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ABSTRACT

A STUDY OF PLATINUM, PALLADIUM, BISMUTH, COPPER AND SILVER FOR THE POTENTIOMETRIC DETERMINATION OF CHLORINE

by Maria A. Gottwald

This research was undertaken to determine which metals would be suitable to be used as electrodes for the determination of the concentration of chlorine in aqueous solutions at various pH levels. Platinum, palladium, bismuth, copper and silver electrodes were constructed and tested to determine their applicability for measuring the concentration of chlorine in drinking water, waste water treatment plant effluent, and swimming pools. Buffer solutions were used which varied in pH from 7 to 8, and in chlorine concentration from 0 to 10 ppm. In addition, the potential variation over time was observed for each electrode in the solutions.

Platinum, palladium, and copper were found the most appropriate metals for the potentiometric determination of chlorine. The data obtained using these electrodes conformed with Nernstian theory. In addition, the response for palladium appeared to be affected by a variation of pH.

A STUDY OF PLATINUM, PALLADIUM, BISMUTH, COPPER, AND SILVER FOR THE POTENTIOMETRIC DETERMINATION OF CHLORINE

by Maria A. Gottwald

A Thesis Submitted to the Faculty of New Jersey Institute of Technology and Rutgers, The State University of New Jersey—Newark In Partial Fulfillment of the Requirements for the Degree of Master of Science in Environmental Science

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APPROVAL PAGE

A STUDY OF PLATINUM, PALLADIUM, BISMUTH, COPPER, AND SILVER FOR THE POTENTIOMETRIC DETERMINATION OF CHLORINE

Maria A. Gottwald

Dr. Barbara B. Kebbekus, Thesis Advisor Professor of Chemistry, NJIT

Dr. Richard Trattner, Committee Member Date Professor of Chemistry and Environmental Science, Associate Chairperson of Chemical Engineering, Chemistry and Environmental Science, ΝЛΤ

Dr. Kenneth R. Farmer II, Committee Member Associate Professor of Physics, NJIT

Date

Date

BIOGRAPHICAL SKETCH

Author:	Maria A. Gottwald
Degree:	Master of Science in Environmental Science
Date:	January 2000

Undergraduate and Graduate Education:

- Master of Science in Environmental Engineering, New Jersey Institute of Technology and Rutgers, the State University of New Jersey, Newark, NJ, 2000
- Bachelor of Science in Chemistry, Saint Joseph's University, Philadelphia, PA, 1998

Major: Environmental Science

To my family, for their invaluable love and support.

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CHAPTER 1

INTRODUCTION

1.1 Objective

The objective of this research is to determine which metals would be appropriate to use for an array of electrodes for measuring pH and free available chlorine in aqueous solutions. The metals chosen for the initial research were platinum, palladium, bismuth, copper, and silver.

Chlorination is the method most commonly used for the disinfection of swimming pools, drinking water, and wastewater treatment plant effluent. When chlorine is added to water, hydrolysis occurs, according to the reaction,

$$Cl_2 + H_20 \longrightarrow H^+ + Cl_- + HOCl_2$$

and has an equilibrium constant of

$$k = [\underline{H^+}][\underline{Cl}-][\underline{HOCl}] = 4.5 \times 10^{-4}.$$

[Cl₂]

The hypochlorous acid, HOCl, which is a weak acid, dissociates through the reaction

$$HOCI \longleftrightarrow H^+ OCI^-$$

and has an ionization constant of 2.7×10^{-8} .

Hypochlorite salts, such as calcium hypochlorite, are usually substituted for chlorine gas in disinfection, because they are safer and more efficient. Chlorine gas lowers the pH of water, is inexpensive, and is 100 percent available, but is lethal if used inappropriately. Hypochlorite is unstable, slow dissolving, leaves sedimentation, has 65% available chlorine, and raises the pH of water. This is used as a shocking agent in superchlorination. Superchlorination, also known as free residual chlorination, is the process of adding a very large amount of the chlorine product used to provide sufficient chlorine for foreign matter to absorb, with enough left over to oxidize and kill bacteria.[29] The free residual process is implemented by the breakpoint phenomenon. When chlorine is first added to water containing ammonia, the hypochlorous acid initially oxidizes ammonia to form monochloramine, a combined chlorine compound. When more chlorine is added, monochloramine is further oxidized by chlorine and forms dichloramine, and then trichloramine. At this point, when more chlorine is added, the trichloramine is oxidized to simple nitrogen and chloride salt. This is considered the "breakpoint". Any more chlorine which is added to the water would be free chlorine.

The application of calcium hypochlorite for potable water and waste treatment gives the same products as for chlorine gas, according to the equation:

$$Ca(OCl)_2 + 2H_2O \longrightarrow 2HOCl^+ + Ca^{++}(OH_{-})_2$$

The hypochlorite ion (OCI-), hydrolyzes and forms hypochlorous acid. The difference between the addition of chlorine and hypochlorite is the side reaction of the end products. The addition of hypochlorites increases hydroxyl ions by forming calcium hydroxide. The success of the free residual process depends on the pH of the system. Through the addition of chlorine gas, the chlorine and water increase H⁺ concentration by forming hydrochloric acid. A chlorine gas solution of pH 2 to 3 will differ from a hypochlorite solution at pH 11 to 12 at the point of application. More HOCI, an active ingredient, and very active molecular Cl₂ are in low pH chlorine gas solutions. At pH 11-12, however, HOCl is almost entirely dissociated to the ineffective hypochlorite ion. The germicidal efficiency of HOCl is believed to by 100 times more than the OCl- ion. [34]

The chlorine oxidizes the organic material in the water. However, chlorination does not completely oxidize all organic materials to carbon dioxide and water.

Intermediate oxidation products such as chlorinated hydrocarbons may be produced which are hazardous to the health. Trihalomethanes (THMs), such as chloroform, which is carcinogenic, are formed. There must be a balance, in other words, the system should have oxidizing conditions throughout so that septic conditions do not develop, but without excess. [2,27,33] The US Environmental Protection Agency has set the maximum residual disinfectant level for chlorine at 4.0 mg/l, for chloramine at 4.0 mg/l, for chlorine dioxide at 0.8 mg/l, for total trihalomethanes at 0.080 mg/l, and for haloacetic acids at 0.060 mg/l.[35] Residual chlorine monitoring and control for disinfection are needed because chlorine demand varies with water composition. Monitoring for control of pH is also essential because the application of chlorination chemicals tends to change the pH. As mentioned previously, the effectiveness of chlorination is seriously impacted by pH.

An electrochemical thin film microsensor would be useful to determine and monitor the concentration of chlorine and the pH in swimming pools, drinking water, and wastewater treatment plant effluent. A microsensor would be ideal due to its wide applicability and transportability. For example, the microsensor weighs less, has a smaller volume, and has a lower cost of manufacture because there are fewer materials needed than for the larger conventional instruments currently used. [9] Currently, methods used for the determination of chlorine residuals include colorimetry, but this method requires extreme visual differentiation. This method has also been used with spectrophotometers. However, many various chemicals are necessary for such determinations. Many titrimetric methods are currently available, but this as well requires a number of chemicals.[34]

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Continuous chlorine residual analyzers for wastewater chlorination were first used in the 1960s. The initial purpose was to control the chlorination system. The first successful installation on secondary effluents occurred in Napa Sanitary District, in Napa, California. This analyzer contained a motorized filter installed on the analyzer cell sample line.[34]

To be useful for determining chlorine concentration in swimming pool chemistry, the sensor should show a sensitivity to approximately 1.0 ppm free available chlorine, with a range from 0.1 ppm to 10 ppm for superchlorination. Ideally, a swimming pool should have a chlorine residual of 1.0-3.0 ppm and a pH of 7.4 to 7.6.[29]

Four of the five metals chosen for this project were used based on previous experiments found demonstrating their utility in determining either free chlorine concentration or pH. It has been found that bismuth and palladium are useful in measuring pH, but bismuth is sensitive to dissolved oxygen. [11] Platinum has been shown to be sensitive to pH and free available chlorine concentration. [32] Copper has been used in this research based on unusual characteristics demonstrated in preliminary experiments when the copper wire was used to test the reliability of the equipment. Silver is normally used with a silver-chloride film as a reference electrode, so this metal has been studied without the silver-chloride film to observe the results in a chlorinated solution.

