

Development of A Potentiometric Portable Extractor for Phosphate using Water Absorbent Materials and Cobalt Wire Electrodes

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Abstract. Soil phosphorus is an essential nutrient in the soil and is very necessary for plants, so measuring the content of elements or their derivatives in the soil is very necessary. This study aimed to develop a portable measuring instrument for phosphate based on the potentiometric principle using cobalt electrodes. The choice of absorbent material to support portable measuring instruments is based on water absorption and the potential response of the cobalt electrode when used with an absorbent. The phosphate electrode was made from cobalt wire and Ag/AgCl as a reference electrode. A comparison of analysis results was carried out between portable extraction potentiometric and conventional potentiometric methods. The results showed that polyvinyl alcohol (PVA) was the best absorbent. Using potentiometric measurements in a portable extractor prototype with PVA as an absorbent material offers promising prospects. The comparison of measurement results between the portable extractor and conventional potentiometric had 0.8039 as the correlation coefficient. Phosphate in conventional potentiometric was measured 1.2809 times higher than portable extraction potentiometric. The potentiometric slopes were -23.69 mv/decade and -26.63 mv/decade for the portable extractor potentiometric and the traditional potentiometric methods, respectively.

1 Introduction

Plant nutrients are classified by their needs. Macro nutrient is needed upper than 500 ppm. Phosphorus is one of the macronutrients essentially required for a plant's physiological and biochemical function [1]. This nutrient is essentially found in the phosphate form. In plants, phosphate plays an important function in biochemical reactions. The high-energy Adenosine triphosphate (ATP) releases its energy for plant activity if the bonding is converted to adenosine diphosphate (ADP). The soil phosphorus has a different form, such as H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-} ions. The form of soil phosphorus depends on soil pH [2]. Precision agriculture is information and technology that is applied for agriculture management system for identifying, analysing, and managing the variety information of soil analyte [3]. In here, the farmers get the ability to crop input effectively include

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fertilizer, pesticides and water irrigation [4]. The soil analysis is the main key that must be done for applying this precision agriculture system. This analysis can give a good recommendation of fertilization. The fertilization can accord with the plant required. Soil analysis can be carried out by conventional spectrometry [5,6] or calometry titration methods [7,8]. This method has several advantages, namely easy, inexpensive, and simple, but it also has limitations; namely, it cannot be carried out for direct analysis on agricultural land, and the analysis process must be carried out in the laboratory.

One method of soil analysis that can be improved is a portable potentiometric extractor, which offers field analysis to detect soil nutrients quickly without taking soil samples to the laboratory. Chamois absorbent material is used as a supporting component for this method [9]. Chamois has not been determined to be the best absorbent for portable extractor support components, as seen from the correlation value of 0.5 in the nitrate measurement results between the portable extraction potentiometric and standard spectrometric methods. Studying several absorbent materials suitable for soil nutrient measurement applications is necessary.

The absorbent material is a supporting component of the portable extractor potentiometric method. This absorbent must have hydrophilic characteristics that can absorb the analyte and filter the soil interferences. This material generally has a higher degree of swelling and water absorbance. Both natural and synthetic polymers have water absorption abilities, such as chitosan, cellulose, polyacrylamide, and polyurethane have been widely used as water-absorbent [10]. By using the absorbent, interferences from soil material cannot come into contact directly with the electrode. This step substitutes the filtration process in the conventional potentiometric method and spectrometric method. Only the tip of the cobalt electrode will come into contact with the absorbent's top surface to measure the analyte's potential.

Application of cobalt electrodes in the flow analysis method for phosphate analytes has been carried out [11]. The electrode produces a fast and selective response to phosphate ions in the sample. Phosphate electrodes from cobalt wire can detect phosphate quickly and cheaply. Apart from pure cobalt metal in the form of wire, our group is also researching the development of cobalt-based electrodes that are electrodeposited on carbon, and cobalt oxide composites with several polymers and other materials, but their performance has not been tested. A cobalt wire electrode, developed with a portable extractor, can directly solve the precision agricultural problem of measuring soil phosphorus in the field. The research objective is to develop an alternative method for measuring phosphate using a portable extractor potentiometric (PEP) based on cobalt electrodes and water absorbent materials.

