Phosphorus Detection Sensor in Agricultural Drainage Water

> Lana Saleh Bacha Nianchao Luo

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Abstract

Phosphorus usually occurs in the form of phosphate (PO4-P) in natural water and can cause eutrophication if it is in high concentration. A sensor that can measure phosphate levels in agricultural drainage water is presented. This system is an alternative to field sampling and in-lab spectrophotometric phosphate measurements that take time and manual labor and is costly. Electrochemical, colorimetric, fluorescent sensors and biosensors were explored. Through careful analysis of existing products and sensor designs that fit our client's criteria, an ISE sensor design was chosen. The following report will describe different phosphate detection methods and the design process of the phosphate sensor. The design is fabricated with a potentiometer, a reference electrode, a gold working electrode that is to be coated and tested for phosphate detection. The total sensor costs 2450\$ with a recurring cost of 1.50\$ per sample. The coating deemed unnecessary as it only decreased the sensor's response time and did not improve sensor accuracy after calibrating the sensor and testing raw water samples and standard phosphate samples.

1. Introduction

The Brace Center for Water Resources Management at Macdonald Campus of McGill University is an important research and training center. The center's vision is to be able to provide food and water in rural communities through staff research. Dr. Chandra A. Madramootoo's current research interests are irrigation and drainage water quality. More specifically, he is interested in water table management systems and field testing to reduce nonpoint source pollution, algal blooms and cyanobacterial contamination of rivers and lakes. Monitoring water quality is important for his and his students' research. The driving force among others is the legislation that is becoming more stringent regarding the quality of water bodies and aquatic ecosystems. The government of Quebec wants to intensify agricultural clean-up efforts by limiting the phosphorus surpluses that usually occur from plant fertilization (MDDELCC, 2002). In order to achieve balanced phosphorus levels, it is highly important to be able to monitor and assess water quality (MDDELCC, 2002).



Fig. 1 Lake Simcoe. Source: Simcoe.com/news

Lake Simcoe, one of the larger lakes in Ontario for tourism and recreation is one of the research areas our client is interested in. Located in Northern Ontario, this lake provides residents drinking water and recreation on and around the lake throughout the seasons. Nearby and adjacent to the lake, the Holland Marsh is an intensive agricultural area located nearby. Unfortunately, runoff from the Holland Marsh, that contains pollutants such as Nitrogen and Phosphorus from manure or pesticides from the farmland, enters Lake Simcoe causing eutrophication. The water from the Holland Marsh tile drains enter the lake. Overall, the lake's health has been compromised due to the agricultural and recreational activities occurring nearby. The current Phosphorus loads are higher than the recommended limit of 44 tons/ year, set by the Lake Simcoe conservation authority. The Phosphorus load of the Holland Marsh, the load percentage it contributes is very high. Although the lake's health is slowly improving, the Phosphorus concentration level has not reached the target level yet.



Fig. 2 Holland Marsh Source: Madramootoo & Grenon

Previously, Dr. Madramootoo's team would use manual sampling techniques and lab analysis to measure phosphorus concentrations. The problem is that the cost per sample is high and that it takes a significant amount of time to analyze as well as manpower (Engblom, 1998). That is why he has tasked us to find a way to measure phosphorus concentrations in water as it drains from the agricultural fields using sensor technology.



Fig. 3 Tile drain Source: Madramootoo & Grenon

The issue is that current sensors on the market are made for the wastewater industry, for high water volume and high nutrient concentration detection. That is our task is to come up with a sensor design that can detect phosphorus concentrations per the following criteria. The concentration levels of phosphate we need to be able to measure is 0.01 to 1.05 mg/l of phosphate. The drainage water volume has to be between 0 to 20 ml. Thus we need to design a portable low-cost sensor to measure Phosphorus concentrations in agricultural drainage water. We must build and test the sensor in the lab as the first project step. As our mentor and client, the team will consult with Dr. Madramootoo to find the best solution for this specific need. With the

help of our mentor as well as Ph.D. student Genevieve Grenon, we are able to find an appropriate way to measure phosphorus, and build the first prototype in the lab.

The objectives are to successfully build a sensor that can detect 0.01 to 1.0 mg/l of phosphate, with a volume of water of 0 to 20 ml. This report aims to document the first phase of the sensor production, the in-lab prototyping of the phosphorus sensor.

The <u>Vision Statement</u> of our team is monitoring and protecting our water.

1.1 Initial Needs Statement

The client stated that he needs a way to measure concentrations of phosphorus in agricultural drainage water in a fast, portable and low-cost way. Genevieve Grenon, the PhD student of our client has research interests in Lake Simcoe located in the North of Ontario. Due to agricultural activities in the adjacent Holland Marsh, eutrophication occurred in Lake Simcoe. The water draining from the tile drains of the agricultural fields into the lake, has been polluted with agrochemical components (Nitrogen and Phosphorus). The high nutrient content of the drainage water due to high phosphorus loads as well as fluctuating low volume of agricultural drainage water made for a need of an easy detection system of Phosphorus concentrations in water. The current in-lab method is time consuming and costly.

1.2 Customer Needs Assessment

Table 1 below shows the initial customer needs list obtained from interviews and observations. First, the sensor must be portable, cost under 3000\$ and most importantly be functional for phosphate concentrations of 0.01 to 1 mg/L, which is the usual concentrations found in the agricultural drainage water from the Holland Marsh. Table 2 shows the same needs in a hierarchical list with weighting factors assumed.

Portable Easy to manufacture in Jab
Easy to manufacture in-fab
Cost under 2000
Cost under 50005
Small tootprint
Sale
Light
Durable
Autonomous
Easy maintenance
Functional for P concentrations of 0.01 to 1.0 mg/l
Functional for water volume of 0 to 20 ml

Table 1. Initial Customer Needs List

1.	Portable
	1.1 Small Footprint
	1.2 Safe
	1.3 Light
2.	User friendly
	2.1 Easy to manufacture
	2.2 Easy to operate
	2.3 Autonomous
3.	Durable
	3.1 Easy maintenance
	3.2 Cost under \$3,000
4.	Functional
	5.1 Detects 0.01 to 1.0 mg/l PO4
	5.2 Detects using 0 to 20 ml water

Table 2. Hierarchical Customer Needs List

2. Literature Review

2.1 Phosphorus & Phosphate

Phosphorus is a limiting factor in the environment and contributes to eutrophication and toxic algal blooms (Pitois et. al., 2001). Phosphorus exists in water in different forms but the most common are phosphates. Phosphates occur as orthophosphates, condensed phosphates (pyro-, meta-, and poly-phosphates) and organically bound phosphates. Phosphates can also be found in bottom sediments and biological sludge, either in organic compounds or precipitated in inorganic forms (Greenberg et al., 1992). Orthophosphates are usually used as fertilizers and then runoff to the surface water (Young et. al, 2009). The analysis of Total Phosphorus (TP) is complicated and has not been cost effective yet because the release of Phosphorus from organic matter needs a digestion step to then become orthophosphate (Taylor et al., 2016).

The problem with current classical methods of measuring phosphate is that the sample can acidify which changes the phosphate content (Burton, 1973). Engblom recognized the need for a phosphate sensor that was simple, accurate and compact that can actually be put to real use (1998). Most popular and current phosphate determination in water cannot be direct, reagent-based methods are needed (Duffy et al., 2017). Different technologies are available in the literature, and in this report the ones we chose to highlight are the following. These methods are colourimetric detection, fluorescence detection and electrochemical detection, and finally biosensors.