1.2 Potentiometric Theory

Potentiometry is a very adaptable analytical method. It can be used to measure a wide range of concentrations without much procedural change. The instruments may be battery powered or automatic for continued monitoring inside a plant or remote location. Such a method can analyze solutions which are colored, viscous, or contain suspended or dissolved ionic or organic solids. The technique can measure a single chemical form without disturbing the equilibria. [21]

The potentiometric method depends upon the relationship between the concentration of the determinand and the electromotive force (e.m.f.) of the electrochemical cell containing the determinand. This relationship is illustrated using the Nernst equation:

$$\mathbf{E} = \mathbf{E}^{\circ} + \mathbf{k} \cdot \log(\mathbf{c})$$

where

E = measured cell potential E° = constant for given temperature c = concentration of determinand k = RT·log10/nF R = gas constant T = absolute temperature F = Faraday's constant n = charge on ionic form of determinand However, for real solutions, $E = E^{\circ} + k \cdot log(a)$

Where a is the activity of species in question, which is related to the concentration by

$$a = cf$$

where f is the activity coefficient.

The activity coefficient is the measure of the interaction of the ion with all the other ions in the cell. The magnitude of the activity coefficient depends upon the total ionic composition of the solution. The total ionic strength is

$$I = 0.5\Sigma c_i z_i^2$$

Where c_i is the molar concentration and z_i is the charge of ith species

The calibration graphs for the ion-selective electrodes are plotted as electromotive force versus the logarithm of the concentration of the determinand, which corresponds to the Nernst equation. This plot may be used to determine E^o and k, where E^o is the standard cell potential.[21]

A chloride or oxide film, however, may form on the electrode surface, which could shift the potential so that the electrode does not demonstrate Nernstian behavior. In this case, the detection limit is determined by the solubility of the slightly soluble chloride or oxide salt formed as the film. When the electrode is placed in the solution, some material dissolves off of the electrode, thus satisfying the solubility product equilibrium. If the concentration of the determinand is greater than that gained by the dissolution, the ratio of e.m.f. to the log (c) is Nernstian. However, as the concentration decreases, the plot of e.m.f. versus log(c) becomes curved, lowering the precision and accuracy.[21]

1.2.1 Formation of Oxide Films

All metals form an oxide layer when in contact with gaseous oxygen. Usually the initial reaction is rapid, but slows when a limiting film of 20-100 Å thick forms. When metal

oxidizes, the films are very strong, coherent, adhesive, and self-repairing after damages occur. They are very protective and form barrier layers. The films conduct electricity only under high potential gradients, but then are passivated, when the exchange currents for the electrochemical processes have fallen to zero.

In some cases, however, oxidation proceeds beyond this stage, when a recrystallization or fracturing process alleviates the strain in the thickening film. For example, in the case of copper, the mechanism for further film growth depends on the ease with which charged particles may permeate the film. Oxygen is dissociatively adsorbed and forms a layer of ions on the outer layer of the film. Electrons from the metal provide the charge. This layer of charge establishes a high potential gradient in the film, and cuprous ions move outward. When the ions reach the outside, the combine with oxide ions to form a new layer of cuprous oxide. The film must possess semiconducting properties to provide the mechanism for extended film growth, which is nonstoichiometric. This cuprous oxide is an oxygen-excess semiconductor.

Oxidation in an aqueous solution with dissolved oxygen proceeds by a similar mechanism or by local cell action. If the air-formed film is nonuniform, then the thicker sections are the sits of cathodic action, where oxygen is used to from hydroxyl ions. On the thinner areas, anodic action sends metal ions into solution. In solution, the metal ions can combine with the hydroxyl ions and form precipitates different from the original oxide film.

A newly plated copper electrode which has been submerged in buffer solutions not containing copper ions has been shown to behave as a copper-cuprous electrode. The electrode responds in the theoretical way to pH from 4.7 to 8.0. However, the electrode potentials deviate positively from the thermodynamic values when the electrode is used in aerated solutions.[11]

Passivation, the hinderence observed from anodic metal dissolution, may occur as a result of oxide layers. Passivation greatly lowers the dissolution of metal when they are in contact with electrolyte solutions. This quality is observed when, during anodic polarization, the potential becomes more positive. This may also occur when the metal is in the presence of oxidizing agents, but is not being anodically polarized by an expternal power source. This phenomenon is observed by a great decrease in the rate of spontaneous dissolution of the metal to solution. Some metals may be made passive when in contact with the oxygen present in air.

Passivation which occurs in solution depends on the composition of the solution, the pH, and anions present. Generally, passivation increases with increased pH, but decreases in extremely basic solutions.

The passive state is caused by factors which initiate the formation of various layers on the metal surface. Many times metals are passivated by a mechanical blocking of an area of the surface by a chemically inert insulating layer. On the other hand, for platinum metal, the electrical double layer is restructured when an adsorbed oxygen layer forms on the surface. The surface potential increases due to the polar nature of the Pt-O bond. The interfacial potential and potential of the ionic electric double layer decrease. The rate of dissolution is reduced by rearrangement of the electric double layer caused by adsorption. Therefore, the passivation of platinum is caused by a redistribution of charges and potential drops in the surface layer.[1]

1.2.2 Reference Electrode

When the working and reference electrodes are in the same solution, it is considered a "cell without liquid junction."[21] The reference electrode should have a known potential which remains constant. The electrode should be insensitive to the components of the solution. An ideal reference electrode would be reversible, would be Nernstian, have a potential which is constant over time, would return to the original potential after being subjected to small currents, and show little hysteresis, or internal friction, due to temperature cycling.[27]

A double-junction reference electrode has been used in this research. In some cases the conventional reference electrode is inappropriate because the electrode would either release ions that interfere with the working electrode or react with another species in the solution. Therefore, the conventional one is separated from the sample solution by another solution with ions compatible with the reference and working halves. [19] The reference electrode chosen for this research was a silver-silver chloride electrode with potassium chloride as the inner filling solution and potassium nitrate as the outer filling solution. In this case, if a conventional silver-silver chloride electrode with potassium chloride solution had been used, the chloride ion would have passed into solution and interfered with the measurement.[13]

1.2.3 Polarization Effect

Polarization occurs if there is a non-linear relationship between the cell voltage and current. The three locations where the polarization can occur are in the electrode itself, on the surface film of the solution immediately adjacent to the electrode, and in the bulk of the solution. There are intermediate steps of the cell reaction which can limit the reaction rate and the size of the current. If the rate of formation or decomposition of an oxidized or reduced species is slow enough to limit current, it is considered reaction polarization. Adsorption, desorption, or crystallization polarization may occur if any of these processes limits the current. If the rate of electron transfer from the electrode to the oxidized species in the surface film or from the reduced species to the electrode occurs is slow, it is considered charge-transfer polarization.

The mass transfer step occurs when the oxidized species moves from the bulk of the solution to the surface film, potentially reducing the reaction rate and current. This step causes concentration polarization, which occurs when the rate of transport of the reactive species to the electrode surface is not great enough to maintain the current needed, and diffusion overvoltage occurs. Overvoltage is the degree of polarization of the electrode, or in other words, it is the difference between the actual electrode potential E and the equilibrium potential E_{eq} . When a potential is applied to the electrode, the surface layer of the solution equilibrates with the electrode. A brief current is generated that brings the surface concentration of ions to the equilibrium concentration c_0 shown by the equation

$$E = E^0 - 0.592/n \cdot \log 1/c_0$$

The current approaches 0 as the concentration of the surface film approaches the equilibrium concentration c_0 . The surface concentration often differs from the bulk of the solution. The surface equilibrium is achieved immediately. However, the equilibrium between the electrode and the bulk of the solution requires minutes to hours to be achieved. A mechanical means, such as stirring, for moving the reactants decreases

concentration polarization. Concentration polarization is more likely to occur at lower concentration of reactants, higher electrolyte concentration, and at an electrode with a relatively small surface area. [26]

However, the electrometer used in this research has possessed very high input impedence and a very low input offset current. These qualities provide measurements which are more accurate than other instruments such as voltmeters, which have too low input impedence.[21] Since the electrometer draws minimal current, the effect of concentration polarization should be minimized.