2 Material and methods

2.1 Materials

Soil samples were taken from four different areas: smallholder agricultural land in Secaba Summersari (A), UNEJ Tegal Boto Agrotechnopark land (B), UNEJ Jubung Agrotechnopark land (C), and smallholder agricultural land in Kranjingan (D). Soil samples were taken with a trowel or shovel to a depth of 10-20 cm and placed in a container that was free of contaminants and protected from the sun. The used sampling technique was a simple random sampling by taking as many as 10 sections that can be represented as a whole [12]. All chemicals used are analytical grade. Three types of absorbent materials, absorbent sodium polyacrylate, absorbent polyvinyl alcohol, and absorbent polyurethane, were obtained from local authorized dealers. Cobalt electrodes were prepared from 0.3 mm OD of high-purity cobalt wire (99.99%, Minihua Store, China) designed according to

previous work [11], used in pairs with ELIT Ag/AgCl reference electrodes (Nico2000 Ltd., UK).

2.2 Procedures

Water absorption capacity (WAC). WAC measurements were carried out using the gravimetric method on three commercial water-absorbing materials, namely chamois (polyvinyl acetate-based material), diapers (polyacrylamide-based material), and foam (polyurethane-based material). Each absorbent material was soaked in distilled water for 48 hours at room temperature. The WAC value is the difference between the mass of the absorbent absorbing water and the initial mass of the absorbent divided by the initial mass and then multiplied by 100%. [13].

The best absorbent selection. The best absorbent material is determined by involving it in the potentiometric phosphate analysis process. The absorbent here plays the role of replacing the extraction filter as well as the medium that interacts with the surface of the measuring electrode. 10.00 grams of soil sample mixed with 100.00 mL of Kelowna extractant solution [14] and then shaken for 5 minutes. The Kelowna solution is a mixture of 5 mL of 5M glacial acetic acid and 5 mL of 0.M ammonium fluoride which is diluted to 100 mL with distilled water. The mixture is poured to separate the soil and extraction liquid, then 2.5 mL of the liquid is taken and placed in a second container, added with 50 μ L potassium hydrogen phthalate (PHP) solution (pH 4). The absorbent is placed on top of the mixture in the second container, and the liquid below can absorb upwards. The cobalt electrode and reference electrode are placed right in contact with the liquid above the absorbent, and the potential difference is measured with a high-impedance millivolt meter. This process was repeated three times for each absorbent material. Fig. 1 shows the process scheme above.

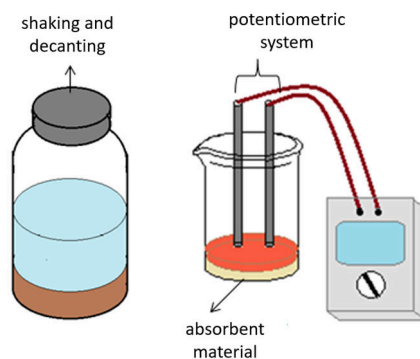


Fig. 1. Illustration of a potentiometric portable extractor for phosphate determination

Phosphorus determination in soil samples. Phosphate measurement in soil samples using the PEP method is carried out in the same way as the procedure for selecting the best absorbent, but using selected absorbent materials and equipped with measurements of standard phosphate solutions for the calibration curve. The results of PEP phosphate measurements were compared with conventional potentiometry. Measurements using conventional potentiometrics were carried out by extracting 10.00 grams with 100 mL of Kelowna extract. The soil and extractant solution were stirred for 5 minutes and then filtered. A total of 10 mL of filtrate was added to 0.2 mL of PHP 0.025 M (pH 4) solution, and the potential difference was measured potentiometrically. Repetition is done three times. Preparation of calibration curves using potentiometric methods (PEP and

conventional) was carried out in the concentration range of 0.01 phosphate standard solutions, 0.1, 1, 10, 20, 30, 40, 50, 60, 70, and 100 ppm, and the linear range was determined before being used to calculate phosphate levels in soil samples.

3 Result and discussion

3.1 Water absorption capacity (WAC)

WAC is an absorbent ability to bind water as much as possible. Sodium polyacrylate, polyvinyl acetate, and polyurethane absorbent material capable of absorbing water are classified as hydrogel physics. The water absorbed by the hydrogel physics will be maintained unless pressure is exerted on the absorbent [13]. Water absorption depends on the presence of functional groups attached to the absorbent. The more and more polar hydrophilic functional groups cause the ability to bind water more and more.

