Development ion phosphate sensor system for precision farming

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Abstract. Indonesia as an agricultural country has agricultural lands are quite spacious and most of the people working in this sector. However, agricultural production has not yet fulfilled domestic demand. One effort to increase agricultural production is to apply precision farming method where conducted monitoring and analysis of soil conditions prior to land management activities by using sensor technology. This paper described the development of sensor systems for measuring ion phosphate concentration as the main nutrient. The sensor employs an electrochemical amperometric measurement technique, based conductive polymer as an ion-sensitive membrane through electro-polymerization technique and electrode fabrication using thick film technology. Three configuration electrodes has been used for the sensor and working and auxiliary electrode was made by carbon while the reference electrode fabricated use silver|silver chloride. The ion phosphate sensor was characterized using a standard phosphate solution 10⁻⁶ - 10⁻² M and produced current about 4 to 41 μA with 98 % linearity, and 150 seconds average of response time. In addition, signal conditioning and data acquisition as electronic circuit system which has support the sensor have been designed and fabricated.

1. Introduction
Phosphate is one of the main nutrients required by plants for proper growth. Phosphate (P) is a naturally occurring element in the environment that can be found in all living organisms as well as in water and soils. Phosphate also plays an important role in photosynthesis, respiration, seed and fruit production, energy production. Adequate supplies of P can enhance early root formation, growth and seed production of fruit and vegetable. The primary functions of P in plants are structural component of proteins, enzymes, nucleic acids, and DNA, photosynthesis (production of sugars and starches) and respiration (producing energy by oxidizing sugars and starches). Therefore, the presence of P in soil is very important for agriculture. However, P is easy losses from agriculture field and it can be a major source of P entering lakes and streams that can stimulate weed and algae growth. The major concern with elevated phosphate levels in aquatic ecosystems is eutrophication, a process in which water bodies receive excess nutrients that stimulate excess plant growth.¹ ²
Nowadays, in-field sensor technology is developing into an advantageous alternative due to some benefits such as in situ measurement, fast response and compact compare than conventional nutrient monitoring involving sophisticated analyses in the laboratory. Sensors can be used to measure many chemical properties including pH, salinity, conductivity, calcium, potassium, phosphate and nitrate. In-field monitoring sensors provide real time data over a large area of land and have relatively low production costs. Several analytical techniques have been used for nutrient measurement such as spectroscopic and electrochemical detection.

Precision farming (PF) is defined as management system of an agriculture field was employed information and technology to measure, identify, analyze and manage variability to gain optimum profitability, sustainability, and protection of resources. PF which has been growing and gaining attention rapidly in many countries aims to reduce the environmental impact of agricultural activities but at the same time to increase productivity, by optimizing the input and output and maintaining soil quality by apply the sensor technology. PF technology can be employ in all of the plant production cycle aspects starting from pre-planting up to harvesting activity. This technology is implement for soil testing, soil tillage, planting, fertilizing, spraying, crop scouting, and harvesting. The practical use of PF needs a good integrated system approach that combines hardware including sensor to detect amount of fertilizers in soil with software systems.

In this paper, we designed and fabricated ion phosphate sensor system including signal conditioning and data acquisition circuit. The device sensor consists of two main parts, electrodes and sensitive layer. The electrodes of ion phosphate sensor have follow amperometric three electrodes mechanism: working, counter and reference electrode. All electrodes have been fabricated by thick film technology or screen printing use Au (gold) for working, counter and Ag|AgCl (silver|silver chloride) for reference electrode. The sensitive layer of ion phosphate sensor was employ conductive polymer (polypyrrole) and doped by ion phosphate through electrochemical deposition process.

2. Material and methods

2.1. Ion phosphate sensor fabrication

All chemical reagents were analytically pure grade and used as purchased from Aldrich or Merck without further purification. Pyrrole was refrigerated in the dark and purified before use by passing pure pyrrole through an alumina (Al₂O₃) column. Ammonium phosphate (hygroscopic grade reagent) was dried in an oven at 80–100 ºC before use. Thick film Carbon and Ag|AgCl paste were purchased from DuPont. All aqueous solutions were prepared using deionized water with a resistivity of 18 MΩ-cm. The ion phosphate sensors were fabricated in bulk using screen-printing technology on an alumina substrate. Figure 1a shows a detailed configuration of ion phosphate sensor including the dimension. Each sensor comprised of three electrodes: Carbon (C) working and Silver (Ag) counter electrodes, and an Ag/AgCl reference electrode.