1.3 Previous Research

1.3.1 Free Available Chlorine Sensors

Various free available chlorine sensors have been developed and investigated over the years. One such sensor is a free-chlorine sensor which detects chlorine in the form of hypochlorous acid. The sensor uses a planar three-electrode electrochemical cell which is covered with a poly(hydroxyethyl methycrylate) hydrogel membrane. The membrane has been photolithographically patterned on-wafer. A diffusion limiting membrane is used for such situations to define the stagnant surface layer in which diffusion is the only process determining mass transfer. Diffusion limiting membranes are used to limit the diffusion of unwanted species to the metal surface. In the study mentioned, the sensors which have membranes of 10 and 50 µg have given a linear calibration between 0.1 - 5 mg/l free chlorine with sensitivities of 2.0 and 0.4 nA(mgL⁻¹)⁻¹ respectively. The sensor is unique in that the entire sensor is on silicon with standard IC-fabrication technique.

The instrument uses thin-film platinum working and counter electrodes. Measurements have been made using cyclic voltammetry.[31]

Another similar sensor has been developed. The sensor is planar silicon based, and also measures chlorine in the form of hypochlorous acid. The sensor uses three electrochemical cells with thin film platinum working and counter electrodes and a thin film partially chloridized silver reference electrode as well. The working electrode, however, is covered by a photopolymerized poly HEMA hydrogel diffusion-limiting membrane. The sensor provides excellent linearity and a sensitivity of approximately 10 nA/(mg chlorine/l), with a detection limit of 1 µg chlorine/l(1 ppb). [32] However, evidence concerning the effect of pH on the previous two determinations has not been reported.

Another instrument developed has been a membrane covered polarographic sensor for dissolved molecules and hydrated halogens. The solid plastic membrane of polyethylene is permeable to aqueous chlorine. The researchers have designed a sensor with a dialysis membrane to be used as an automatic controller for maintaining a constant level of free available chlorine in swimming pool water, with good results. The sensitivity of this instrument to pH has not been reported, however. [4]

Another technique used for determining chlorine has been flow injection analysis (FIA). One such method uses iodometric detection and ion chromatography (IC) with conductivity detection. These techniques have been used to measure chlorite and chlorate in drinking water, with good results. The IC method is not affected by other oxidants including chloramines. The FIA response, however, is affected by chloramines and other oxidants in drinking water, providing inaccurate readings. [7]

12

Other researchers have studied flow-injection amperometry with two polarized platinum electrodes to determine the residual chlorine, based on the oxidation of iodide. The detection limit has been found to be 2 μ g l⁻¹, and a linear calibration has been obtained up to 0.8 mgl⁻¹. [19] A gold electrode has also been used in flow-injection amperometry of chlorine. This method shows a sensitivity of 70 nA μ M⁻¹ for chloramine and 0.2 μ M for hypochlorite. The calibration gives a linear range down to 0.4 μ M for chloramine and 0.2 μ M for hypochlorite. Flow injection, however, requires substantial instrumentation to implement, and this method, as it was studied in the previously mentioned research, has not been reported for the determination of pH. [30]

An optochemical thin-film chlorine sensor has been studied. The sensor is based on an electrochromic thin-film sensing layer over planar waveguides. The sensor, which combines optical technology and electrochemical techniques, gives good results, with a sensitivity below 1 ppm, but its sensitivity to pH has not been reported. [23]

1.3.2 pH Sensors

Sputtered thin-film pH electrodes of platinum, palladium, ruthenium, and iridium oxides have been developed. The technique used is reactive sputtering of platinum, palladium, ruthenium, and iridium metal oxides in an argon-oxygen atmosphere to produce 1 μ m thick electrodes on alumina and silicon. The pH response has been measured from pH 2-11 versus a glass electrode. [15]

Wire palladium-palladium oxide pH sensing electrodes have been found to be useful from pH 3-11, and stable for more than six years with no change in pH response.

The various ways of making pH-sensing electrodes have been studied using monocrystalline or polycrystalline antimony, iridium, and palladium. The methods have been compared by each electrode's preparation, pH response with reproducibility and time response, and the effect of complexing ligands in solutions on electrode response, redox-response of electrodes, and the effects of different oxygen pressures on electrode potentials. [14]

Ruthenium trioxide has been studied as a pH microsensor. The electrode has been fabricated using microlithographic technology for the deposition on a flat surface. The technique has been applied to a thick-film voltammetric sensor. Ruthenium trioxide is found to be a useful electrocatalytic material due to its excellent stability. [21]

Another sensor has been developed which combines pH-sensing capabilities with the ability to detect dissolved gaseous species in water. The sensor uses electrochemically conditioned gas-permeable membranes with optical fiber colorimetricbased pH sensing capabilities. [5]

Even though these aforementioned sensors are ideal for the determination of pH, none have yet been reported for their sensitivity to free available chlorine.

1.4 Thin Film Technology

The proposed microelectrodes would be sputtered thin film devices. Microelectronic solid-state devices are based on material structures generated by thin-film deposition. There have recently been advances in technology, with improved, economical, *in situ* process monitors and measuring parameters. Engineers have a better understanding of

the physics and chemistry of the films, surfaces, interfaces, and microstructure materials, which has led to new applications.[24]

Sputtering is a physical vapor deposition process in which material is transferred from a solid cathode. Positive ions emitted from a rare gas discharge bombard the cathode. The resulting momentum is transferred from the impacting ions to the surface atoms. This sputtering technique is used to deposit most materials. The method is mechanical in nature, and refractory materials can be deposited at temperatures below their melting points. Appropriate substrate materials are alumina, glass, beryllia, or beryllium oxide-based ceramic, aluminum nitride, silicon, and metal.[8]

Copper is an excellent electrical and thermal conductor, and may be evaporated and deposited by sputtering. The material is non-magnetic, solderable, and easily wetted by lead and tin solders. The copper surface must be made passive because the metal oxidizes at low temperatures and does not easily adhere to dielectrics. A SiC inert coating protects the copper from degradation, high temperature, and corrosion. During chemical vapor deposition, nucleating copper to the metal oxide and silicon oxide is difficult due to the difficulty of chemical bonding between the species, which lowers copper adhesion to such surfaces. To improve adhesion, chromium, titanium, niobium, aluminum, or magnesium are used as interface layers. Small amounts of alloying elements may also be added.[8]

Palladium is easily evaporated, and is often used in thin-film technology as a protective layer against surface oxidation of other metals. The metal may be used for the adhesive underlayer of titanium or chromium to glass or ceramic substances. Palladium is electrodeposited from baths based on diamino-dinitro-palladium buffered with ammonium nitrate and sodium nitride. The hardness and resistance of the film is similar to that of gold.

