
- 3) Calibrate the pH meter
- 4) Use the newly calibrated pH meter to monitor the pH of the solution
- 5) Put a magnetic stirring bar in the beaker
- 6) Put the beaker over a magnetic stirrer
- 7) Set the magnetic stirrer to 200 rpm
- 8) Slowly add phosphate buffer until the pH is 8.9

**Prepare the pencil lead electrode**

- 1) Polish the pencil lead
  - (a) Wrap the pencil lead with lab tissue
  - (b) Apply pressure 180° across the pencil lead
  - (c) Slide the pencil outward from the wrapping of lab tissue
  - (d) Check the mark of pencil lead on the lab tissue
  - (e) Stop if the mark is almost indistinguishably faded compared to the previous mark
  - (f) Rotate the pencil lead for about 30°
  - (g) Use another location on the lab tissue
  - (h) Repeat polishing one more time
- 2) Wrap the pencil lead with Parafilm to limit the area to expose of the pencil lead electrode

**Set up the electrochemical reaction**

- 1) Pick a prepared lead graphite electrode
- 2) Connect the prepared pencil lead to the terminal for the working electrode on EmStat 3
- 3) Wash the counter electrode
- 4) connect the counter electrode to the terminal for the counter electrode on EmStat 3

- 5) Carefully remove the reference electrode from the storage vial
- 6) Make sure the metal connector is completely dry
- 7) Connect the reference electrode to the terminal for the reference electrode on EmStat 3
- 8) Avoid exposing the reference electrode in the air for prolonged period
- 9) In my experiments, this time was less than a few seconds
- 10) Secure all electrodes inside the beaker
- 11) Make sure there are no electrodes touching the wall of the beaker
- 12) The reference electrode should be close to the working electrode
- 13) The reference electrode should be at least 5 mm away from the top of the magnetic stirring bar
- 14) Add 10 mL blank solution into the beaker
- 15) Make sure the exposed area from the working electrode is fully submerged in the solution
- 16) Start the stirring at 600 rpm

#### **Set the program for EmStat**

- 1) Select amperometric detection (aka chronoamperometry) function
- 2) Set the voltage to 1.0 V (1.1 V in chapters 3,4,5)
- 3) Set the time to 7200 s
- 4) Set the sampling interval to 2 s
- 5) Start the electrochemical reaction
- 6) Take the working electrode out between 7200 s and 7203 s
- 7) Rinse with deionized water
- 8) Discard the solution for modification according to safety regulations
- 9) Store the working electrode in a clean glass vial filled with deionized water

**Measurement of free chlorine**

- 1) Set up the electrochemical reaction
- 2) Set the program for EmStat 3 to use 0.1 V dc potential for Amperometric Detection (also known as chronoamperometry) to collect a data point per 0.5 s
- 3) Start the measurement
- 4) Add 10  $\mu\text{L}$  of free chlorine stocks using a mechanical pipette
- 5) This procedure tests for increasing free chlorine in fixed steps

**Prepare the free chlorine stocks**

**Warning: DANGER!** Free chlorine stocks are high corrosive. Read SDS carefully and remember it, and use proper Personal Protective Equipments. Discard hazardous waste according the safety regulations.

- 1) Dilute the stock around 20000 times and measure the chlorine concentration with DPD colorimetry
  - (a) Add 10  $\mu\text{L}$  of stock into 990  $\mu\text{L}$  of water, and then take 50  $\mu\text{L}$  of diluted stock into 10 mL water to dilute 20000 times
- 2) Test the free chlorine using High Range
- 3) Note the number, e.g. 6.0 ppm
- 4) Adjust the stock solution so that the next dilution measures 5.0 ppm
- 5) Calculate the volume to add by the following mass conservation
- 6)  $\text{Current reading} \times \text{current volume} = \text{target reading} \times \text{target volume}$
- 7)  $\text{Adjustment volume} = \text{target volume} - \text{current volume}$
- 8) Adjust the stock solution
- 9) Measure the free chlorine stock using 20000 dilution
- 10) Proceed if the reading is 5.0 ppm
- 11) Use the stock solution in 10  $\mu\text{L}$  additions. Each addition of 10  $\mu\text{L}$  into a 10 mL beaker results in 1 ppm increase
- 12) Use a 20 mL beaker for 0.5 ppm increase per addition