2.2 Phosphorus in Agricultural Drainage Water

The importance of Phosphorus originating from agricultural sources to the nonpoint source pollution of surface waters has been an environmental issue for decades because of the well-known role of P in eutrophication. Most previous research and nonpoint source control efforts have emphasized P losses by surface erosion and runoff because of the relative immobility of P in soils. Consequently, P leaching and losses of P via subsurface runoff have rarely been considered important pathways for the movement of agricultural P to surface waters. Ryden et al. (1973) cited eight studies where dissolved inorganic P (DIP) concentrations in

subsurface runoff in artificial drainage systems were higher than values usually associated with eutrophication of surface waters 0.01-0.US mg/L; (Foy and Withers, 1995; Sawyer. 1947: Sharpley et al., 1996: Vollenweider, 1968; USEPA. 1986). Mean DIP concentrations in these studies were from 0.012 to 0.44 mg/L. They also cited studies where P export (kg/ha per yr) in subsurface flow equaled or exceeded values typically found in surface runoff (Bolton et al., 1970; Sylvester, 1961). In Quebec, total P losses from poorly drained clay soils through tile drainage may range from 0.01 to 1.17 mg/L P or higher (Beauchemin et al., 1998; Simard et al., 2000). Particulate P (> 0.45 μ m) tends to be the dominant form of P transported to tile drains, perhaps because most of the dissolved P (< 0.45 μ m) is adsorbed by the soil matrix; however, the quantity of P leached is affected by soil texture, tillage and cropping practices, and rainfall events (Sims et al., 1998; Simard et al., 2000). Quebec provincial surface water quality standard indicates the accepted concentration is 0.03 mg/L total P (Ministère de l'Environnement du Québec, 2000). Next, phosphate detection methods will be explored to find the best method for building a functional phosphate sensor.

2.3 Fluorescent Phosphate Detection

An optical instrumental method to measure phosphate is by fluorescence. Fluorescence occurs when a molecule absorbs energy in the form of light and an electron is raised to an excited state. The phosphate sensing method is based on fluorescence recovery; it is when a competing ion, quantum dot or nanoparticle is replaced with phosphate (Duffy et al., 2017). There's many ways to determine phosphate using fluorescence one of them is by a reaction of vanadomolybdophosphoric acid and molybdophosphoric acid with thiamine determines phosphate (Duffy et al., 2017). Another way is using synthetic receptors that are then used to generate signals when phosphate is detected under aqueous conditions (Ojida et al., 2004). These signals occur when a phosphate binding protein and two fluorescent reporter proteins are embedded within polyacrylamide nanoparticles (Sun et al., 2008). Another way is using reverse injection analysis by detection of diffusely emitted fluorescence in a glass capillary to measure the phosphate analyte concentration (Krockel et al., 2014). The lowest level of detection for that specific method was 0.22 to 40 microgram per liter for pure water with a 15-40 microliters of injected water sample (Krockel et al., 2014). Overall, fluorescent methods use little amount of

reagent and could measure phosphate rapidly (Frank et. Al, 2006). The low limit of detection as well as narrow sensor range makes it a good method to use when sensing in surface or under seawater (Krockel et. al, 2014). This method features simple equipment and relatively low levels of detection depending on the fluorescent method used. However, fluorescence and electrochemical sensors, which will be explored next, have not yet been fully automated like the colorimetric methods (Cleary et al., 2008).

2.4 Colorimetric Methods

Colorimetric testing is a major method of chemical compounds detection in lab. The detection is based on the measurement of colour change after mixing the objective water samples with a specific chemical solution. The basic theory is called "Beer-Lambert Law". In 1700s, Johann Heinrich Lambert defined the relationship between the chemical concentration and the light absorption in the liquid (Beer, 1996). He found that light gets harder to go through the mixer as the concentration gets higher.

$$A = \log_{10}(\frac{I_0}{I})$$

(A is absorbance, is incident intensity, is the transmitted intensity)

$$A = a_{\lambda} \times b \times c$$

(A is absorbance, a_{λ} is the molar absorptivity of the species of interest, b is the path length of light through solution, c is the concentration of the analyte)

Therefore, the intensity of transmitted light is proportional to the concentration of the objective chemical compounds in the liquid. Scientists use this method to measure the concentration of phosphate in the mixed liquid. Yellow method (vanadomolybdophosphoric acid) and blue method (phosphomolybdic acid) are the two methods used in phosphate detection. Either yellow method or blue method is using optic instrument to detect the formation of yellowish or bluish compounds in the liquid. To observe this color change, a colorimeter is required in the lab.

The yellow method was adopted in the autonomous microfluidic sensor (Cleary, 2008). The water sample is mixed with an acidic reagent containing ammonium molybdate and ammonium metavanadate (Cleary, 2008). In 1962, a study used a more efficient colorimetric molybdenum blue method by adding antimony into the phosphate solution (Murphy, 1962). The author found that the addition of antimony added into the original single solution accelerates the formation of bluish compound (Murphy, 1962). Overall, the colorimetric detecting method is easy to operate and has a relatively low cost. The only limits are when we need to detect a low concentration of phosphate. The optical system does not work functionally if the concentration is lower than the proportional designed light intensity. Also, the results showed that some discrepancies occurred during the experiments (Cleary, 2008). The major cause is the imperfect connections in the sample line and interference with the passage of light through the optical cuvette. The air bubbles within the microfluidic chip rose the phosphate level to the peak (Cleary, 2008).

2.4.1 Microfluidic Technology

Microfluidic technology is an important field that is gaining a lot of interest from academia and industry namely because of its advantage in bio sensing (Burger, 2015). It enables laboratory analyses in a compact, portable and automatic way that is affordable called lab-on-adisc system (Burger, 2015). Another study introduced the 'miniaturized total analysis system' (µTAS) and the advantages of such microfluidic sensing systems are many (Manz et al., 1990). First, small sample sizes can be used and that reduces the reagent volume as well as waste that could be generated (Cleary et al., 2013). The microfluidic system makes for a compact sensing system that can be portable, an important feature when an environmental monitoring sensing system is required. Since the operation of microfluidics is in the micro scale, chemical analysis can be performed in a faster way compared to regular laboratory operations (Cleary et. al, 2013). There are downsides to this technology. First of all, it is difficult to represent a complete water body when we are operating in the micro-scale and using microliter sample sizes (Cleary et. al, 2013). However, since this technology is portable and compact, taking many water samples onsite can mitigate this possible issue (Cleary et al., 2013). Secondly, fine particulate matter could interfere and block the microfluidic channels; to avoid this problem micro filters need to be used at the sampling point (Cleary et al., 2013). The two microfluidic systems that are of interest in

this report is the microfluidic disc and chip. Some microfluidic technology in sensors rely on centrifugal forces namely when it is a microfluidic disc that has a motor (Gorkin et al., 2010). When the disc is rotated and a centrifugal force is created, the fluid gets pumped through the microfluidic channels (Gorkin et al., 2010). The fluid gets driven from the center to the edge of the disc (Gorkin et al., 2010). The fluid velocity depends on fluid viscosity, fluid density, distance from the center of the disk to the fluid, the cross-sectional area of the channel and the channel wetness (Gorkin et al., 2010).

2.5 Biosensors

Biosensor technology is based on biological recognition elements that can bind to a chemical compound and then get transduced into an output that could be measurable (Storer, 2017). An example in the literature is the combination of enzymatic substrate recycling using a sensor made of xanthine that can determine inorganic phosphate, the limit of detection being 0.5 to 100 micromoles (Wollenberger et al., 1992). While being cost effective and a good portable sensing method, the biggest limitation biosensors have is that ambient conditions such as temperature and pH are extremely important as the enzyme's protein can denature or the biological macromolecule can decompose when unsuitable conditions occur (Storer, 2017). The short shelf life of enzymes is the main challenge to current commercialization of biosensors, and producing enzymes that can withstand different environmental conditions is important to overcome this challenge (Law al et al., 2013).