Polyurethane has isocyanate functional groups and hydroxyl groups. Isocyanate groups tend to be less polar than the hydroxyl group. When forming the polymer, the hydroxyl group binds to isocyanate groups of different monomers and causes polarity decreases (Fig. 2). The presence of the hydroxyl group in PVA (Fig. 3) causes water absorption greater than polyurethane.

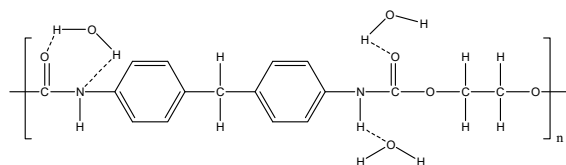


Fig. 2 Interaction between water and polyurethane-based absorbent by hydrogen bonding

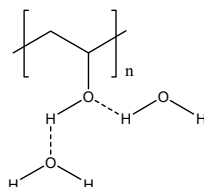


Fig. 3 Interaction between water and polyvinyl acetate-based absorbent by hydrogen bonding

The greatest of water absorption is owned by absorbent sodium polyacrylate-based. Water absorption on the absorbent sodium polyacrylate reached 8247% (Table 1). Monomers, acrylic acid, and sodium acrylate have a hydrophilic carboxyl group. This group is capable of binding water. Hydrogen bond is formed in two parts: the oxygen atom that has a double bond and the hydroxyl group (Fig. 3).

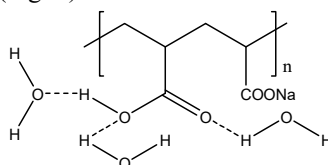


Fig. 4 Interaction between water and polyacrylamide-based by hydrogen bonding

Table 1 Water absorption capacity (WAC) for polyvinyl alcohol-based (PVA), sodium polyacrylate-based (Na-polyacrylate), and polyurethane-based absorbent.

Absorbent	m absorbent (gram)		WAC (%)
	Dry	Wet	
PVA	0.50	3.01	502
Na-polyacrylate	0.72	60.93	8247
Polyurethane	0.13	0.54	315

3.2 The best absorbent selection

Determination of optimum absorbent was calculated by the PEP method. Comparison of potential as analyte response to some absorbent material has been conducted. Absorbents will absorb the sample solution from the bottom surface toward the top surface, or in other words the sample solution will be absorbed by the absorbent. Small pores in the absorbent material cause the impurities in the sample solution was not contact directly with the electrode. The shrinkage of impurity in direct contact with the electrode allows the electrode for a longer lifetime. The absorbent substitutes the filtration process carried out in a conventional potentiometric measurement. Based on Table 2. The lowest potential response to phosphate was demonstrated by measuring analytes using absorbent sodium polyacrylate and polyvinyl alcohol.

Table 2 Soil phosphate potential measurement with absorbent variation

Absorbent	potential (mV)	SD (mV)	Cv (%)
PVA	-386.9	2.25	0.58
Na-polyacrylate	-404.3	2.19	0.54
Poliuretana	-385.1	2.04	0.53

The potential result of using absorbent sodium polyacrylate is -404.3 mV, while the absorbent polyvinyl alcohol is -386.9 mV. Absorbents will absorb phosphate analytes to the surface of the absorbent. The hydrogen bonds are possibly formed between atoms of hydrogen and oxygen atoms of H_2PO_4^- ions (the phosphate is available in the form of H_2PO_4^- ions at pH 4) with atoms of hydrogen and oxygen on absorbent material.

Electrode responses to variations of phosphate concentration in each absorbent are shown in Fig. 5. The highest sensitivity was produced by the absorbent polyurethane, which is 20.71. Polyvinyl alcohol has 20.5 sensitivity, while sodium polyacrylate has the lowest sensitivity, 14.36. However, the slowest ability to absorb analyte was polyurethane material than others. The use of absorbent sodium polyacrylate-based produces the lowest sensitivity, which indicates that changes in the phosphate concentration will result in a small change in potential.

The low value of the potential in the use of absorbent sodium polyacrylate was suspected because of the low concentration of the carboxyl group (COO^-) derived from sodium polyacrylate polymer. Ion selectivity of acetate was a second after cobalt phosphate with electrodes on the Kelowna solution [14]. This indicates that the measured response is actually a response to the interaction of the carboxyl group on absorbent.