Silver is electrodeposited to 0.1 to 1.5 mm for contacts, switches, and coating bearing surfaces. The electrodeposition is performed in baths based on potassium silver cyanide. High-speed baths are usually used, with a higher silver content, higher pH, and higher temperature. [8]

1.5 Array-based sensing and Pattern-Recognition

Array-based sensing involves four steps. The first is to develop appropriate chemically sensitive interfacial materials. The suitability of the materials depends on their application and the environment in which they will be used. There are a number of factors for deciding which materials would be most appropriate. Some of these factors are the material's thickness and structure, durability, cost, ease of synthesis, and the degree of uniqueness of its response to the analytes. Chemical independence is important. A material is chemically independent when it responds to the analyte in a manner unique from the other materials used for the array. The next step is integrating the materials onto sensor transducers. The third step, which has been explained below, is developing pattern-recognition algorithms. Finally, the entire system must be integrated and packaged.[6]

Chemometrics is a method of studying and analyzing chemical data by using statistics, logic, and mathematics. The goal is to design experimental procedures, provide enough chemical information by analyzing data, and obtain knowledge about chemical systems. The aim of chemometrics is not always obtaining new knowledge, but to gain quality information.[18]

Pattern recognition started as a collection of tools used by the computer to solve classification-type problems in artificial intelligence. Artificial intelligence competes with the human's ability to recognize patterns in two or three dimension. The computer is taught to recognize patterns in large data sets not recognizable by humans. Within a collection of objects with a set of measurements for each object, a property is found or predicted which is not directly measurable. This property would be indirectly related to measurements by an unknown or undetermined relationship. [25]

Pattern recognition uses modern mathematical methods which are based upon multivariate statistics and number analysis to illustrate relationships in multidimentional sets. Because pattern recognition is not affected by human bias, it enhances the extraction of chemical information from chemical data. Interference effects are reduced and there is an improvement in selectivity in analytical measurements. Computerassisted pattern recognition is used if the complexity of information makes data analysis by ordinary means difficult. [28]

Today many researchers use pattern recognition techniques to both quantify and identify analytes on the basis of the multivariate responses of chemical microsensor arrays. Previously obtained array responses of a class category of interest, also called training sets, are used as the chemical identities or concentrations of the analytes. Each sensor provides the response for one of the dimensions of a multidimensional response vector. Each of the array responses is a well-defined geometric location in multidimensional response space.

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There are two advantages in using pattern recognition techniques in microsensorbased chemical sensing. The first is that chemical identification may be accomplished by using only partially chemically selective microsensors rather than highly selective microsensors, which are more difficult to develop. Also, a large number of chemical species may be identified by a small set of sensors. Quite a number of researchers have been combing pattern recognition techniques with sensor array hardware for portable, low-power chemical analysis. The pattern recognition techniques used for such analysis may be feature selection techniques and statistical and non-statistical based methods.[20]

The premise of pattern recognition as it relates to electrochemical sensor array analysis is based on the following:

- 1) The chemical species' and instrument's response are related.
- 2) The chemical species is adequately represented as a set of sensor responses.
- The relation can be discovered between compounds and their responses by applying pattern recognition to a set of tested compounds.
- 4) A relation can be extrapolated to untested compounds from similar cases.[26]

The electrodes in this research have been used to study their response to two parameters—pH and chlorine concentration. Each has provided unique responses to varying pH and chlorine concentration, thereby demonstrating chemical independence. Chemometrics may be used to recognize a pattern throughout the data sets. New information concerning their sensitivity to pH and free chlorine concentration not available otherwise may be generated by pattern recognition. To apply chemometrics, however, one would desire an electrode that varies sufficiently to both pH and chlorine concentration.

CHAPTER 2

EXPERIMENTAL

2.1 Equipment

2.1.1 Electrodes

The platinum electrode used had been previously sealed in glass. About 1 inch of the metal was exposed.

The bismuth electrode was made by first melting bismuth in a covered crucible on a hot plate under a hood. Two inches of the narrow tip of a Pasteur pipette was broken off. Copper magnet wire was sanded to expose approximately two inches on each end. The magnet wire was placed through the wide end of the Pasteur pipette to about two inches from the narrow end. A pipette bulb was expelled of air and placed on the wide end of the pipette. The narrow end was placed in the melted bismuth, and the bulb was released quickly in order to suck the bismuth into the pipette around the magnet wire. The connection was checked carefully to make certain it was secure, and that the glass of the pipette had not cracked from rapid heating and cooling. The narrow end of the electrode was sanded and polished. Super glue was applied to exposed bismuth to ensure a waterproof seal. Small amounts of glue were applied so that enough glue would fill the small space between the bismuth and pipette. The pipette was moved by hand to make sure that enough glue had flowed into the space. When the glue had dried, the end of the pipette was sanded to expose the bismuth again.

The palladium, copper, and silver electrodes were made by the following method. The tip of a Pasteur pipette was broken off. About 3 inches of the metal for the electrode

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was cut and placed through the narrow end of the pipette. The metal was adhered with superglue in the pipette, allowing about one-half an inch of the metal to be exposed.

Magnet wire was soldered to the other end of the palladium, silver, and platinum electrodes.

The reference electrode used was a double junction Ag-AgCl electrode. The inner filling solution was saturated AgCl. The outer filling solution was 10% KNO₃. The electrode solutions were replaced as necessary. The electrode was stored in deionized water when not in use.

2.1.2 Circuitry

Twelve holes large enough to hold BNC connectors were drilled in the top of aluminum box. A grounded BNC connector was placed in each hole. On the side of the box holes were drilled for a triaxial connector and a 12-position switch. Each was placed in the appropriate hole and a knob was placed on the outside of the box on the switch. Eleven of the twelve BNC connectors were connected to the switch with insulated copper wire. These were labeled 1 through 11. The corresponding locations around the knob were also labeled 1 through 11. The common of the switch was connected to the center contact of the triaxial connector with wire. The twelfth BNC connector, designated for the reference electrode, was connected directly to the side contact of the triaxial connector and was labeled "Reference."

Each six-foot RG-58 BNC cable was cut in half. Approximately 2 inches of the black outer insulation was stripped off. The shielding wires were pulled back and insulated with masking tape. The insulation around the center wire was stripped to
approximately one-half to three-quarters of an inch. The magnet wire on the electrodes were looped and soldered to the inner wire of the BNC cable.

For the reference electrode, a BNC cable was similarly stripped, but instead of directly connecting the electrode to the cable, the inner wires were looped around the screw in an alligator clip. The alligator clip was clipped to the end of the cable from the reference electrode.

A Triaxial cable connected the triaxial connector to the Keithley Instruments Model 617 Programmable Electrometer. Figure 1 illustrates the layout of the circuitry, and Figures 2 through 5 show the equipment used in this research.

2.1.3 Solutions

Buffer solutions were made to pH 7.0, 7.5, and 8.0 with 200-ppm sodium bicarbonate and 0.1 M hydrochloric acid. To determine the pH of the buffer solutions, an Orion Research Ionanalyzer Analog pH meter was used. Calcium hypochlorite was added in varying concentration from 0-10 ppm free chlorine.

2.2 Procedure

2.2.1 Potential Variation with Concentration

100 milliliters of buffer solution was placed in a 250-ml beaker which was over a magnetic stirrer. The beaker was insulated in a Styrofoam container after it was noted that the stirrer was heating up gradually throughout the procedure, in turn changing the temperature of the solution. All measurements were taken at room temperature.



Figure 1 Layout of circuitry

The initial circuitry was constructed to provide a means for rapidly switching from one electrode to another. Originally, all of the electrodes were to remain in solution throughout an entire data set collection. However, it was noted that for most electrodes the potential increased while in solution. Therefore, to obtain the true potential reading without the effect of time, each electrode would need to be removed after each reading. The next method of data collection tested was to remove each electrode from solution and re-immerge in solution of equal concentration without grounding the surface. However, the initial potential for the second immersion was approximately that of the final potential of the first. When the electrode was polished, however, the results were reproducible.

Each electrode was sanded with crocus cloth before the initial measurement was taken, and between consecutive measurements. Bismuth was further polished with notebook paper until its surface was reflective. For each measurement, the electrode was clamped above the stirred solution so the end dipped into the solution. An initial measurement was taken of the buffer solution without the chloride solution. The chloride solution was then added in one-milliliter increments. A measurement was taken after each milliliter was added. Each measurement, except for the measurements for copper, was taken 60 seconds after the electrode was dipped in solution. The measurements for copper when the chloride had been added were taken at the highest potential reading.

All measurements were taken in millivolts. Six measurements were taken for each electrode at each pH.

2.2.2 Potential Variation with Time

A constant potential reading could not be obtained for any of the electrodes. Measurements were taken to illustrate how the potential reading varied over time. Potential readings were taken at the following times: 30, 60, 120, 180, 240, and 300 seconds except for copper. The readings for copper were taken every second for 30 seconds to illustrate how the potential reached a peak. For such data acquisition, the electrometer was set to the recording mode to record a data point for each second. The concentrations that these measurements were taken were 0, 1, 2, 3, and 4 ppm Cl- in buffer solutions of pH 7.0.