In this particular research, the authors developed a highly sensitive chemiluminescent flow-injection analysis sensor that uses maltose phosphorylase and is coenzymeless (Nakamura et al., 1999). The linear range of this method is attractive since it ranges from 10 nanomoles to 30 micromoles of phosphate ions. The low detection level makes it a good option for environmental monitoring, however making this system automatic is currently still in progress. There was a pre-treatment involved that was needed, filtering the water using a hydrophilic membrane and then adding EDTA (ethylenediaminetraacetic acid) to remove the cation in the water sample (Nakamura et. al, 1999). As mentioned previously, the biggest problem with most biosensors is their short lifetime, this specific biosensor for example only has a lifetime of 2

weeks. Another research made a sensor that consisted of a bi-enzyme membrane and uses a platinum amperometric electrode to detect hydrogen peroxide (D'Urso et al., 1990). One mole of phosphate ions leads to 2 moles of hydrogen peroxide, that is how phosphate is then determined. The detection limit of 0.1 to 10 micromoles makes it very suitable. Nonetheless, there is a strict pH range between 7.4 and 8.2 for this enzymatic system to work (D'Urso et al., 1990). This system electrochemically detects hydrogen peroxide, making it a viable option and seems promising, but uses lots of reagents and is mainly an in-lab method not a portable sensor.

2.6 Electrochemical Phosphate Detection

2.6.1 MEMS

Micro-Electro-Mechanical systems, or MEMS, is a technology that is composed of several miniaturized technical and electro-mechanical elements that are used in various fields. MEMS could be varied with respect to the different movement of elements under the control of integrated microelectronics (Berchmans, 2012). In chemical science study, there are different kinds of sensors based on the technology of MEMS. Chemiresistor sensors, chemi-capacitor sensors and chemi-mechanical sensors are the main applications of MEMS in the chemical sensor industry. Numerous previous studies on the determination of phosphate in water showed the advantages of adopting electrochemical sensors in field. It has the advantages of having a relatively small size, low power consumption , low cost (Jinbo et al., 2016), easy integration, and highly resistant to the natural caused vibration, shock and radiation. For specifically, the following three applications of MEMS have been studied of detecting phosphate level: potentiometry, voltammetry and amperometry (Berchmans, 2012).

2.6.2 Potentiometric Electrochemical Sensor

The potentiometric electrochemical sensors are mainly measuring the potential difference between the ion-exchange rate which is generated on the surface of the working electrode and the ion-exchange rate which is generated on the surface of the reference electrode. The potential difference can be correlated to the Nernst equation then transformed into phosphate concentration. Transduction consists in measuring the variation of the potential at the electrode interface as a function of the phosphate concentration. The previous study narrows the research onto the ion selective electrodes (ISE). Potentiometric ion selective electrode is the most important component of the potentiometric electrochemical sensor system. It has the properties of easy fabrication and reproduction. The ion selective electrode has the following categories: metal/metal phosphate electrode, solid state membrane electrode, liquid membrane electrode, coated wire electrode, heterogeneous membrane electrode and redox exchange electrode (Al et al., 2013). However, previous studies indicated that the ion selective electrochemical sensor can be involved in a disturbed interference with other anions due to the hydrophilic nature of phosphate. The hydrophilic nature of phosphate is indicated by the anion's position at the end of the Hofmeister series. This limits the selectivity of a potential phosphate selective membrane, as phosphate remains in solution more readily than the more hydrophobic anions (Warwick et al., 2013). To improve this, a cobalt coated electrode or a conducting polymer coated electrode is preferred in the ISE system. Previous study showed that the cobalt matrix has a better selectivity of different ions. It is the earliest method in phosphate sensing and has the advantage of being highly portable, and inexpensive to produce (Dimeski et al., 2010).

The alternative system that is also used for phosphate detection called ISFET (ion sensitive field effect transistor). It is another type of chemical potentiometric sensor which integrates ISE and microelectronic technology. The difference between these two ISEs is the field-effect transistor (FET) (Dimeski et al., 2010). The movement of the current which is produced by the system to the targeted liquid is controlled by a gate electrode coated with an ion-selective membrane. The current is moving between two conductor electrodes. Compared to ISE, ISFET does not need an internal solution. The ion-selective membrane is directly attached to the electrode surface. It has the advantage of smaller size, low output impedance, short response time, long-life use and low cost (Dimeski et al., 2010).

2.6.3 Voltammetric Electrochemical Sensor

The voltammetry electrochemical sensor is using anion receptor with a proper signal unit and an effective binding site to detect phosphate in water. Compared to potentiometric electrochemical determination, voltammetry electrochemical sensors highly depends on the selection of the ion receptor. The use of voltammetric devices to measure orthophosphate activity is largely inhibited by the oxygen ions around the central phosphorus atom. Consequently, voltammetric analysis of orthophosphates has tended to rely on indirect methods. Voltammetry has also been used together with an alternative means of indirectly quantifying phosphate levels, using bis-thiourea receptors on the surface of gold electrodes (Berhmans et al., 2011). Orthophosphate ions, attracted to the bis-thiourea receptors, inhibited the redox reaction of potassium hexacyanoferrate, an electron transfer agent used in cyclic voltammetry. The method was highly selective for phosphate, compared to sulphates, nitrates and chlorides but only permitted the (indirect) measurement of phosphates down to 16 mg/l (Warwick et al., 2013).

2.6.4 Amperometric Electrochemical Sensor

Amperometric sensors measure the current produced by the target analyte at an electrode with a constant voltage. Ferrocene based macrocyclic synthetic receptors investigated the selectivity for dihydrogen phosphate detection based on a ferrocene based macrocyclic synthetic receptors (Beer et al., 1996). It showed that the selectivity is highly affected by the importance of pH value of the targeted solution. There are other indirect amperometric methods detecting the phosphate concentration by measuring the reduction of the phosphomolybdate complex, and the reduction of the anodic oxidation of molybdenum (Quintana, 2004; Jonca et al., 2011). However, both of these two quantification methods require highly requirement of safe disposal of the reagents used in the detection.

An alternative glassy carbon electrode was developed in 2005. The surface of the electrode was modified with ammonium molybdate, a chitosan matrix and another layer of ammonium molybdate in an ionic liquid. This invention avoided the need for additional reagents. The signal produced from the reduction of ammonium phosphomolybdate, allowed measurements of phosphate between 0.02 and 1 mg/l. The sensor performed in aqueous solution and did not suffer from interference from arsenate, chloride or nitrate. However, due to the silicate particles of the glassy electrode, it caused the interference and the effect of sulphate was not reported (Berchmans et al., 2011). In contrast to the potentiometric sensors, none of the amperometric methods offer detection covering the range of phosphate typically found in wastewater (0.1-5 mg/l). Furthermore, the principal problem with many of the electrochemical

affinity sensors discussed here was the lack of specificity for phosphates, without interference from other ions.

3. Design Approach

3.1 Design Criteria

After consulting with our client and with Ph.D. student Genevieve Grenon, the following criteria were established to help us aid our sensor selection

Functionality The sensor must be able to measure low concentrations of phosphate, namely 0.01 to 1.0 mg/l, and be able to measure low volumes of sample water. Additional functions of the sensor is preferred but not necessary.

Ease of Operation The sensor must be easily operated by anyone wishing to make phosphate measurements with little or no previous sensor knowledge.