**Use of DPD colorimetry to determine free chlorine**

1. Add 10 mL of water to the supplied container as a blank sample
2. Measure the blank sample
3. Empty the container
4. Add 10 mL of the solution to test to the container
5. Add one pouch of the DPD free chlorine chemicals to the container
6. Wait for three minutes
7. Measure the free chlorine concentration using the handheld device
8. Clean the container

**Pretreatment of all free chlorine contacting containers**

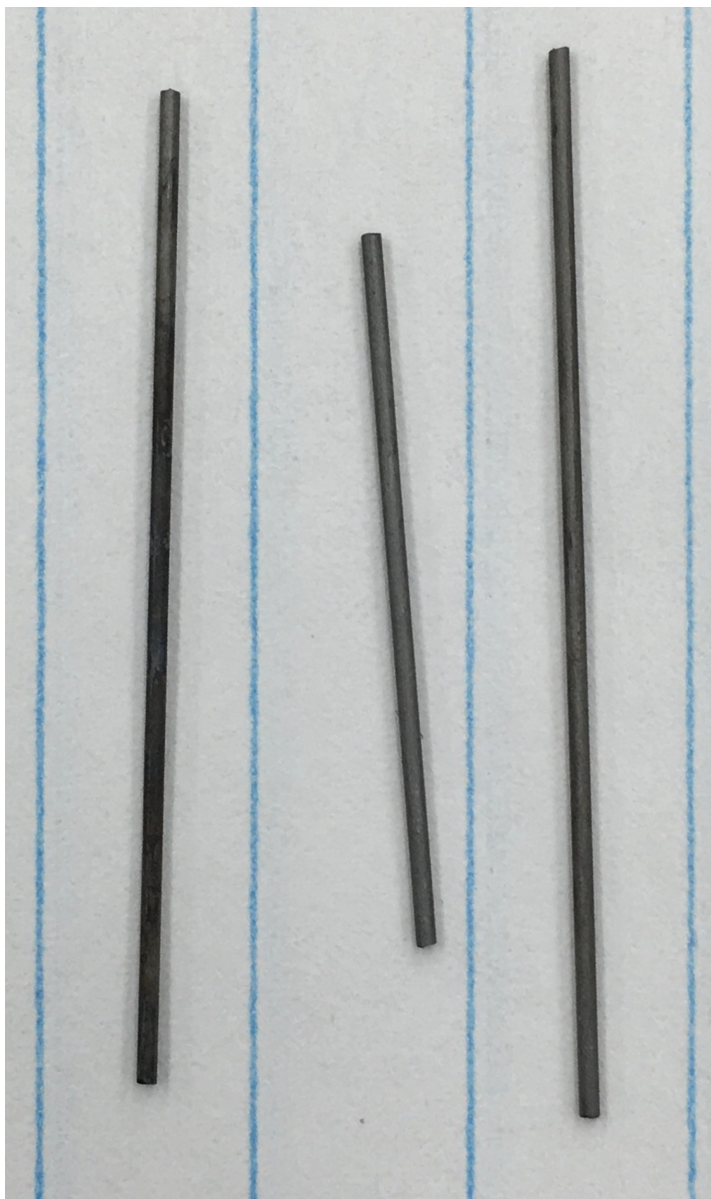
Make free chlorine solution at around 2 ppm and fill the containers to contact free chlorine for 24 hours.