2.3 Materials Used

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1.	Calcium hypochlorite, tech, available $CI = 65\%$, Aldrich
2.	Sodium Bicarbonate, powder, Fischer Chemical
3.	Super Glue Gel, CVS®
4.	Bismuth, 99.999% Shot, Matheson Coleman & Bell
5.	Palladium, wire, 1.0 mm diam., 99.9%, Aldrich
6.	Silver, wire, 1.5 mm. diam., 99.99+%, Aldrich
7.	Platinum, wire, 1 mm. diam., unknown source
8.	Enamel-coated Magnet Wire, 22 ga., Radio Shack
9.	Programmable Electrometer, Keithley Instruments Model 617
10.	Hot Plate, Thermolyne Sybron Corp., Type 1900
11.	Ionanalyzer, Analog pH meter, model 399, Orion Research

- 12. Reference Electrode, Double- Junction, Orion Model 90-02
 - a) d/j ref. electrode, inner filling solution, 90-00-02, saturated with AgCl
 - b) d/j ref. Electrode, outer filling solution, 90-00-03, 10% KNO₃
- 13. Utility Case, 0.040 in. aluminum, 6.0 x 3.0 x 3.0 in., Hammond Manufacturing
- 14. 12 Positions, 1 pole Rotary Switch, Rating: 0.3 A 12 V AC, Type: Shortening, Mounting Hole = 0.375", GC
- 15. 52-Ohm, RG-58 BNC RF Cable Assembly, 6 ft., Radio Shacka) BNC Connectors
- 16. Magnetic Stirrer, Precision Scientific





Figure 3 Equipment set-up. Left to right: beaker in styrofoam, utility box, electrometer.



Figure 4 Reference electrode (left) and working electrode (right) in buffer solution.



Figure 5 Close-up of utility box and electrometer.

CHAPTER 3

RESULTS

The tables located in this chapter display a summary of the results for each type of electrode. The results in the table displaying the linear regression equation and least squares for the electrodes at each pH were obtained through the calibration plots located in Appendix B. These calibration plots were obtained by plotting the data displayed in Appendix A. These tables display each data point, averages for each concentration of free chlorine, and the standard deviation at each concentration. The tables displaying the variation in potential over time illustrate the magnitude of potential change at each concentration from the first data point taken at 30 seconds, to the last data point collected, at 5 minutes, or 300 seconds. These tables are also located in Appendix A, with the plots located in Appendix B.

3.1 Platinum

Table 1 Linear regression equation and R^2 for platinum.

pН	Equation	R^2
7.0	y = 268.65x + 23.298	0.9692
7.5	y = 220.94x - 2.5861	0.9092
8.0	y = 238.12x + 10.675	0.9731

 Table 2
 Time-potential variation for platinum.

[Cl ₂](ppm)	Δ potential from 30 seconds to 5 minutes
0	127.6
1	166.81
2	156
3	171
4	163.19

The calibration plots for the platinum electrode showed somewhat Nernstian behavior and a large slope. The response does not appear to be affected by a change in pH. The standard deviation is relatively high. The potential for the platinum electrode increased rapidly over 5 minutes. Within this time, equilibrium had not been achieved, but the slope decreased.

3.2 Palladium

Table 3 Linear regression equation and R^2 for palladium.

pН	Equation	\mathbf{R}^2
7.0	y = 192.35x + 488.32	0.9144
7.5	y = 227.61x + 425.83	0.9594
8.0	y = 152.75x + 433.99	0.8798

 Table 4 Time-potential variation for palladium.

[Cl ₂](ppm)	Δ potential from 30 seconds to 5 minutes
0	27
1	235.1
2	339.3
3	263.9
4	179.3

The calibration plots for palladium demonstrate Nernstian behavior with a large slope.

The response appears to be affected by changing pH, the potential decreasing with increased pH. However, the standard deviation is relatively high. The potential of palladium increases rapidly within the 5 minutes. Within this time, equilibrium had not been achieved, but the slope somewhat decreased.

3.3 Bismuth

Table 5 Linear regression equation and R^2 for bismuth.

pН	Equation	R^2
7.0	y = 17.113x - 270.59	0.6128
7.5	y = 38.395x - 272.76	0.7955
8.0	y = 61.076x - 282.57	0.9407

 Table 6
 Time-potential variation for bismuth.

[Cl ₂](ppm)	Δ potential from 30 seconds to 5 minutes
0	9.6
1	24.6
2	44.4
3	75
4	118.87

The calibration plot for the bismuth electrode varies in demonstrating Nernstian behavior. The plot for pH 7.0 is not linear. At pH 7.5 and 8.0, the linearity increases, and R² improves. The slope of each plot is low, but increases with increased pH. The standard deviation is lower than that of platinum and palladium. The time vs. potential plot, however, shows that the potential changes very little. The degree of change appears to depend upon the concentration of chlorine in the solution, increasing with increased concentration of chlorine. In all cases, though, the potential increases over time.

3.4 Copper

Table 7 Linear regression equation and R^2 for copper.

pН	Equation	R^2
7.0	y = 46.183x + 15.489	0.9472
7.5	y = 31.297x + 30.753	0.8713
8.0	y = 34.388x + 33.859	0.9831

The calibration plot for copper demonstrates Nernstian behavior with a linear trend, but the slope is small. The result does not appear to be affected by pH. However, the change of potential when the electrode is in a solution which contains chlorine differs from that of other electrodes used in this research. The potential of copper in buffer solutions without chlorine initially increases, then reaches equilibrium at 3 minutes (180 seconds). However, when the chlorine is added to the solution, the behavior changes. The potential increases rapidly but briefly, reaches a peak, and then decreases. Over time, the slope decreases. With increased chlorine concentration, the potential of the peak increases according to Nernstian theory, as stated above.

3.5 Silver

The calibration plot for silver does not demonstrate Nernstian behavior. The plot for pH 7.0 shows a positive slope initially. At levels above 6 ppm chlorine, the potential does not change with increased concentration of chlorine. The plot for pH 7.5 is similar, the potential becoming constant above 4 ppm chlorine. For pH 8.0, the slope is negative, but all the readings are within close range. The potential for silver does not change drastically over time.

CHAPTER 4

DISCUSSION AND CONCLUSION

4.1 Discussion

Platinum, palladium, and copper appear to be the most appropriate metals for the potentiometric determination of chlorine. These results agree with previous research performed on platinum for such determinations, which had provided evidence that the response would be Nernstian. However, the results for platinum and palladium had a high standard deviation, indicating low reproducibility. The slope of the linear regression equation of the calibration plot was the highest for platinum and palladium, a factor which is favorable for the use in potentiometric determination. Even though the plot of the calibration for copper was relatively linear, the slope was lower than that for platinum and palladium. However, the standard deviation for data for this electrode was low.

Platinum and copper do not respond well to various pH levels, in contrast to palladium, which gives a lower potential for higher pH. The response for palladium in chlorinated solution was previously unknown, but the data obtained in this research showed that palladium does respond well to various concentrations of chlorine. The calibration plot illustrates that palladium gives a Nernstian response. The palladium electrode was expected to respond to varying pH. The data obtained agrees with this evidence.

The response for copper was previously unknown for the determination of chlorine and pH. However, the data obtained in this research shows that copper behaves in a Nernstian manner when used in chlorinated solution. The response is very reproducible, as indicated by the low standard deviation. The trend of the response over

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time, however, varied from that of the other electrodes used in this research. The peak obtained was most likely caused by the growth of a film formed by the combination of copper and chlorine. The potential of the peak, however, varied with chlorine concentrations in a Nernstian manner. The copper electrode did not respond to varying pH.

The bismuth electrode did not respond in a Nernstian manner. The results were more reproducible than for platinum and palladium. Bismuth was expected to respond to pH, but the data obtained in this research does not provide evidence of this behavior. However, the change of the potential over time was small, even less than the other electrodes used in this research. This result was unexpected because the amount of exposed bismuth metal had a smaller surface area than that of the other metals. Previous theory concerning such a quality states that the change would be greater for electrodes with a smaller surface area.