Portability The sensor must be portable and can be deployed on the field without any necessary in-lab steps.

Data Acquisition and Storage The sensor must have a simple way to acquire phosphate data and preferably have an easy data storage system.

Manufacturability The sensor must be fairly simple to manufacture and sourcing the components must be doable, on the sensor markets are considered as easily manufacturable.

Affordability The cost of the sensor must be affordable and comparable to on the market nutrient sensors available and must be under 3000\$.

Autonomous The sensor we would prefer to employ would be autonomous, taking phosphate data without manual labor.

3.2 Alternative Sensor Designs

A flow injection biosensor previously developed uses enzyme reactors and a chemiluminescence detector (Nakamura et al., 1999). However, due to Cr, Cu and Mn interference, pre-treatment of the water was necessary with EDTA (Ethylenediaminetetraacetic acid) and activated carbon. After the enzyme reaction, hydrogen peroxide gets mixed with luminol and the chemiluminescence is measured (Nakamura et al., 1999). The advantage of this potentiometric biosensor is the high sensor performance and detection range that fits what we need 10 nanomol/L - 30 micromol/L. Two main disadvantages of this system is the small

lifetime of 2 weeks and that it is not a portable system, it can be made and used in-lab only. This system is not yet automated and still needs further work, but seems like a promising option. The schematic diagram below demonstrates how the system works.



Fig. 4. Schematic diagram of the chemiluminescence phosphate-ion sensor system. Source: Nakamura et al., 1999

The Autophos system uses a syringe pump and a reusable microfluidic chip system based on the vanadomolybdophosphoric acid colorimetric method (yellow method). It is designed for continuous autonomous in-field use. The linear range of detection of this system is 0.4-10 milligram/Liter phosphate, which cannot detect the low range of phosphate we encounter in the field. The cost to make this sensor is about 3000\$ with a recurring reagent cost (Duffy et al., 2017). The system works by a pump that collects the sample and pumps the sample and reagents on the chip, which measures the absorbance after 7 mins. The chip must be rinsed after each use (Duffy et al., 2017). The disadvantages of this autonomous system is the high initial cost, the fact that reagents must be purchased and disposed of for all sample uses and that most importantly, it cannot detect the low phosphate concentrations of 0.01 to 0.4 mg/L for our desired system.

Phosphasense, a lab on disc design, determines phosphate, with a centrifugal disc that automates the colorimetric method. It can be applied to river and wastewater samples. It is a handheld sensor that uses the blue method. The fluid moves through the disc using centrifugal force, loaded fluids are then mixed and are forced through microfluidic channels, into the optical detection zone (Duffy et al., 2017). The low cost optical detection system consists of an LED-photodiode transducing pair that measures absorbance of light by the molybdenum blue complex formed at 880 nm. It has a mass of two kilograms and the range of detection is 5 to 800 microgram/L while what we need is a system that can measure from 10 to 1050 microgram/L of phosphate, the upper range cannot be detected by the Phosphasense system. The component cost is around 150 Euro, sample intake is manual, power source is a 12 Volt main supply. Since it's a

manual system, it does not need to withstand harsh environmental conditions as autonomous sensing systems (Duffy et al., 2017). It has an initial design cost of about 230 \$ but might have a high running cost due to the microfluidic disk that gets disposed of as well as the reagent. The main problem is when taking into its environmental effect and assessing the impact of the disposable nature of the microfluidic disk, it makes this system unsustainable and not ideal to implement.

An alternative to designing the sensor we also considered as a backup was purchasing the sensor from the market. Companies such as Hoskin IQ, Fisher Scientific, Hach were explored and the products found in the companies' websites were good choices if we did not have our low detection range of phosphate that is a big constraint. However, it was important to get an idea of the general cost of such sensors on the market for comparability reasons. The first product Hoskin IQ SensorNet P 700 IQ Orthophosphate Analyzer is used mostly in wastewater treatment plants and has 3 different ranges of orthophosphate it can detect, the range that is closest to our needs is 0.05 to 15 mg/L while what we desire is a system that can detect 0.01 mg/L of orthophosphate. It operates in a pH range of 5 to 9 and temperature range of -20 to 40 °C with a 5 minutes maximum response time. It uses the vanadomolybdate yellow colorimetric method. Another big issue with this system is that it can't use low volumes of water to detect the phosphate.

Hach's DR1900 Portable Spectrophotometer was also explored as a possible option. It is a compact portable spectrophotometer which can be used to test phosphate levels in field. It includes and uses 4 alkaline AA batteries and can operate in 10 to 40 °C. It can detect many parameters not only Phosphate such as Nitrogen, which is quite favorable. The cost is quite high, Hach company provided a 4701 \$ quote for this product. However, the reagents must be purchased separately and the closest range desirable to us is the Ascorbic Acid reagent that can detect 0.02 - 2.50 mg/L PO4. Another thing to note is that the battery life is only 15 day with 5 readings per day and that means for a high amount of sample analysis, we would need to buy and dispose a lot of batteries which is not favorable for a sustainable design (USA, n.d.).

The previous products discussed use the colorimetric method to detect phosphate. This next particular innovative product by the CleanGrow company based in the UK is a multi-ion sensitive analyzer. One of the ions it can measure is the HPO4 2- hydrogen phosphate ion (CleanGrow, 2018). It is a portable device that uses advanced ion selective electrode (ISE) sensor technology. It does not need any maintenance with automatic calibration and data transmission through the smartphone application. The innovative part of this product is their "use of carbon nanotubes as the transducing layer in the sensor" (CleanGrow, 2018). The two main problems of this system is that it has a high initial cost of 3800\$, with no recurring cost since it uses no reagent or batteries, and needs no maintenance unlike most other sensors. It is the only manufacturer and seller of ISE phosphate sensor but the main problem is that the CleanGrow sales representative claimed ISE cannot measure easily such low concentrations of phosphate, the typical range it can measure is 2 to 200 ppm or mg/L, which is outside of our range unfortunately. This innovative sensor product does not solve our problem, which is why we rejected this product, despite its cutting-edge technology but it has inspired our final design.

Many sensors were researched and evaluated for feasibility of design, however our desired concentration range is so narrow and limited. The previous sensors have innovative designs but do not fit in our specific range needed. The next section aims to describe all detection methods considered for comparison and selection of the best detection method for the sensor design.

Detection method	Brief Description	Advantages	Disadvantages	Cost
1- Autophos Colorimetric method	Consists of a syringe pump and microfluidic chip, uses the yellow method, with a detection range of 0.4 to 10 mg/L PO4	 Reusable microfluidic chip system Covers a wide detection range Could be automated 	 Has a recurring reagent cost Might be difficult to manufacture or acquire microfluidic chip Not easily portable 	Around 3000\$
2- Phosphasense lab-on-disc (colorimetric)	Composed of disposable microfluidic disc, and a centrifugal force pump to mix reagents. Uses blue detection method. Low range of detection of 8-1000 µg L-1 PO4-P	 Cheaper startup cost than Autophos Only 2kg, it could be portable Not a wide range of detection 	 Microfluidic disc gets disposed of every time Reagent gets disposed of every time High running cost Difficult to automate 	Around 300\$
3- ISE electrochemica 1	Consists of a reference electrode, a working electrode coated with chemicals, and an ion meter to read measurements.	 Easy to manufacture Simple materials Could use recycled material 	1. Depending on sensor, must be done in lab	Depends on material of electrode 2000- 3000\$ expected cost
4- Biosensor by Nakamura et al.	Uses enzymes to detect phosphate levels, with a limit of detection of 0.5 to 100 micromoles	1. The limit of detection fits our desired range	 Short shelf life of 2 weeks Need to purchase specific enzymes Difficult to manufacture 	Unknown

3.3 Selection of Detection Method

Table 3. Phosphate detection methods description, advantages, disadvantages and overall cost

Criteria	Weight	A Autophos	B Phosphasense	C Electrochemical sensor ISE	D Biosensor
Portability	5	5	-5	5	-5
Manufacturability	3	3	-3	3	-1
Lifecycle	4	4	-4	4	-4
Cost	1	-4	4	-4	0
Data Acquisition	2	2	2	2	-2
Ease of operation	2	-2	-2	2	-2
Additional functions	1	-2	-2	2	-2
Autonomous ability	2	2	-2	-2	-2
Net Score	20	8	-12	12	-18

Table 4. Pugh Matrix of Accepted Sensing Systems.

