

Development and Application of Co-C Electrodes for Potentiometric Determination of Phosphate Ion in Agricultural Soils Compared to Spectrophotometric Method

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Phosphorus is a nutrient in the soil that is used by plants to grow, so its presence needs to be known as basic information in land management. Phosphorus content analysis is usually carried out by measuring phosphate ions extracted from soil samples using spectrophotometric methods. This paper reports the results of the development of an alternative phosphate measurement method through the design of a cobalt-based potentiometric electrode capable of selectively detecting phosphate ions. The electrodes were made voltammetrically to reduce the cobalt ions in solution and attach them to the ends of the carbon rods. The cobalt thin layer on the carbon tip is an active part of the Co-C electrode in the process of potentiometric detection of phosphate ions. The results of the characterization of the electrode performance on the measurement of a series of standard phosphate solutions showed that this electrode had a sensitivity value of 28.01 mV/decade. Meanwhile, the selectivity coefficient for interfering ions (NO_3^- , NH_4^+ , K^+ and Cl^-) is <1 which indicates that the interference of these ions does not significantly affect the measurement of the main ion. The electrode also has good precision by showing the value of variation coefficient $<5\%$. Compared with the spectrometric method in the measurement of agricultural soil samples at four locations, it was shown that the Co-C electrodes showed equivalent results, as evidenced by the correlation coefficient of 0.998. It can be stated that the Co-C electrode is very promising to be used as an alternative method of measuring phosphate.

Keywords: Soil phosphate; Co-C electrode; potentiometric method; spectrophotometric method; soil sample analysis

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Soil serves as a medium that provides nutrients and water that plants need to live and grow. Good soil is soil that can provide nutrients needed by plants, one of which is phosphorus which functions for the formation of new cells, activates growth and flowering, accelerates maturation [1], and improves the performance of plant chloroplasts [2]. The availability of phosphorus in the soil is usually insufficient because of its small amount and mostly in a form that cannot be absorbed by plants [3]. The importance of phosphorus in the soil which can affect the quality of plant growth requires an adequate amount of phosphorus, this adequacy can be determined by measuring the form of phosphorus that can be absorbed by plants, namely in the form of phosphate. Measurement of phosphate in soil usually begins with extracting phosphate from the soil, one example is by using a Kelowna extracting solution [4]. Kelowna solution was reported to extract 2.5 times more than 0.5 N NaHCO_3 extractant and was as good as Bray-1 extractant [5].

The most widely used method for measuring phosphate levels today is the spectrophotometric method. This method is known to require a long preparation

stage and requires quite a lot of materials [6]. The equipment is also quite large so that it is not easily applied by the farmer or directly on the spot, so other methods are needed that can cover these shortcomings, one of which is using the potentiometric method. The potentiometric method is an analytical method based on measuring the potential difference of an electrochemical cell consisting of a pair of electrodes and an electrolyte solution. This method has several advantages compared to the spectrophotometric method, including being simpler, energy efficient and easy to adopt for direct measurements in the field.

Many studies have been carried out to determine phosphate levels in the soil using potentiometric methods, one of which is using a cobalt ion selective electrode (ESI) with flow injection analysis (FIA) technique. It has been developed and obtained a low sensitivity of 7,890 mV/decade [7]. Research on the performance analysis of potentiometric methods using pure cobalt wire electrodes has been carried out and provides a low sensitivity value, because the cross-sectional area of the wire electrode used is small [8]. Several researchers have carried out a development to

increase the cross-sectional area of the cobalt electrode by the electrodeposition method. Cobalt can be electrodeposited on a substrate, one of which is on carbon. The result of cobalt deposition on carbon is in the form of a Co-C electrode. This study developed a Co-C electrode as a working electrode with the aim of studying its characteristics in measurements using the potentiometric method. The application was then carried out by analyzing the phosphate content of soil samples in rice fields and compared with the results of measurements using the spectrophotometric method.

EXPERIMENTAL

Chemicals and Materials

The chemicals used in this study were cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) Ammonium fluoride (NH_4F), Potassium Hydrogen Phthalate (KHP) Sodium dihydrogen phosphate monohydrate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$), Ammonium molybdate ($\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$), Antimony potassium tartrate ($\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$), Ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$), Sodium nitrate (NaNO_3), Potassium chloride (KCl), Sodium chloride (NaCl), Ammonium chloride (NH_4Cl). All of these chemicals are analytical grade.