The silver electrode behaved in a non-Nernstian manner. Silver is normally used as the base of a reference electrode for such research. Usually the metal is coated with a silver chloride layer. The potential change with varying concentrations of chlorine gave unusual results. The potential increased with increased chlorine concentrations at low concentrations, then became constant. This result was expected. This response was most likely due to the formation of a film of silver chloride, creating a silver-silver chloride electrode. If this theory were true, the response indeed would have been constant with varying concentration and time. The silver electrode did not respond to varying pH.

4.2 Summary

In summary, the platinum, palladium, and copper electrodes showed Nernstian behavior with varying free chlorine concentration. The slopes of platinum and palladium were higher than that of copper, but the standard deviations were higher. Palladium is the only electrode used that was effected by a change in pH. Copper and silver most likely form a film on the metal surface with chloride ions. The formation of this film causes the potential of the copper electrode to reverse direction at a point in time, while this quality causes the potential of the silver electrode to become constant with varying concentration of free chlorine. Bismuth does not show Nernstian behavior.

If one were to apply chemometrics to the information provided by the data, one would expect that the palladium electrode would provide the most useful information, due its response to both pH and chlorine concentration. Silver, on the other hand, does not respond well to either parameter. However, this information would be useful in investigating silver's suitability for use as a reference electrode in similar determinations. Copper and platinum have provided some useful information for their response to chlorine concentration, but not for the determination of pH.

However, each electrode has responded to the two parameters in unique manners, each demonstrating chemical independence, which is an important factor in determining materials for use in an array. More similarities and differences most likely exist within the various responses of the electrodes. Through the use of computer-assisted chemometrics, future researchers may uncover new information and relations between the electrodes and parameter not obvious to the author presently.

4.3 Future Research

The irregular response of bismuth may have been due to the different manner in which the electrode was constructed. In the future, researchers should attempt to construct such electrodes in a similar fashion as the others used. Perhaps researchers could form a bismuth rod and adhere this in glass. Also, further research may include introducing interferents, such as oxygen, into the solutions. Some attempt should be made to construct and test thin films of palladium, platinum, and copper in chlorinated solutions. Research may be performed to improve the surface of such metals. A diffusion-limiting membrane over the bare metal surface may alleviate the drifting of potential over time. Also, other various metals and metal-oxides, such as palladium, iridium, and ruthenium oxide, that have been useful as pH sensors, may be studied to investigate their response to varying chlorine concentration. As previously mentioned, future researchers may obtain new information and recognize new patterns throughout the various responses of each of the electrodes through the use of chemometric, and apply these to their use in a microsensor array.

APPENDIX A

TABLES OF DATA FOR POTENTIAL CHANGE WITH CONCENTRATION

[Cl 2](ppm)	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	average	st. dev.
0	-152	-160	-125	-132	-114	-192.7	-145.95	28.544
1	79	16	69.89	-29.66	-13	90	35.3717	51.036
2	103	154	42.12	8.14	124	116	91.21	54.921
3	145	188	20.56	119	137	179	131.427	60.208
4	214.6	219.6	202.2	189	185	218.8	204.867	15.228
5	258.4	235.8	137	150	175	280.5	206.117	60.07
6	310.5	215.5	246.6	246.2	171	313	250.467	54.928
7	179	241.3	187.94	230.8	232.5	321.7	232.207	50.763
8	291.1	318.9	210.9	271.5	202.4	321.9	269.45	52.14
9	158	330	320.8	269.3	188	347.9	269	79.387
10	251.8	320	350.6	350.4	227.5	330.4	305.117	52.625

Table 8 Potential for platinum electrode at various Cl- concentrations in pH 7.0buffer solution.

Table 9Potential for platinum electrode at various Cl- concentrations in pH 7.5buffer solution.

[Cl 2](ppm)	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	average	st. dev.
0	-90	-204.6	-68	-65	-215.2	-210.1	-142.15	74.865
1	10	-73	58	26	-6.22	-25	-1.7033	44.978
2	7	-3	120	109	52.84	16	50.3067	53.296
3	59	63	188	189	121	60	113.333	62.752
4	134	88	241.3	246.2	54	78	140.25	84.285
5	199	159	261.5	237.2	69	45	161.783	88.624
6	283	201	246.6	152	101	113	182.767	73.422
7	290	185	163	148	155	72	168.833	70.681
8	227.6	241.4	161	147	127	78	163.667	61.803
9	223.1	243.2	167	123	103	240.6	183.317	61.327
10	190	250.3	124	126	205.4	669.7	260.9	206.05

[Cl 2](ppm)	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	average	st. dev.
0	-98	-136	-81.52	-189.2	-248.7	-202.8	-159.37	65.006
1	-40	9.72	40	58.13	-29	11	8.30833	38.004
2	35	110	114	73	85.44	81.07	83.085	28.648
3	67	100	148	165	132	125	122.833	35.04
4	122	167	171	159	142	190	158.5	23.772
5	355.4	177	165	166	171	145	196.567	78.555
6	166	228.4	161	187	162	204.3	184.783	27.298
7	119	253.5	206.7	244.8	147	189	193.333	53.176
8	240.9	267.1	196	290.7	205.5	220	236.7	36.788
9	203.3	259.9	103	286.2	240	240.6	222.167	64.403
10	292.6	284.4	149	294.2	271.1	283.6	262.483	56.2

Table 10 Potential for platinum electrode at various Cl- concentration in pH 8.0 buffer solution.

Table 11 Potential for palladium electrode at various Cl- concentrations in pH 7.0buffer solution.

[Cl 2](ppm)	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	average	st. dev.
0	202.5	188	189.75	182	45	153	160.042	58.708
1	542.2	549.6	521.3	433.8	234.5	433.7	452.517	118.69
2	623.4	635.4	588.6	600	406.8	569	570.533	83.676
3	666.4	658	626.5	610.5	443.4	600.1	600.817	81.37
4	673.4	656.8	621.7	633.3	499.3	623.7	618.033	61.554
5	691	690.3	649.7	657.5	532.4	558.8	629.95	67.966
6	678.9	684.7	667.9	671.8	519.9	633.7	642.817	62.797
7	680.8	689.6	673.1	663.8	605.7	615.2	654.7	35.445
8	687.5	685.8	679.9	662.8	549.1	647.4	652.083	52.739
9	702.2	699.9	670.8	688.2	556.8	657.1	662.5	54.6
10	705	697.5	680.8	659.5	572.7	650.4	660.983	48.108

[Cl 2](ppm)	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	average	st. dev.
0	186	184	153	127	139.8	37	137.8	54.717
1	498.8	486	466.4	403.4	427.3	258.5	423.4	88.386
2	572.9	555.8	396	473.4	514.4	327.8	473.383	95.458
3	600.1	604.6	514.2	540	554	425.3	539.7	66.034
4	614.4	613.5	569.5	576.9	519.5	591.8	580.933	35.27
5	634.4	650	530.1	536	607.3	605.3	593.85	50.04
6	653.9	634.6	606	663	571.7	593.3	620.417	35.922
7	673.4	653.8	663	625.4	592.9	586.9	632.567	36.755
8	660.7	659.3	620.6	588	596.9	584	618.25	34.746
9	673	630.8	636.2	637.1	624.3	605.3	634.45	22.191
10	674.3	644.9	652.6	627.8	633.5	573.3	634.4	34.091

Table 12 Potential for palladium electrode at various Cl- concentrations in pH 7.5buffer solution.

Table 13 Potential for palladium electrode at various Cl- concentration in pH 8.0buffer solution.