**Measurement of hysteresis**

- 1) Measure for increasing free chlorine in fixed steps to 6 ppm
- 2) Use a preequilibrated pipette to take out 1 mL of test solution from the beaker
- 3) Bring the test solution to its original volume by adding back 1 mL of blank buffer using a clean pipette
- 4) Take notes of the serial number of operations of additions and dilutions
- 5) Calculate the theoretical concentration resulted from each operation
- 6) Plot the concentration reading on the y axis and the theoretical concentration on the x axis to demonstrate hysteresis
- 7) Find the difference on the y axis between the calibration curves, if the calibrations curves have similar slopes

**A.2 Pictures of unmodified, modified electrodes and set of electrodes**

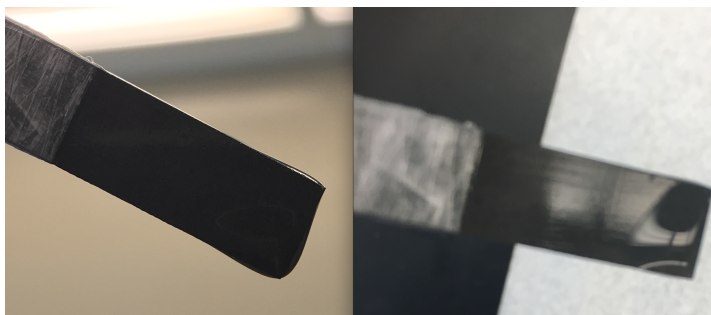




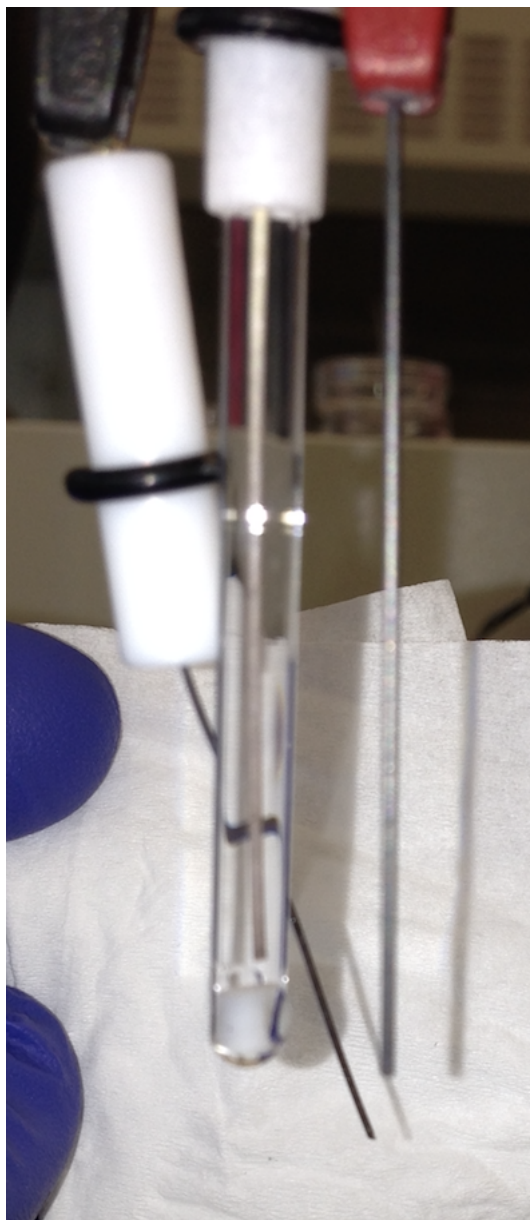
**Figure A.1:** Picture of a modified pencil lead electrode (left) and unmodified ones (center and right). The appearance slightly changed.



**Figure A.2:** Picture of a modified pencil lead electrode wetted and holding water. Unmodified pencil lead would not wet and hold water.



**Figure A.3:** Pictures showing modified graphite cuboid wetted and holding water as seen from different angles. Unmodified ones will not wet and hold water. Due to the dimensions, these pictures show better the wettability than do those of pencil lead electrodes.



**Figure A.4:** A set of electrodes to measure free chlorine: (From left to right) The counter electrode, reference electrode and working electrode. The area of the working electrode is not limited in this example. The depth of dipping will affect the signal.



# Appendix B

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Low-Cost Graphite-Based Free Chlorine Sensor

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