Electrode Development and Characterisation

The main equipment used in the development of the electrode is the Amel 433 potentiostat which is equipped with a glass cell chamber, Ag/AgCl reference electrode, stainless steel counter-electrode, and a carbon electrode as a working electrode as well as a substrate for depositing cobalt metal. The deposition solution was made by mixing 50 mL of 0.01 M cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) with 10 mL of 1 M ammonium chloride (NH_4Cl), then slowly adding 0.02 M ammonium hydroxide (NH_4OH) to adjust the pH of the solution to 6 [9].

The fabrication of Co-C electrodes was carried out by taking the carbon rods of a 1.5 V AA (ABC) battery and cleaning it from the remnants of the battery material using sandpaper, rinsed with distilled water and dried. The carbon rod is inserted in the plastic hose and the remaining space between the carbon wall and the plastic hose wall is filled with slow-drying epoxy-resin (Araldite blue), then left for 24 hours to dry and harden completely. One end of the carbon is then rubbed with sandpaper until the surface is flat and then the carbon surface is smoothed with fine alumina powder, while the other carbon end is connected to a copper wire for connection to the potentiostat. The surface of the carbon rods was rinsed with distilled water, then put into an ultrasonic cleaning bath for 8 minutes and dried at room temperature.

Electrodeposition was carried out using the cyclic voltammetry (CV) technique at a potential range of 0 to -1000 mV, a scan rate of 3 mV/s and performed for 15 cycles. The electrodes resulting from the electrodeposition were then removed from the electrochemical cell, rinsed with distilled water and dried. The electrodeposition was made 3 times so that 3 electrodes were produced.

The initial characterization of the Co-C electrode was carried out by testing it on the measurement of a series of standard phosphate solutions (0.01; 0.1; 1; 10; and 100 ppm) using the potentiometric method. A total of 10 mL of standard phosphate solution was put into a beaker and 0.2 mL of ISA KHP pH 4 solution was added. The solution was homogenized with a magnetic stirrer, then the potential difference was measured using a Co-C electrode and an Ag/AgCl electrode for 3 repetitions. The potential difference obtained is plotted as the y-axis and the concentration log as the x-axis to obtain a calibration curve. The resulting calibration curve data is processed to characterize the performance of the Co-C electrode which includes the sensitivity, selectivity, and precision values.

Sample Analysis using Spectrophotometric and Potentiometric Methods

Agricultural soil samples were taken from 4 rice fields in the Tegalgede area, Jember Regency. Soil samples were taken as much as 1 point and repeated 3 times in each area using a shovel, then put into a plastic container. Phosphate analysis in agricultural soil samples was carried out using potentiometric and spectrometric methods, namely the sample was extracted before measuring. In both methods, 10 grams of sample were weighed, put into a bottle, added 100 mL of Kelowna extractant. The mixture was homogenized with a magnetic stirrer for 10 minutes and filtered through filter paper.

RESULTS AND DISCUSSION

Electrodeposition Carbon-Cobalt Electrode

The voltammogram generated from the electrodeposition process shows clear evidence of a reduction process of Co^{2+} ions to Co which is shown at the reduction peak in the potential area close to -1000 mV when the potential scan is directed towards the reduction process, namely from 0 to -1000 mV relative to the reference electrode Ag/AgCl. (Figure 1: orange line). Meanwhile, when the solution was left in the absence of cobalt $2+$ ions, the potential sweep in the same range resulted in a voltammogram which did not show any redox activity (Figure 1: blue line).

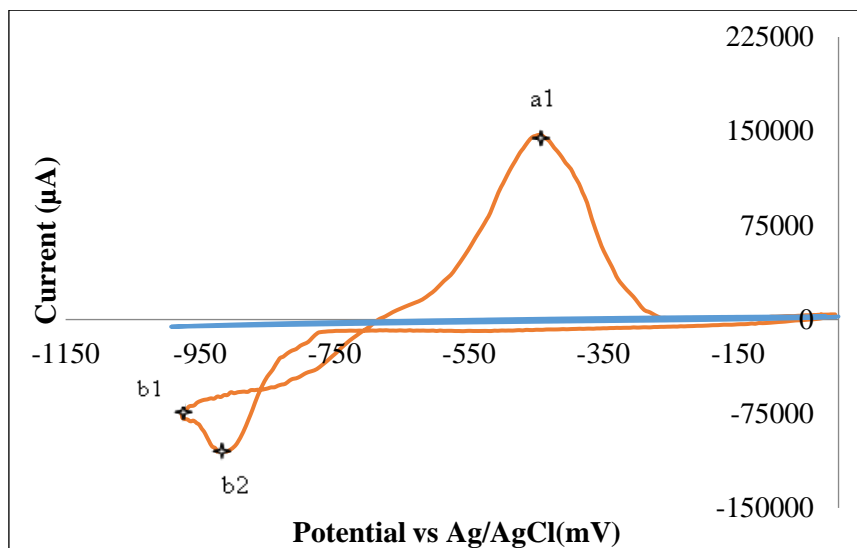


Figure 1. CV Voltammogram of electrodeposition cobalt onto carbon surface (orange) and CV control (blue).