[Cl 2](ppm)	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	average	st. dev.
0	188	172	153	129	68	50	126.667	56.277
1	499.7	444	332.8	375.6	430.3	436.8	419.867	58.123
2	573.3	560	499	367.7	460	460.5	486.75	75.61
3	590	606.1	530	383.5	500.3	525.1	522.5	79.274
4	606.1	632.2	478	459.9	520.4	524.7	536.883	68.833
5	626	653.3	412.3	487.6	562.7	580.7	553.767	89.8
6	632.5	652.8	557.6	498	592	391.1	554	97.008
7	659.9	654	449	491.1	454.2	470.8	529.833	99.573
8	643.6	668.8	464	560.6	497.5	473.3	551.3	88.331
9	668.3	666.1	649.2	453.6	509.7	509.7	576.1	95.675
10	680.7	673.6	681.9	603.5	536	489.5	610.867	82.761

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[Cl 2](ppm)	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	average	st. dev.
0	-300.8	-250.3	-235.2	-282.8	-300.3	-304.3	-278.95	29.413
1	-289.3	-247.7	-213	-290.9	-297.1	-298.8	-272.8	34.849
2	-271.7	-246.3	-190	-284	-289.4	-283.8	-260.87	38.018
3	-264.7	-246.4	-222.8	-287.7	-281.3	-283.4	-264.38	25.472
4	-264.1	-233.8	-217.1	-284.4	-277.5	-278.8	-259.28	27.552
5	-261.1	-218.1	-223.4	-276.9	-275.6	-277.5	-255.43	27.592
6	-254	-223.5	-227.3	-282.8	-279.2	-282.8	-258.27	27.669
7	-257.2	-229.6	-222.2	-280.8	-279.9	-276.6	-257.72	26.206
8	-264.6	-232	-228.2	-287.1	-281.4	-286.8	-263.35	27.054
9	-252.1	-242.1	-224.6	-276.5	-277.7	-260	-255.5	20.494
10	-262.2	-226.6	-153	-279	-278.3	-277.1	-246.03	49.774

Table 14 Potential for bismuth electrode at various Cl- concentrations in pH 7.0buffer solution.

Table 15 Potential for bismuth electrode at various Cl- concentrations in pH 7.5buffer solution.

[Cl 2](ppm)	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	average	st. dev.
0	-290.2	-299.1	-273.6	-295.4	-308.1	-315.5	-296.98	14.603
1	-280.2	-292.9	-268.3	-287	-280.8	-282.5	-281.95	8.2026
2	-279.2	-216.6	-260.1	-232.5	-283.6	-269.2	-256.87	26.8
3	-217.9	-220.2	-260.6	-260.4	-236.4	-273.1	-244.77	23.209
4	-219.5	-220.2	-247.9	-259.2	-251.9	-268.8	-244.58	20.437
5	-227.2	-245.5	-243.2	-276	-260.7	-265	-252.93	17.608
6	-206.6	-214.2	-245.1	-253.3	-257.7	-250.2	-237.85	21.789
7	-224.1	-220	-238	-251.9	-238.8	-257.1	-238.32	14.665
8	-219.7	-209.8	-231.9	-237.4	-268.8	-268	-239.27	24.522
9	-215.3	-208.5	-225.7	-231.3	-274.1	-278.7	-238.93	30.12
10	-217.4	-213.5	-227.9	-230	-276.1	-277	-240.32	28.744

[Cl 2](ppm)	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	average	st. dev.
0	-285	-296	-279.5	-346.4	-352.5	-320.4	-313.3	31.386
1	-261.1	-296.9	-248.7	-291.1	-306.5	-290.5	-282.47	22.458
2	-255.4	-274.6	-234.3	-308.8	-258.9	-283.9	-269.32	25.799
3	-207.2	-284.8	-227.7	-265.2	-266.7	-279.6	-255.2	30.868
4	-215.8	-278.1	-219.6	-267.1	-193.3	-253	-237.82	33.194
5	-207.5	-275.1	-223.6	-229.6	-232.2	-247	-235.83	23.113
6	-235.8	-272.9	-200.4	-207.6	-220.9	-241.8	-229.9	26.359
7	-223.3	-271.1	-236.7	-241.5	-227.7	-203.2	-233.92	22.551
8	-227.1	-254.6	-225.2	-226	-220	-259.2	-235.35	16.932
9	-207.4	-234.4	-213	-212.6	-210.1	-256	-222.25	19.149
10	-219.3	-238.8	-213.2	-206.2	-211.1	-249.6	-223.03	17.267

Table 16 Potential for bismuth electrode at various Cl- concentrations in pH 8.0buffer solution.

Table 17 Potential of copper electrode at various Cl- concentrations in pH 7.0buffer solution.

[Cl 2](ppm)	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	average	st. dev.
0	-61	-75.36	-79.66	-81.91	-83.77	-84.19	-77.648	8.7736
1	21	18	18	24	29	14	20.6667	5.2789
2	45	24	16	11	14	21	21.8333	12.287
3	50	35	31	34	30	33	35.5	7.3417
4	57	48	45	45	42	39	46	6.1968
5	64	46	50	39	46	46	48.5	8.3845
6	67	37	49	47	47	48	49.1667	9.7656
7	72	54	52	55	49	50	55.3333	8.4774
8	72	55	61	52	58	55	58.8333	7.1391
9	79	60	60	55	56	58	61.3333	8.8919
10	81	57	57	58	54	57	60.6667	10.053

[Cl 2](ppm)	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	average	st. dev.
0	-81	-39	-80.35	-107	-110	-110	-87.892	27.704
1	79	50	18	3	3	0	25.5	32.192
2	93	72	36	15	16	15	41.1667	33.666
3	97	85	41	26	21	21	48.5	33.94
4	97	96	35	34	34	33	54.8333	32.283
5	105	101	39	35	32	32	57.3333	35.489
6	97	90	46	36	36	41	57.6667	28.09
7	90	82	47	39	36	35	54.8333	24.637
8	83	75	60	39	34	34	54.1667	21.646
9	78	86	64	38	38	41	57.5	21.483
10	82	89	72	44	38	43	61.3333	22.304

Table 18 Potential of copper electrode at various Cl- concentrations in pH 7.5buffer solution.

Table 19 Potential of copper electrode at various Cl- concentrations in pH 8.0buffer solution.

[Cl 2](ppm)	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	average	st. dev.
0	-81.81	-82	-84	-78	-81	-80	-81.135	2.0272
1	38	33	35	31	28	26	31.8333	4.446
2	58	57	54	38	36	33	46	11.507
3	55	62	54	43	44	44	50.3333	7.8145
4	68	68	65	48	46	48	57.1667	10.852
5	69	64	55	55	46	52	56.8333	8.3287
6	76	58	66	53	55	55	60.5	8.8713
7	77	75	66	57	50	54	63.1667	11.268
8	73	72	66	63	62	58	65.6667	5.8878
9	76	7 1	71	65	52	57	65.3333	9.2232
10	75	76	70	62	64	57	67.3333	7.5807

[Cl 2](ppm)	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	average	st. dev.
0	92.6	40.68	38.48	-4.08	-10.35	-17.93	23.2333	42.23
1	21.46	39.91	40.34	25.87	51.09	31.77	35.0733	10.85
2	68.3	91.25	115	100.36	21.69	18	69.1	41.071
3	124	120	133	133.79	137.28	123	128.512	7.0437
4	39	50	44	112	137	135	86.1667	46.791
5	134	136	136	136	133	93	128	17.193
6	140	141	139	139	135	130	137.333	4.1312
7	142	139	137	137	138	137	138.333	1.9664
8	139	138	137	137	135	137	137.167	1.3292
9	136	137	136	136	133	138	136	1.6733
10	134	133	133	133	135	135	133.833	0.9832

Table 20 Potential of silver electrode at various Cl- concentrations in pH 7.0 buffer solution.

Table 21 Potential of silver electrode at various Cl- concentrations in pH 7.5buffer solution.