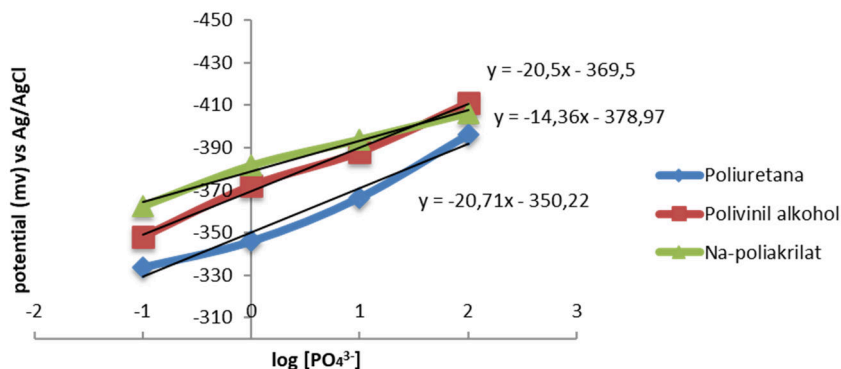
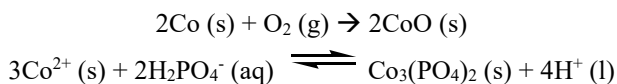


Fig. 5 Potential response of the cobalt electrode to the variation of phosphate concentration with various commercial absorbents

3.3 Phosphate determination in soil.

Based on the measurement results using both methods were obtained the concentration of phosphate in the soil are shown in Figure 6. Measurements using the conventional potentiometric (CP) method produces the higher than measurement of the PEP method. This is because the surface area of the cobalt wire that contacts with the solution is broader than the PEP method. The occur reaction in the cobalt electrode and ion $H_2PO_4^-$ are as follows [11].



Cobalt wire oxidizes to form cobalt oxide when contacts with the solution. Then cobalt oxides formed will form an equilibrium with $H_2PO_4^-$ ions forming a thin layer of cobalt (II) phosphate. The formation of cobalt oxide will be greater if the surface area. Consequently cobalt oxide which reacts with dihydrogen phosphate ion will be more so the potential is greater as well. While on the surface area of PEP method in contact with the absorbent is so small that reduction-oxidation process will be a little smaller. It causes the concentrations measured smaller than conventional method.

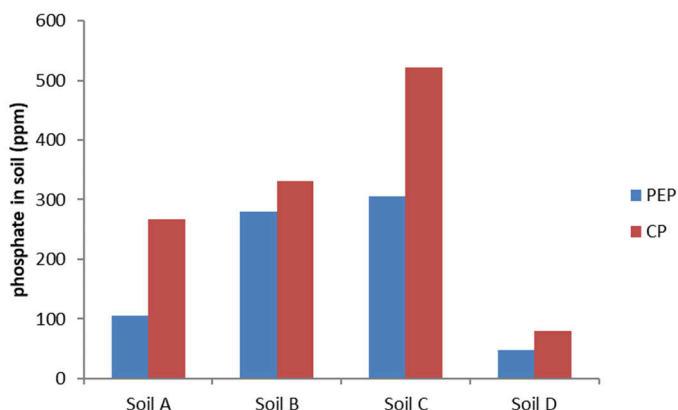


Fig. 6 Comparison of soil phosphate concentration using portable extractor potentiometric (PEP) method and conventional potentiometric (CP) method

The correlation between the concentration of phosphate potentiometric method with a portable extractor and conventional potentiometric was shown in Fig. 7. Correlation value of conventional potentiometric and potentiometric method with a portable extractor is 0.8039 with a slope of 1.2806. This value indicates that the resulting concentration of conventional potentiometric method 1.2806 times higher than the potentiometric method with a portable extractor. However, differences in the results of these measurements have a tendency or trend indicated a fairly good correlation of values. This means that the dependence of the two is 80.39% while the remaining possibilities influenced by other factors.