The sensor systems in the Pugh Matrix, shown in Table 4 above, are all systems that fit our low concentration of phosphate criteria. The first criteria we are considering in our Pugh matrix is portability. We gave it a weight of 5 because the sensor must be portable and not need in-lab or difficult operations to give a phosphate reading. The whole point of our system is to reduce manual labor and in-lab spectrophotometer device use that is costly and time consuming. Sensor A and C are portable. The fluorescent and biosensor are not as easily portable and need more steps in lab for phosphate measurements.

The second criteria manufacturability is based on how easy to manufacture the sensor in question. The electrochemical sensor needs an electrochemical measurement system and an electrode system which is fairly easy to assemble. The biosensor system needs MP (maltose

phosphorylase), MT (mutarotase), and GOD (glucose oxidase) which must be purchased from pharmaceutical companies from the US and Japan making it more difficult to build and use for the long term. The lifecycle is also important to consider. The biosensor life cycle is only 2 weeks, which is very undesirable. The electrochemical sensor's lifecycle is unknown which is why we inserted a 0 in the Pugh matrix. The colorimetric sensors that could be purchased all have a recurring cost which is the purchasing of the reagent, which is quite undesirable for cost and environmental implications.

From the above Table 4 of the constructed Pugh matrix, the electrochemical detection method seems most promising due to its manufacturability, ease of operation, and affordable cost. Finding an electrochemical sensor design that fits our low concentration of phosphate range, has a possibility of end of lifecycle use, and making the sensor easy to manufacture and use is our main challenge.

4. Final Design

4.1 Standards Relating to Design

Before delving into the sensor design chosen, it is important to follow and keep in mind standards related to our designs. IEEE (Institute of Electrical and Electronics Engineers) issues standards and the main one that fit our sensor design were chosen and studied. The IEEE standard 1554 written in 2005 "Recommended Practice for Inertial Sensor Test Equipment, Instrumentation, Data Acquisition, and Analysis Calibration of equipment" was consulted. First, it states that there should be at least a once per year calibration of the sensor or at the start of a long test sequence. Since we will be using a voltage to determine the concentration of the ion, the standard also states that a true root-mean-square (rms) or a rectifying ac voltmeter might be useful since our system requires great precision. Furthermore, sensor output might not be precise enough if using commercial equipment, so the IEEE standard claims that test equipment should be bought as commercial-off-the-shelf (COTS) procurement if possible (1554, 2005). This standard was kept in mind when designing the phosphate sensor. ASTM and ASABE standards were also consulted, however not many other standards fit our specific sensor project.

4.2 Design Selection & Implementation

After massive research on previous study on manufacturing an effective and precise electrochemical sensor for detecting phosphate, a potentiometric electrochemical sensor is chosen to be our final design. The context of potentiometric electrochemical sensor is explained in the above section of this paper. The ion-selective electrode was found to be the most important component of the sensor system. Usually, the potentiometric electrochemical sensor is composed of one working electrode and one reference electrode and both are connected to a potentiometric meter through wires. The signal transferred is analyzed using a computer software. The more successful approach of detecting a wider concentration range of the targeted ion is to use an ionselective liquid membrane. The liquid membranes are hydrophobic and immiscible with water, and most commonly made of plasticized poly(vinyl chloride) (PVC). The selectivity is achieved by doping the membranes with a hydrophobic ion (ionic site) and a hydrophobic ligand (ionophore or carrier) that selectively and reversibly forms complexes with the analyte (Shigeru, 2007). Based on the principle of liquid membrane ion-selective electrodes, three main categories of ISEs are listed below: ionosphere-free ion-exchanger electrode, neutral-ionosphere-Based electrode and charged-ionosphere-based electrode (Shigeru, 2007). However, the manufacturing and application of the liquid membrane is too complicated for this project. The liquid membrane requires regular calibration to approach the precise detection goal. Due to the structure of the liquid-membrane based ISEs, with the inner filled with liquid, as a result, this kind of ISEs is sensitive to evaporation of these inner filling solutions and changes in the sample temperature and pressure (Jinbo et al., 2016). Also, the osmotic pressure from the difference in the ionic strength of samples and the inner filled solution will cause the liquid transport into out of the inner filling solution. This leads to an undesired volume change and delimitation of precision of the sensing membrane (Jinbo, et al., 2016). On the other hand, the liquid-membrane based ISEs does not meet the design criteria of portability.

Thus, solid contact ion-selective electrodes are considered as a better choice for our design scope. Instead of the inner filled liquid, an electron-conducting substrate is applied onto the electrodes. Since the first invention of the solid contact ion-selective electrodes, it has been four decades. Hirata and Date proposed a Platinum (Pt) based electrode coated with a $Cu^{2+}S$ -

impregnated silicone rubber sensing membrane (Hirata and Date, 1970). Another invention followed this work from Cattrall et al., they also used a platinum wire coated with a calcium ion ionosphere-doped poly metric membrane, which was considered as the ancestor of the present-day ionosphere based solid contact state ion-selective electrochemical.

The measured electromotive force is the difference in electrical potential between the connecting leads of the ISE and of the reference electrode. In the 1960s, several scientists developed varied choices of ion-selective electrodes for phosphate ion sensors. Grabber et al. used glassy carbon electrodes modified by Bi/BiPO4A, however it was found that the Bi/BiPO4 electrodes are hard to reproduce. Years later, Ag/Ag3PO4 modified electrodes was proposed to replace the initial invention for the same purpose. Nowadays, conventional ion-selective electrodes usually use an Ag/AgCl coated electrode as the reference electrode (Jinbo, 2016, Yu et al., 2015).

To replace the inner filling solution which interacts with the interfacial potential change from Ag/AgCl electrode, conducting polymers are introduced to the composition of the solid contact ion-selective electrodes. Conducting polymers are effective ion-to-electron transducers because they are both electrically conductive and exhibit ionic conductivity through doping. They can be conveniently deposited on an electron-conducting substrate by electrochemical polymerization or drop-casting of a polymer solution (Jinbo, 2016). The conductor polymers can be either doped with a large immobile polyelectrolyte or small anion.