[Cl 2](ppm)	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	average	st. dev.
0	-18.9	-9.03	-19.5	-24.41	-20.9	-38	-21.79	9.4534
1	37.43	40.03	40.58	33.8	34.6	68	42.4067	12.836
2	108	113	126	56.68	50	45.18	83.1433	36.293
3	132	109	82	107	75	131	106	23.866
4	132	133	132	137	133	132	133.167	1.9408
5	133	132	135	131	132	130	132.167	1.7224
6	131	126	133	132	133	130	130.833	2.6394
7	133	133	131	130	131	130	131.333	1.3663
8	132	130	128	129	128	128	129.167	1.6021
9	128	129	130	128	130	129	129	0.8944
10	129	129	128	127	129	128	128.333	0.8165

[Cl 2](ppm)	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	average	st. dev.
0	116	113	111	109	103	96.4	108.067	7.1907
1	162.56	155.47	155	159	158	155	157.505	2.9908
2	159	156	155	154	154	157	155.833	1.9408
3	158	158	156	155	157	155	156.5	1.3784
4	153	152	150	151.3	151	153	151.717	1.1839
5	151	150.9	150.7	148	152	151	150.6	1.352
6	151	150	149.7	150	152	152	150.783	1.04
7	151	150.7	149	149	151	150	150.117	0.939
8	150	149	150	148	150	153	150	1.6733
9	153	150	150	151	1 49	147	150	2
10	151	149	148	150	150	146	149	1.7889

Table 22 Potential of silver electrode at various Cl- concentrations in pH 8.0buffer solution.

APPENDIX B

CALIBRATION PLOTS



Figure 6 Calibration graph for platinum electrode in pH 7.0 buffer solution.



Figure 7 Calibration graph for platinum electrode in pH 7.5 buffer solution.



Figure 8 Calibration graph for platinum electrode in pH 8.0 buffer solution.



Figure 9 Calibration graph for palladium electrode in pH 7.0 buffer solution.



Figure 10 Calibration graph for palladium in pH 7.5 buffer solution.



Figure 11 Calibration graph for palladium electrode in pH 8.0 buffer solution.



Figure 12 Calibration graph for bismuth electrode in pH 7.0 buffer solution.



Figure 13 Calibration graph for bismuth electrode in pH 7.5 buffer solution



Figure 14 Calibration graph for bismuth electrode in pH 8.0 buffer solution.



Figure 15 Calibration graph for copper electrode in pH 7.0 buffer solution.



Figure 16 Calibration graph of copper electrode in pH 7.0 buffer solution.


Figure 17 Calibration graph for copper electrode in pH 8.0 buffer solution.



Figure 18 Calibration graph for silver electrode in pH 7.0 buffer solution.



Figure 19 Calibration graph for silver electrode in pH 7.5 buffer solution.



Figure 20 Calibration graph for silver electrode in pH 8.0 buffer solution.

APPENDIX C

TABLES OF DATA FOR POTENTIAL CHANGE WITH TIME

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Time(sec)	0 ppm	1 ppm	2 ppm	3 ppm	4 ppm
30	-291.5	-122	-48	22	43.81
60	-262.3	-55.77	11.72	72	74.73
120	-220.6	1.44	50.78	112.56	124.57
180	-192.8	23.81	68.03	149.81	159.33
240	-175	37.55	88.07	174	186
300	-163.9	44.81	108.43	193	207

 Table 23
 Potential change of platinum electrode over time.

 Table 24
 Potential change of palladium electrode over time.

Time(sec)	0 ppm	1 ppm	2 ppm	3 ppm	4 ppm
30	144	284	202.3	313.5	416.2
60	151	363.3	303	413.8	476.8
120	161	430	417.5	493.6	545.6
180	166	469.4	475.8	537.5	564
240	169	498.9	512	561.2	581.4
300	171	519.1	541.6	577.4	595.5

 Table 25
 Potential change of bismuth electrode over time.

Time(sec)	0 ppm	1 ppm	2 ppm	3 ppm	4 ppm
30	-275.3	-228.4	-247	-236	-216.8
60	-270.6	-222	-238.5	-222.7	-195.2
120	-268.6	-215.1	-226.6	-203.4	-163
180	-267.5	-210.7	-217.8	-187.7	-137
240	-266.3	-207	-210.4	-175	-115.71
300	-265.7	-203.8	-202.6	-161	-97.93

 Table 26
 Potential change of silver electrode over time.

Time(sec)	0 ppm	1 ppm	2 ppm	3 ppm	4 ppm
30	-13.54	29.92	20.77	113	138
60	-17.93	31.77	18	123	135
120	-24.8	54.11	31.9	127	131
180	-28.85	77	52.09	127	129
240	-31.55	88.3	77.7	129	128
300	-33.43	94.44	95.12	128	127

Time(sec)	0 ppm	<u>1 ppm</u>	2 ppm	3 ppm	4 ppm
1		-62.34	-12.55	-17.82	5.99
2		-47.24	6.49	-0.14	14.13
3		-40.07	7.76	11.29	15.2
4		-28.11	6.17	13.68	14.6
5		-19.68	4.33	11.6	13.84
6		-13.53	2.03	10.45	12.84
7		-9.36	0.08	7.95	12.82
8		-6.89	1.11	7.41	11.22
9		-5.17	-3.14	5.51	9.8
10		-4.79	-4.38	4.41	9.44
. 11		-4.29	-5.5	2.89	8.49
12		-4.04	-6.42	2.08	8.18
13		-5.18	-7.68	0.64	6.9
14		-5.86	-8.29	-0.63	6.35
15		-6.39	-9.42	-1.99	5.9
16		-6.46	-10.39	-2.46	5.26
17		-7.16	-11.05	-3.24	4.82
18		-8.75	-11.38	-3.81	3.96
19		-8.18	-13.14	-4.87	3.66
20		-8.92	-12.93	-5.67	3.19
21		-9.61	-13.94	-6.06	2.55
22		-10.76	-14.43	-6.27	2.05
23		-11.29	-14.43	-6.88	1.85
24		-12.16	-14.81	-7.09	1.24
25		-13.62	-15.18	-7.95	1.05
26		-13.77	-15.51	-8.37	0.57
27		-13.83	-16.04	-8.37	0.45
28		-14.25	-16.86	-8.91	0.17
29		-15.88	-16.5	-8.99	-0.44
30	-82	-15.22	-17.28	-9.58	-0.82
60	-77				
180	-74.23				
240	-74.13				
300	-74.28				

 Table 27 Potential change of copper electrode over time.

APPENDIX D

PLOTS OF POTENTIAL CHANGE WITH TIME



Figure 21 Potential change over time for platinum electrode at 0 ppm chlorine.



time(sec)

Figure 22 Potential change over time for platinum electrode at 1 ppm chlorine.



Figure 23 Potential change over time for platinum electrode at 2 ppm chlorine.



Figure 24 Potential change over time for platinum electrode at 3 ppm chlorine.



Figure 25 Potential change over time for platinum electrode at 4 ppm chlorine.



Figure 26 Potential change over time for palladium electrode at 0 ppm chlorine.



Figure 27 Potential change over time for palladium electrode at 1 ppm chlorine.



Figure 28 Potential change over time for palladium electrode at 2 ppm chlorine.



Figure 29 Potential change over time for palladium electrode at 3 ppm chlorine.



Figure 30 Potential change over time for palladium electrode at 4 ppm chlorine.



time(sec)

Figure 31 Potential change over time for bismuth electrode at 0 ppm chlorine.



time(sec)

Figure 32 Potential change over time for bismuth electrode at 1 ppm chlorine.



Figure 33 Potential change over time for bismuth electrode at 2 ppm chlorine.



Figure 34 Potential change over time for bismuth electrode at 3 ppm chlorine.



Figure 35 Potential change over time for bismuth electrode at 4 ppm chlorine.



Figure 36 Potential change over time for copper electrode at 0 ppm chlorine.



time(sec)

Figure 37 Potential change over time for copper electrode at 1 ppm chlorine.



Figure 38 Potential change over time for copper electrode at 2 ppm chlorine.



Figure 39 Potential change over time for copper electrode at 3 ppm chlorine.



Figure 40 Potential change over time for copper electrode at 4 ppm chlorine.



Figure 41 Potential change over time for silver elctrode at 0 ppm chlorine.



Figure 42 Potential change over time for silver electrode at 1 ppm chlorine.



Figure 43 Potential change over time for silver electrode at 2 ppm chlorine.



Figure 44 Potential change over time for silver electrode at 3 ppm chlorine.



Figure 45 Potential change over time for silver electrode at 4 ppm chlorine.

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