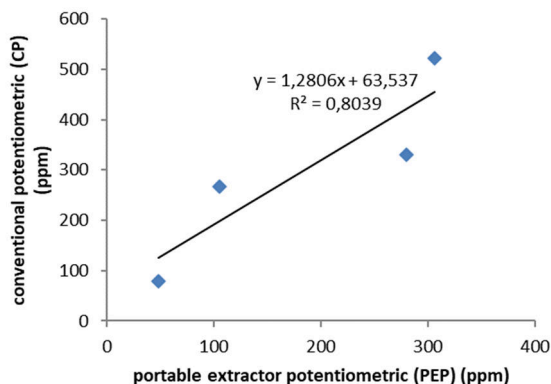


Fig. 7 Correlation of phosphate measurement results in several soil samples between the portable extractor potentiometric method and the conventional potentiometric method

3.4 Characteristic of method

The linear range measurements using the PEP phosphate is shown in Fig. 8, while the conventional method is shown in Fig. 9. Potential measured in both methods when the concentration of 1 ppm to 100 ppm are in the linear region. The detection limit measurement of phosphate using the PK method is 0.36 ppm, while the PEP method is 0.91 ppm. The detection limit indicates that the analyte concentration is still able to provide a significant signal compared to the blank [15,16]. While the value of the coefficient of variation (CoV) method dan metode PK PEP are shown in Table 3. CoV value is less than 2% showed good repeatability for short response time of the electrode.

Table 3 Coefficient of variation (Cv) of Portable Extractor Potentiometric (PEP) method and Conventional Potentiometric (CP) method

[PO ₄ ³⁻] (ppm)	CoV (%) PEP	CoV (%) CP
0.01	0.33	0.13
0.1	0.28	0.31
1	0.69	0.19
10	0.34	0.05
20	0.26	0.11
30	0.22	0.09
40	0.11	0.19
50	0.07	0.18
60	0.18	0.08
70	0.13	0.12
100	0.14	0.10

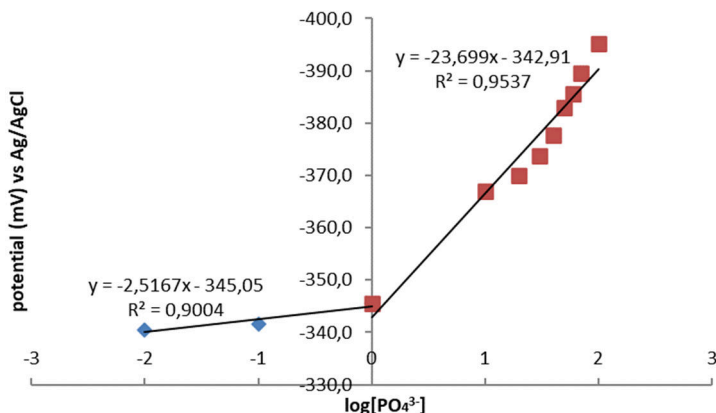


Fig. 8. Relation of log phosphate and their potential with portable extractor potentiometric method and phosphate electrode

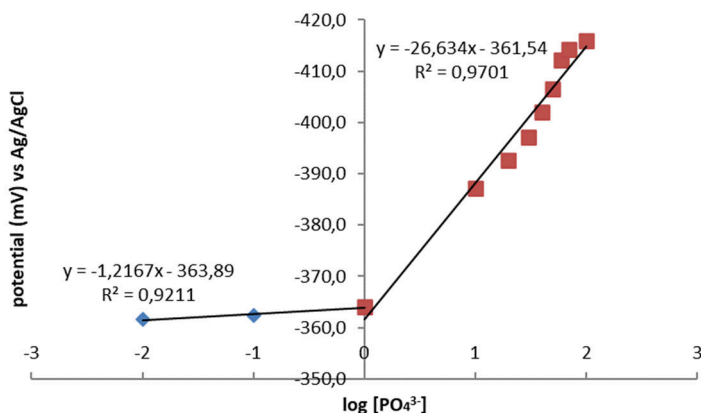


Fig. 9. Relation of log phosphate and their potential with conventional potentiometric method and phosphate electrode

4. Conclusion

The largest water absorption capacity is possessed by sodium polyacrylate absorbent, which reaches a value of 8247%. However, it was found that polyvinyl alcohol absorbent was the best-supporting component for measuring phosphate in soil using a portable potentiometric extractor. A comparison of phosphate measurements using the portable extractor potentiometric method and conventional potentiometric methods shows slightly different results. However, the resulting trend is relatively the same, with a correlation value of 0.8039. Phosphate in conventional potentiometric was measured 1.2809 times higher than portable extraction potentiometric. The potentiometric sensitivities were -23.69 mv/decade and -26.63 mv/decade for the portable extractor potentiometric and the conventional potentiometric methods, respectively. Further research is needed to improve the design of cobalt electrodes for applications in portable extractor potentiometry.

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