Consequently, the interfacial potential at the interface between the conducting polymer and the electron-conducting substrate is also controlled by the redox reactions in the conducting polymer layer, whereas the potential difference across the interface of the ISE membrane and the conducting polymer is determined by the ion distribution. The ability of conducting polymers to be oxidized or reduced gives them redox buffer capacity, although the conducting polymers are not ideal redox buffers due to the continuum of redox potentials that they represent (Jinbo et al., 2016). Overall, there are few materials that can be used as the solid contact conducting polymers: polypyrrole (PPY), poly(3-octylthiophene) (POT), polyaniline (PANI), and poly(3,4-ethylenedioxythiophene) (PEDOT) (Cadogan et al., 1992, Bobacka et al., 1994, Bobacka et al., 1995, Bobacka et al., 1999). The sensing membrane most often coated onto the electrode is PVC (Jinbo et al., 2016). An experiment optimized the capacitance of conducting polymers for solid contact ion-selective electrodes (Zaneta et al., 2015). They found that poly(3,4-ethylenedioxythiophene) (PEDOT) as the conducting polymer was characterized by its high stability, high ionic mobility and fast charge transfer rate. These unique electrochemical properties result in a relatively high redox capacitance. Therefore, PEDOT became the most potential choice for our sensor design project. For an asymmetric all-solid-state ISE that contains conducting polymer as an ion-to-electron transducer between the solid base electrode and sensing membrane surrounding with detected liquid, the detection limit of the ISE can greatly be improved by means of the external current compensation in the process of condition adjustment (Huang et al., 2012).

In addition to coating glass onto the metal metal rial of the electrodes, there is another category of sensors which are polymer-based sensors. Few polymers were used in the ion-selective electrodes fabrication to prevent the hydrophilic nature of phosphate. Gold electrodes coated with polyanilline was built although it showed that the good lifetime but the sensitivity varied in different interference solution (Huang et al., 2017). Satoh et al. proposed an ionosphere-doped polyvinyl chloride (PVC) membrane based electrodes in 2017. The sensitivity result was shown good but with an extremely short lifetime (shorter than five hours). Another research described a novel PVC membrane doped with a chitosan-clay composite (Topcu et al., 2017). After conditioning in Cr(III) solution, the as prepared electrode exhibits anionic response, especially selective and sensitive toward HPO_4^{2-} (Topcu et al., 2017). Metal complex based sensors is another choice of the component of compositing a ion-selective electrode. Copper phthalocyanine (CuPc) can be implemented in the phosphate sensors. The CuPc with a capacitive transduction has a better performance and the ability of preventing the interferences of anions (Forano et al., 2018).

We also looked into the published patent from world intellectual property organization. WO2014/177856 AI by Canfield University described a polymer based phosphate sensor. WO 2012/154028 AI by Technology Park Malaysia described an ion-selective electrode of a cobalt Mano-articles substrate with a conductor layer. They used screen printed electrodes as the substrate of the working electrode. After taking all the existed designs above into consideration with our design criteria, specifically, the detecting range is from 0.01 to 1.00 mg/L, our final working electrode design are referring to these following different ion-selective electrodes: cobalt electrode with oxide layer; carbon paste electrodes modified with zeolite; polyamide **PVC** based ionophore electrode with membrane. in in

4.2.1 Chosen Design Components for Sensor

1- Reference electrode: Ag/AgCl electrode

2- Working electrode: Gold electrode coated with CuPc sensing membrane fabricated by drop casting a solution of 1 ml of tetrahydrofuran and 4 mg of copper phthalocyanine.

3- Potentiometer or voltmeter to read the voltage for different phosphate concentrations

The reference electrode and working electrode are connected using a BNC adaptor and alligator clip wires to the potentiometer. Figure 5 illustrates this sensor design.



Fig. 5. Initial Theoretical Phosphate Sensor Design



Fig. 6 Actual Sensor System with potentiometer (left), reference and gold electrode (right)

The actual sensor assembly is shown in Figure 6 with the potentiometer connected to the reference and gold electrodes using a BNC connector and alligator clips. The final design is expected to fulfill our low phosphate detection requirements. Further test and analysis occurred to see the response time and functionality of the sensor at different phosphate concentrations. The sensor will be easily operated. The sensor is not meant to be built as an autonomous system, it is used for individual water samples and for in-lab use as a first prototype. The water samples need to be brought to the lab where the sensor is set up, as it is not quite robust to be brought to the field where outside air can interfere with voltage readings.

4.3 Design Considerations

4.3.1 Environmental Considerations

Electrical components will be purchased for the sensor fabrication. The individual components after the sensor's lifecycle ends shall be either disposed of in a safe way or preferably recycled or reused. Another option is to give some of the components another life, meaning they are to be reused in other projects. For example, the ion meter (potentiometer) that

will be used as part of our design can be used for other experiments or projects if our sensor design fails or reaches its end of lifecycle.

The electrochemical sensor should not be harming the environment on the contrary, it is meant to be built for monitoring environmental pollutants in water. The electrochemical sensor method was chosen over the colorimetric detection method because less reagents are needed, that means less reagents that are disposed. A consideration to keep in mind when we purchased the components of the sensor was to source the components from as close a supplier as possible. For example, given the choice of a potentiometer or electrode from a European or American company, choosing the American supplier is better as we are not wasting transportation cost and lowering the environmental impact as much as possible of our design. Overall, our specific ISE sensor is meant to help detect environmental analytes that are difficult to measure using conventional techniques especially in-situ contexts and outside of the laboratory and should not be harming the environment because this sensor aims to improve the water quality of drainage water by monitoring nutrient concentrations (Hayat et al., 2014).

4.3.2 Ergonomic and Risk Considerations

The risk involved with handling most sensors is the potential hazards that come with handling and using reagents. The exposure of reagents can occur through the eyes, skin, by inhalation or ingestion and can cause irritation and harm if inhaled or ingested. Fortunately there are no specific effects of such reagents but all chemicals used in-lab or in-field must be handled with caution. It is important to read and be aware of each reagent safety guide and know the first aid measures if there is eye and skin contact, inhalation or ingestion. If there is accidental release, it is important to use protective equipment while cleaning up with an inert absorbent material (Life Technologies, 2013). For hand protection, wearing impervious gloves and safety glasses when handling such material is important. Protective clothing is also vital, wearing a lab coat on top of any outfit is needed. Handling all material in accordance to good industrial hygiene and safety is necessary. All reagent products should not be entering drains and must be disposed of in accordance to local regulations. Even though our method of choice is not the colorimetric detection method but the electrochemical sensor, use and safety handling of electrical components and chemicals while constructing the sensor prototype is crucial. Electrochemical

sensors are shrinking in size and weight making them more portable and easier for people to use, meaning more ergonomically friendly. That is why we chose the ISE system design. Having a probe that can be inserted in water without the need of reagents like the colorimetric method makes for an easy system students, farmers and most people can use without much prior sensing knowledge.

Hazard	Consequences	Severity	Likelihood	Risk	Recommendations
Coating Fabrication for sensor	Toxic fumes	1	3	3	Using a fume hood, mask, lab coat and gloves when handling chemicals
Wire failure	Electrocution	2	3	6	Using wires and alligator clips with insulation
Buffer solution skin contact	Burn or skin irritation	5	2	10	Pouring buffer solutions while wearing protecting gloves

Table 5. Risk Factor Matrix of Sensor System

The risk factor matrix shown in Table 5 above shows different potential hazards with our sensor system, the associated consequences and recommendations to mitigate the risk. The severity of the hazard is quantified from 1 to 5, the likelihood from 1 to 5, and the risk from 1 to 10 where 1 is high and 5 or 10 is low. The risk is obtained by multiplying the severity and likelihood numbers together.

4.3.3 Economic Considerations

Analyzing samples using the in-lab Lachat spectrophotometer costs around 12\$/sample as each sample is analyzed in 3 trials for 4\$ each. Lab supplies needed such as the filter and syringe for each trial costs 2\$/sample approximately. Thus the current method costs around 14\$/sample. Products that are on the market range from 20 to 30000\$ (the hydrocycle PO4 by Seabird Scientific). The Hydrocycle is an autonomous colorimetric sensor that is installed in situ but is very costly and has to be submerged in water like rivers and lakes. The market sensor that is most similar to our design, the ISE portable sensor by CleanGrow costs around 3800 \$. The innovative sensor designed by a UK company measures different ions and monohydrogen phosphate is an option. However, the sensitivity is not low enough and the cost is quite high. The sensor we wish to employ will have the following cost components.