A series of processes of reduction and oxidation of Co^{2+} solution that occurred in the electrodeposition process have been described by previous researchers [10], the resulting voltammogram is also identical. This proves that the carbon coating process by cobalt has been successfully carried out and at the same time shows the prospect of making cobalt electrodes more economical than using whole cobalt wire.

Characterisation of Carbon-Cobalt as Potentiometric Electrode for Phosphate ion

According to Meruva and Meyerrhoff [11], the ability of the Co-C electrode to selectively detect phosphate ions in solution can be explained through 2 reaction stages, namely the cobalt oxidation stage and the formation of a cobalt sulfate thin layer. The first step can occur because the cobalt in the aqueous environment

makes it oxidized and forms an oxide with an oxidation number of +2. Furthermore, in the second stage the formation of a cobalt phosphate thin layer occurs due to the presence of cobalt oxide in the solution environment containing phosphate ions. The most dominant form of phosphate is H_2PO_4^- because the reaction occurs at a pH of around 3-4. Based on this condition, the relationship in Nerst's equation becomes:

$$E = E^0 + \frac{0,0592}{n} \log \frac{[\text{H}^+]^4}{[\text{H}_2\text{PO}_4^-]^2} \quad (\text{Eq. 1}).$$

If the pH value is made constant it will produce a new equation, namely

$$E = E^0 - \frac{0,0592}{n} \log [\text{H}_2\text{PO}_4^-]^2 \quad (\text{Eq. 2})$$

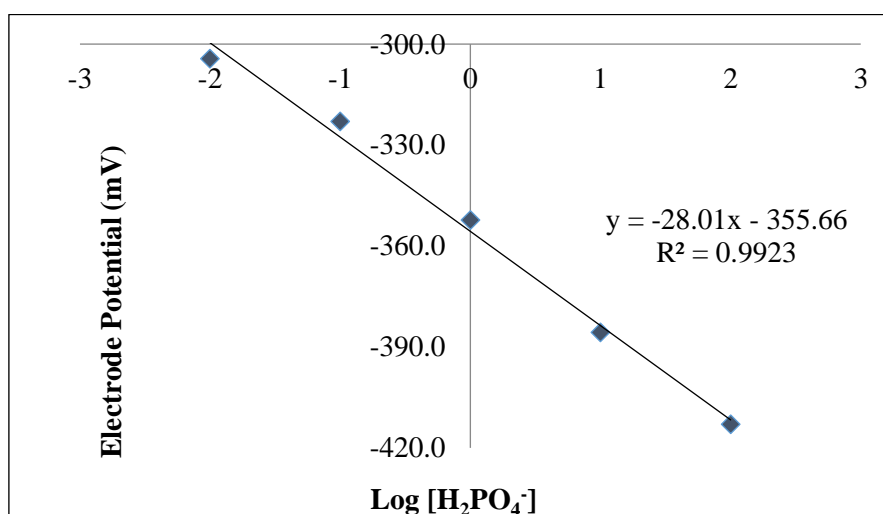


Figure 2. Calibration curve of C-Co electrode using a series of phosphate standard solutions.

Based on equation 2, it can be stated that the greater the log value of the phosphate concentration, the more negative the resulting potential difference. This is very much in accordance with the measurement results of the standard solution as shown in Figure 2.

Based on the calibration graph in Figure 2, phosphate measurement using Co-C electrode showed a sensitivity value of -28.01 mV/decade. The measured phosphate ion is in the form of H_2PO_4 which is a monovalent anion which theoretically has a potentiometric sensitivity value of 50-60 mV/decade. The sensitivity value obtained from this study is smaller than the theoretical value which may be due to the imperfect quality of the cobalt layer so that the interaction process of the cobalt layer with phosphate ions does not fully follow the Nerst equation above (Eq. 2).