![Figure 1](image-url)

Figure 1. (a) The structure and dimension of thick film ion phosphate sensor based on conductive polymer design on alumina substrate. (b) As prepare thick film ion phosphate sensor.
2.2 Preparation of phosphate-doped polypyrrole \((PPy(PO_4^{3-}))\) thick film sensor electrode

Polymerization of pyrrole doped with phosphate onto carbon electrode on alumina substrate was performed electrochemically as known as electro-polymerization. The schematic of electro-polymerization pyrrole monomer doped by ion phosphate on carbon working electrode surface shows in Figure 2. A voltage source was used to supply a constant current for electro-polymerization. The initial polymerization solution consisted of 1 M pyrrole and 0.1 M \((NH_4)_3PO_4\) in aqueous media. The solution was deoxygenated by purging it with nitrogen for 5–10 min before and during polymerization experiment. A one compartment cell was employed including C, Ag|AgCl and Ag printed on alumina substrate as working, reference and counter electrode, respectively. Polymerization was performed under constant current conditions (current densities 1.5–2.1 mA/cm\(^2\)) for 20 min. The freshly prepared phosphate-doped polypyrrole \((PPy(PO_4^{3-}))\) on carbon electrodes were rinsed with water and conditioned for at least 24 h in a 0.01M \((NH_4)_3PO_4\) solution at room temperature in the dark.

![Figure 2. Schematic diagram of the electro-polymerization apparatus, gold electrode of sensor as cathode and platinum as the anode electrode. “d” is the distance between the cathode and anode](image)

2.3 Electronic supported system

Amperometric sensors use transference processes of ionic to electronic charges between electro active sample and an electrode. An electrical current is settled through the sensor device immersed in a solution and directly related to the sample concentration. A two-electrode configuration (working and reference electrodes) can be used when low currents are needed. However, when currents higher than ten microamperes are applied, reference potential losses, become important and subjected to characteristics of the solution. Thus, some changes are generated in the reference electrode that influence the cell stability. Therefore, a counter electrode is added to the cell become three-electrode configuration avoiding current pass by the reference electrode. Hence, instrumentation must be designed and fabricated to fulfill similar requirements to complete a very useful but simple, reliable and portable measuring amperometric system. Figure 3 shows a block diagram of the instrument or electronic supported system.
Potentiostat is a circuit for maintaining a constant voltage between reference and working electrodes. The circuit compensates possible voltage losses due to the chemical solution and also allows a very low current circulation by the reference electrode. The current-voltage converter produces a voltage proportional to the working electrode current and the output circuit adequate its current-voltage values to those corresponding to chemical concentration; at least two amplification factors were required. An adjustable circuit for cell polarization in the range 0-2.5 V and also for compensating purposes when expanded scale is needed, were also included.

The data acquisition including main controller and analog-digital converter circuit has been designed and fabricated as a part of electronic supported system for ion phosphate sensor. The block diagram of data acquisition shows on Figure 4.

2.4 Characterization and measurement
Scanning electron microscopy (SEM) images for morphology of polypyrrole film doped by PO$_4^{3-}$ as sensitive layer was perform using a SEM (SEM, IT-300, JEOL, Japan). The amperometric measurement of ion phosphate sensor device was perform using open source potentiostat (Rodeostat, RSAT-01, IORODEO, USA).

3. Results and discussion
Polypyrrole is one of the most intensive studied conducting polymers because of its easy preparation, high conductivity and more stable. Generally, the polymerization process of pyrrole (C$_4$H$_5$N) requires at least two moles of electron per one mole of pyrrole. In the oxidized state, polypyrrole exist as a polyradical cation, and at the oxidation stage anions (PO$_4^{3-}$) will attracted electrostatically into a polymerize conducting polymer film as a counter ions (dopant). The Figure 1b shows the fabricated ion sensor device and polypyrrole film doped by PO$_4^{3-}$ has successfully deposit on carbon surface as working electrode. The morphology of polypyrrole film doped by PO$_4^{3-}$ has exhibit in figure 5. Based
on the data in figure 5, it is clearly shown the rough surface in amorphous bulk form indicates polymer layer has growth on metal surface. According previous studies, there is an impregnable relationship between synthesis conditions and the morphology of the synthesized polypyrrole film. The electropolymerization conditions that affect the polymerization processes include electrolyte anions, solvents, pH values of the aqueous solutions, and polymerization temperature, current/potential ratio and etc.