Material	Company	Price	Quantity
Gold Working electrode	CH Instruments	1135\$	1
Reference Ag/AgCl electrode	ColeParmer	135\$	1
Handheld Voltmeter	ColeParmer	830\$	1
Sand Paper 700 Grade	Canadian Tire	10\$	1
Chemicals	Company	Price	Quantity
Copper Phthalocyanine	Sigma Aldrich	300\$	1
Tetrahydrofuran	Sigma Aldrich	50\$	1
Total Capital Cos	st 2460\$		

Table 6. Bill of materials for sensor fabrication

The current method to analyze samples usually take 48 hours as well as manual labour and a high cost of 14\$/sample. That includes the cost of lab analysis as well as lab supplies needed, the syringe and filter needed to filter the raw water samples. As for our ISE sensor, the capital cost of the sensor is 2460\$. It is still cheaper than the most similar on the market sensor manufactured by CleanGrow by about 1800\$. As for the operating cost, Kimtech tissues used to dry the electrodes are used as well as Ph buffers. The buffers are used for standardizing the reference electrode thus Ph buffers of 4, 7 and 10 are needed. The total cost of the sensor is 2460\$ and a recurring cost of 1.50\$/ sample.

Using the following formula, we solve for x which is the number of samples it takes for our sensor system to be more cost effective compared to the current method. The current method cost is shown on the right side, it costs 14\$ per sample. The proposed sensor cost is shown on the left side, it costs 2460\$ with a recurring cost of 1.50\$ per sample.

$$2460 + 1.5x = 14x$$

The equation was solved for x which gave 197 samples. Each summer, the Water Innovation's Lab gather and analyze around 600 samples per summer.



Fig. 7 Cost comparison of sensor and current method

Thus, as seen in Figure 7 above, after around 200 samples, the sensor proposed will be beneficial economically. Since around 600 samples are analyzed per year, the sensor proposed will save around 5040\$.

5. Sensor Design Fabrication

5.1 Sensor Assembly

The phosphate sensor was built in the lab with the following purchased materials; an Oakton Ion6+ Handheld Potentiometer Kit, one Ag/AgCl reference electrode purchased from ColeParmer, and one gold working electrode, which is 8 cm long and has a 2mm radius, purchased from CH Instrument Inc. The gold working electrode and the Ag/AgCl reference electrode were connected to a BNC connector adaptor then connected with the alligator clips to the potentiometer.

5.2 Standardization of Reference Electrode

The reference electrode needed to be standardized before calibrating and testing the water samples. The standardization procedure was followed according to the user manual provided by the manufacturer. At least two different pH buffer solution were used in the standardization of the reference electrode. In this case, the pH4 and pH7 buffer solutions were used. The potentiometer was turned into calibration mode for pH reading. The standardization started with the pH7 buffer solution first. The reference electrode and the thermometer were cleaned prior and immersed into the buffer solution. The correlating measurements of two different buffer solutions were adjusted by pressing on the "up" or "down" button on the potentiometer. Adjustment of the reading was restricted to the temperature of the buffer solution. The standardization of the working electrode with the buffer solutions is shown in Figure 8 below.



Fig. 8. Standardization of reference electrode

5.3 Calibration of the Working Electrode

The calibration of the working electrode was conducted before testing the sensor system. First, manual calibration prior was done. This step is for creating a calibration line manually by gathering the corresponding measurements of known phosphate concentration solution from the potentiometer. Multiple trials are needed to achieve this linear line.

During calibration, three known concentrations of phosphate standard solutions were used, 0.01 mg/L, 0.1 mg/L and 1 mg/L. All the standard phosphate solutions were safely stored in the fridge in the lab. First, each of the phosphate standard solution were measured in a fixed volume of 20 ml and transferred into a 100ml beaker for detection. Secondly, the gold working electrode and the Ag/AgCl reference electrode were rinsed with deionized water before use and dried with Kimtech lab-use tissue. Thirdly, the electrode system was dipped into the solution and stirred gently. Then, the potential difference in mV was recorded and its corresponding response time (min). Measurement was taken in a time interval of 2 minutes and lasted for 16 minutes, after the sensor has stabilized values. Finally, the gold working electrode and the Ag/AgCl reference electrodes were rinsed after the measurement with deionized water and dried with Kimtech tissue.

The previous procedure was repeated for the next known phosphate concentration standard solution detection. The response time of the sensor was recorded when the reading on the potentiometer stopped blinking. The measurement of the phosphate ion activities is stable at this time. The calibration line of this measurement was created and recorded manually in the Excel software.

5.4 Gold Electrode Coating

The preparation of the sensing membrane was studied and referred to from the research paper "Novel Sensitive Impedimetric Microsensor for Phosphate Detection Based on a Novel Copper Phthalocyanine Derivative". The amount of chemicals were rescaled to the desired specification of the gold electrode our system uses. Copper phthalocyanine and tetrahydrofuran are the critical chemicals needed in this step. The chemicals were purchased from Sigma Aldrich from the United States and shipped to the lab and stored safely. The in-lab preparation of the chemical mixture was conducted by the following steps. First, 4 mg of copper phthalocyanine were weighed with a scale balance and deposited into a small boat holder. Then, a 5ml syringe was used to take 1 ml of tetrahydrofuran from the bottle and deposited that into the beaker. The CuPC powder was mixed into the 1 ml of tetrahydrofuran beaker. Around 0.025 ml of mixed solution was coated onto the gold electrode tip and dried for 24 hours at room temperature.



Fig. 9. Copper phthalocyanine and tetrahydrofuran mixture



Fig. 10. Coated gold electrode

The authors used a centrifuge because they used a plate gold electrode unlike our system that is using a gold electrode tip that needs to be coated. The disadvantage is that it might not be easy to get a uniform coating to obtain a specific thickness compared to the centrifuge method. Another possible drawback of drop-casting is that even under ideal conditions, differences in evaporation rates across the substrate can lead to variations in film thickness and therefore sensor accuracy. However, drop-casting does serve as a quick and accessible method to make a thin coating film on the small substrate that is the gold electrode, and was used for this sensor system.

6. Results & Discussion

6.1 Pre-coated Electrode Sensor

In order to assess the sensor built, the functionality of the sensor was assessed before coating and after coating the gold electrode for comparison reasons and to see if the chemical coating improved the sensor's ion selectivity and accuracy. Prior to the testing of the electrode, the reference electrode was standardized following the manual. The main target of this whole project is to measure the phosphate level in the agricultural drainage water and due to the acidic property of phosphate solution we used pH 4 and pH 7 buffer solution in the standardization step. The detailed standardization procedure is mentioned in the above section. Calibration and testing of the working electrode was also implemented before the coating of the electrode occurred. The detailed calibration procedure was mentioned in the design section.