Selectivity is the ability of a sensor or electrode to correctly select the target analyte. The presence of chemical species other than the analyte may interfere with its response to the intended analyte. The selectivity value that is commonly used in the measurement using the potentiometric method is the K_{ij}^{Pot} selectivity constant [12]. If the value of $K_{ij}^{Pot} < 1$ foreign ions is considered not disturbing the main ion, while the value of $K_{ij}^{Pot} > 1$ foreign ion is considered to disturb the main ion [13]. In testing the potentiometric response to other ions

such as NO_3^- , NH_4^+ , K^+ and Cl^- , it was shown that the Co-C electrode has good selectivity (KS) as indicated by its selectivity constant value which is smaller than 1 when applied to interfering ions. on. The data from the selectivity measurement can be seen in Table 1.

The precision in this research, which is expressed as the coefficient of variation (Kv) value, still shows good precision, namely the Kv value $< 5\%$. At a concentration of 0.01; 1; and 10 ppm obtained the same Kv value that is equal to 0.190. At concentrations of 0.1 and 100 ppm also obtained the same Kv value is equal to 0.010

Comparison of Soil Analysis between Spectrophotometric and Potentiometric Methods

Phosphate analysis is also carried out on samples with 4 different areas of rice fields (agricultural soils) in potentiometric and spectrometry. Soil samples are used need to be extracted using the Kelowna extractant with extraction time 10 minutes. Kelowna can extract phosphate in the soil because it contains fluoride ion so it is able to replace phosphate which are bound to other compounds [7].

Obtaining the phosphate concentration in the sample in both methods can be used to calculate the value of accuracy (can be seen in Table 2). A good accuracy value is between 80-110% [13].

Table 1. Selectivity constant of Co-C electrode to some ions.

Standard Ion Solution	Average Potential (mV)	Δa_j (ppm)	Δa_i (ppm)	K_{ij}^{Pot}
Phosphate ($NaH_2PO_4 \cdot 2H_2O$)	-385,7	10,00	1,072	0,107
Nitrate ($NaNO_3$)	234,3	10,00	21,06	-2,016
Chloride ($NaCl$)	229,7	10,00	20,89	-2,089
Potassium (KCl)	231,7	10,00	20,97	-2,097
Ammonium (NH_4Cl)	210,3	10,00	20,21	-2,021

Table 2. Comparative result of soil analysis using two methods.

Sample Point	[PO_4]/ppm		Accuracy (%)
	Potentiometry	Spectrometry	
T1	5.41	5.21	105
T2	1.03	0.76	136
T3	4.37	4.29	102
T4	3.02	3.19	95

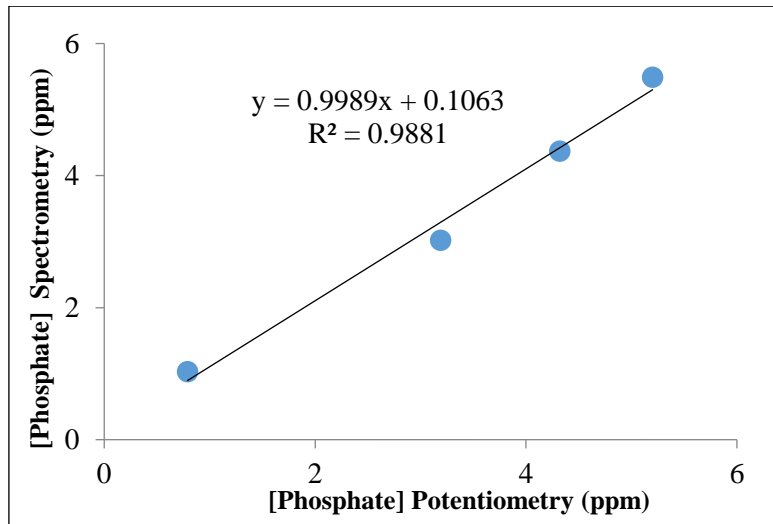


Figure 3. Relationship between soil sample measurement results between two methods

Accuracy (%) was measured based on the results of spectrometry methods which was considered as reference methods.

CONCLUSION

From the series of results and observations presented above, it can be concluded that the development of Co-C electrodes as phosphate sensors produces electrodes that are in line with expectations, namely electrodes that are capable of quantitatively detecting phosphate ions. Although the sensitivity slope is still not maximized, it can be stated that the results of this study are quite adequate with the demonstrated ability of very adequate selectivity. In addition, comparison with standard spectrophotometric methods showed good results with a good correlation coefficient of 0.988.

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