The electro-polymerization process of pyrrole mainly consists of two continuous steps. The first step is the diffusion of pyrrole monomer to the carbon electrode surface, the rate of this step is determined by the monomer concentration. The second step is the oxidation reaction of pyrrole at the interface between the electrode and electrolyte solution. Because the applied current density and the electrolyte concentration were kept constant, therefore the rate of the reaction was determined by the amount of monomer available at the interface at unit time. For higher monomer concentration the positive charge at the working electrode is rapidly consumed by pyrrole, the accumulation of the charge at the electrode is lower, consequently the corresponding reaction potential is lower. At lower monomer concentration, the positive charge cannot be consumed by pyrrole immediately, thus some charge will be accumulated at the working electrode, resulting in a higher reaction potential.10

![Figure 5. SEM image of PPy/PO₄³⁻ on carbon electrode.](image)

The signal conditioning and data acquisition circuit (main controller and output signal processing) as electronic supported system. The system has been successfully fabricated into compact and integrated as shown in figure 6a and figure 6b. The ion phosphate sensor system has equipped with a 90 cm length probe provides a housing for sensor devices and connector for electronic supported system as exhibits in figure 5b and c. The signal conditioning consists of several parts as explained before such as bias source, potentiostat and amplifier. Potentiostat is a circuit for maintaining invariable the voltage between reference and working electrode. This circuit compensates possible due to the chemical solution and also permits a very low current circulation by the reference electrode. Amplifier circuit consist of two amplification features and current-voltage (I-V) converter. The I-V converter convert the working electrode current into voltage which has proportional to concentration of phosphate standard solution.

Ion phosphate sensor device characterization was performing in two steps. Firstly, the prototype Ag/AgCl reference electrode was measure against commercial double junction reference electrode (Accumet, USA) to evaluate the stability for 10 minutes. The stability test curve of three prototype
Ag|AgCl reference electrodes and each of it was compare against commercial double junction reference electrode as shows in figure 7. The average data showed voltage difference around 0.3 mV ± 0.001 with good stability for 10 minutes measurement compare to commercial electrode. Hence, the prototype double junction Ag|AgCl reference electrode can be used for ion phosphate sensor.

Secondly, the sensor need to characterize electrochemically by direct measuring ion phosphate standard solution with different concentration range from 10 µM to 0.1 M and stability of reference electrode Ag|AgCl against commercial product from Accumet. The stability of reference electrode to maintain voltage reference is very important to measure because it will influence the performance of amperometric three-electrode configuration sensor. The stability curve of prototype reference electrode is quite good with average voltage different estimate around 0.3 mV for 200 seconds observation as shows on figure 7a. The amperometric measurement of ion phosphate sensor was conducted by potentiostat and the results shows the output current will rise as the concentration ion PO$_4^{3-}$ increase gradually. The response of sensor due to various ion PO$_4^{3-}$ standard solution as calibration curve is exhibit in figure 7. The response time of the sensor was on the order of a few seconds. The ion phosphate sensor exhibited amperometric behavior (slopes 0.255 ± 0.0214 µA per log cycle of phosphate concentration (n = 5), at T = 25 °C) and a detection limit 10$^{-5}$ M of phosphate.

Figure 6. (a) The prototype of signal conditioning and data acquisition, (b) Integration of electronic sub-system and sensor’s probe, (c) The prototype of ion phosphate sensor’s probe.
Figure 7. (a) The stability curve of prototype Ag|AgCl reference electrode based on thick film technology versus commercial double junction Ag|AgCl reference electrode. (b) Amperometric response of PPy(PO$_4^{3-}$) film on carbon electrodes to PO$_4^{3-}$ ion standard solution (T= 25°C). Deposition of PPy(PO$_4^{3-}$) layer at constant current densities 1.5–2.1 mA/cm$^2$ for 20 min.

According to calibration curve of sensor as showed in figure 7, current amplification factor need to be assigned in signal conditioning circuit and it will help to minimize error during I-V conversion and further processing signal from sensor so it can either store into memory or send to master station through wireless communication. The integration of sensor sensor device and electronic supported system has been conducted into a compact system and perform good for is situ measurement.

4. Conclusion

In summary, we have successfully design and develop ion phosphate sensor system which is apply in precision farming. The system consists of two main parts: sensor device and electronic supported system. The sensor device of ion phosphate (PO$_4^{3-}$) was fabricated based on thick film technology with three electrode configuration (working, reference and counter electrode) and on working electrode has been deposited a sensitive layer to detect made of conductive polymer pyrrole doped by ion phosphate. Similarly, the electronic supported system consists of several part such as signal conditioning, data acquisition and wireless communication circuit has been designed, fabricate and connected to device ion phosphate sensor. The sensor system performed very good measurement response in various concentration of ion phosphate standard solution with low detection limit. Thus, it is applicable for precision farming as sensor nodes through wireless sensor network system.

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