As previously mentioned, 0.01 mg P/L, 0.1 mg P/L and 1.0 mg P/L phosphate solutions were used as the standard calibration solutions. The mV readings and response times were recorded. Two trials of testing with the uncoated working electrode were conducted. The following table is the recorded data:

Potential (mV)	0	2 min	4 min	6 min	8 min	10 min	12 min	14 min	16 min
0.01 mg P/L	33	37.2	39.3	40.6	42.2	43.1	44	44.6	45
0.1 mg P/L	210	191.2	185.2	181.1	178.1	175.1	173.2	172.4	170.4
1.0 mg P/L	2.96	20.8	225	207	208	209	209	209	209

Table 7. First trial mV readings of gold electrode without coating

Potential (mV)	0	2 min	4 min	6 min	8 min	10 min	12 min	14 min	16 min
0.01 mg P/L	352	344	319	290	294	296	300	300	301
0.1 mg P/L	347	333	327	317	316	312	309	308	309
1.0 mg P/L	364	338	331	324	319	315	311	310	309

Table 8. Second trial mV readings of gold electrode without coating



Fig. 11. Response time of first trial without coating



Fig.12 Response time of second trial without coating

As shown in Figure 11 above, the first trial calibration of the uncoated electrode was not too successful, understandably, as it was the first time the sensor was being used. The second trial had better results and is shown in Figure 12 above. Due to the inaccuracy of data that is difficult to analyze for the first trial, the calibration line was only done for the second trial which had more stabilized values and a response time of about 12 minutes. Figure 13 below shoes the calibration line and equation of the second trial with the uncoated gold electrode. It is not very linear and has a very low R^2 value.



Fig.13 Calibration line of second trial without coating

6.2 Coated Electrode Sensor

The gold electrode was coated after the 2 trials were conducted pre-coating. Three standard solutions were used to calibrate again, 0.01 mg P/L, 0.1 mg P/L and 1.0 mg P/L. The mV readings and response times were recorded. Three trials of testing with the uncoated working electrode were conducted. The following table 10, 11 and 12 show the recorded data:

First Trial (mV)	0	2 min	4 min	6 min	8 min	10 min	12 min
0.01 mg P/L	160	178.7	189.4	196.6	200	205	209
0.1 mg P/L	247	244	243	242	243	243	243
1.0 mg P/L	227	247	236	232	231	231	231

Table 10. mV readings of first trial with coating

Second Trial (mV)	0	2 min	4 min	6 min	8 min	10 min	12 min
0.01 mg P/L	222	222	221	221	222	222	222
0.1 mg P/:	243	243	243	243	243	243	243
1.0 mg P/L	258	248	241	240	239	239	239

Table 11. mV readings of second trial with coating

Third Trial (mV)	0	2 min	4 min	6 min	8 min	10 min	12 min
0.01 mg P/L	233	229	227	227	228	228	228
0.1 mg P/:	254	247	245	245	245	245	245
1.0 mg P/L	259	249	246	244	244	244	244

Table 12. mV readings of third trial with coating



Fig. 14. Response time of first test with coating



Fig. 15. Calibration line of the first test of coated electrode



Fig. 16. Response time of second test with coating



Fig. 17. Calibration line of second test with coating



Fig. 18. Response time of third test with coating



Fig. 19. Calibration line of third test with coating

The following discussion relates to all the results combined and shown previously from figure 14 to 19. First of all, compared to the uncoated gold electrode system that had a response time of 12 minutes, the coated sensor system has a response time of 6 minutes shown in the

figures 14, 16, and 18. It is safe to say that coating the gold electrode with the CuPc and THF chemical mixture improved the response time of the sensor, an important characteristic of sensors.

Secondly, by comparing the calibration lines generated in both the pre-coated and postcoated tests, it was found that both electrodes did not respond well to a relative high concentration of standard phosphate solution. With each trial, the R^2 value improved of the calibration line, an indicator of the perfect fit with 1 being perfectly correlated data points. The first trial had an R^2 of 0.06145, the second trial 0.17042, and the third and best one was 0.27628. However, this is still a low R^2 value and shows that our sensor's different data points are not showing a good linear calibration line and consequently will show inaccurate results possibly.

To examine the accuracy of the calibration lines generated, the 0.5 mg P/L standard was detected using the sensor. The coated electrode gave a 32% error and the pre-coated electrode gave a 20% error using the calibration line. After coating, the calibration results were worse than the pre-coated results, an unexpected and unfortunate outcome.

The response time of the coated working electrode is much shorter than the pre-coated electrode. The average response time of the phosphate ion detection decreased from 12-14 mins to 4-6mins. The CuPc sensing membrane improved the response time of the sensor system. However, the stability of the sensing membrane needs to be studied and researched more in the future as it was not extremely worth the time and cost in our sensor case. In chart 5, a big fluctuation was observed during the beginning 2 minutes.

Next, the following are raw water test results recorded in Table 13. This is to see if the sensor works in raw water samples similarly to the standard phosphate samples. The raw water samples are similar to what the research team collects from the field.

	Concentration	0min	4min	6min	8min	10min	12min
1 st trial	unknown	273	259	258	258	258	258
2 nd trial	unknown	190.8	202	208	211	211	211
3 rd trial	unknown	235	232	232	232	232	232

Table 13. Measurement of raw water samples with coated electrode



Fig. 20. Response time of raw water sample

	Known	0	4 min	6 min	8 min	10 min	12 min
	Concentration						
1 st trial	0.05 mg P/L	281	276	281	281	281	281
2 nd trial	0.05 mg P/L	286	281	281	281	281	281
3 rd trial	0.05 mg P/L	268	277	276	276	276	276

Table 14. measurement of 0.05 mg P/L with coated electrode



Fig. 21. Response time of 0.05 mg/L sample

The coated electrode showed a good response time, both raw water and known concentration water measurements stabilized around 4 to 6 minutes. We took the stabilized potentiometric reading back to the calibration line we created; the result showed a 1660% error regarding the 0.05 mg P/L water sample. From the graph and linear interpolation, the actual concentration found from the sensor gave a value of 0.88 mg/L when the actual concentration is 0.05 mg/L.

The raw water sample was sent to the soil lab and analyzed using the colorimetric method with the LaChat spectrometer. The concentration of the raw water was found to be 0.025 mg P/L while using the sensor system, a value of 0.4 mg/L was found. The calculated result showed a 1500% error. Overall, the sensor did not perform very well with lower phosphate concentration. Furthermore, it seems that the sensor coating was decaying with time because the raw water sample and 0.05 mg/L sample were detected around 2 weeks after coating of the electrode. Also, the measurements are highly affected by the surrounding environment and if it is to be taken to the field, a housing unit is highly recommended.

In summary, the gold electrode chemical coating improved the response time by half, from 12 minutes to 6 minutes. However, the coating has drawbacks. It is very time consuming and challenging to do in perfect conditions. The possibility of contamination and inaccurate measurement of chemicals makes the coating challenging to execute perfectly. Despite the

difficulty of the coating, it did not improve sensor accuracy by much. The sensor also has limitations. First, calibration using 0.01, 0.1, and 1 mg/L is needed before each analysis. Also, the sensor needs to be used in the lab as it is very sensitive to the environment. Therefore, if it is to be potentially taken to the field, a housing unit is recommended to keep the sensor in a controlled environment.

After 3 weeks of testing, we obtained inaccurate concentration results from a raw water sample, shown in Table 13 and Figure 20, and a standard P sample (0.05 mg/L) shown in Table 14 and Figure 21. The assumption is that the sensor coating decay was the reason of such a high % error found between the sensor and actual concentration values.

7. Conclusion

To conclude, although there are many innovative sensors and different detection methods available, the electrochemical sensing system is most promising. The Ion Selective Electrode design proposed was built, calibrated using known low phosphate levels, and finally tested with different water samples. The coating of the gold electrode improved the response time. However, the extra cost and time to do the coating did not improve accuracy of measurements. The cost analysis showed that the sensor payback period occurs after 200 samples are analyzed. Further research is needed to improve the sensitivity of the sensor. The challenge persists to fabricate a phosphate sensor for drainage water with low phosphate concentrations.

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