

Optimisation Of Extractant And Extraction Time On Portable Extractor Potentiometric Method For Determining Phosphate In Soil

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Abstract-Phosphorus is one of the nutrients which is needed by plants in large amounts. Fertilisation is a popular solution for supplying a sufficient amount of phosphorus in the soil. However, phosphorus can pollute water bodies and lead to eutrophication if fertilisation is carried out without considering prior information about the soil condition. Thus, analysis of phosphorus needs to be done before fertilisation. This paper is reporting a result in development an alternative strategy for analysing the phosphorus in soil agriculture using potentiometric method. The aims of this research were to find the optimum condition of extractant and extraction time for determining phosphate, one form of phosphorus, in soil and evaluate a portable extractor potentiometric (PEP) method for determining phosphate in soil. Measurement of phosphate was undertaken by using cobalt working electrode, silver-silver chloride reference electrode and 0,025 M potassium hydrogen phthalate at pH 4 as ionic strength adjuster. Evaluation of PEP method was carried out by comparing this method with both the conventional potentiometric (CP) and the standard spectrometric (SS) methods. It was found that Kelowna was the optimum extractant for measuring phosphate potentiometrically in soil by CP method. Extraction time of 10 minutes was the optimum time for extracting phosphate in soil using Kelowna extractant solution. The result also shown that correlation between PEP and CP method was 0.883 whereas correlation between PEP and SS method was 0.924. Linear response characterisation of both PEP and CP method has obtained slope of (-28.47) and (-23.67) mV per decade respectively, in other hand the PEP and CP has resulted the detection limit 0.72 ppm and 0.83 ppm respectively. Repeatability for both PEP and CP method were less than 5%.

Keywords: extractant, phosphate, portable extractor, potentiometric, extraction time.

Introduction

Phosphorus is one of the nutrients which are needed by plants in large amounts. Phosphorus is absorbed by plants in the form of orthophosphate ions (H_2PO_4^- and HPO_4^{2-}) [1]. Phosphorus plays an important role in the process of nucleic acid and membrane synthesis, photosynthesis and the activation or inactivation of the enzyme [2]. The important role of phosphorus is inversely proportional to its presence in soil. It is said that phosphorus is the least nutrient that is available in soil [3]. So, phosphorus deficiency may occur. Fertilisation is a popularly solution that done by most of farmers. However, if fertilisation is done not on target, phosphorus can pollute water bodies and lead to eutrophication [4]. Thus, analysis of phosphorus needs to be done.

Potentiometric method is promising for phosphate analysing because it uses affordable equipment, has rapid detection and good sensitivity. Therefore, there were many studies developing this method for phosphate such as potentiometric flow injection (FIP) using a cobalt wire electrode [5]. The result of FIP method was good, but the equipment for the flow system is less efficient when it's applied in the field. There was a modification of the extraction process on nutrient analysis using potentiometric method called the portable extractor-potentiometric (PEP). PEP method has been done for analysis of nitrate and potassium [6]. The advantages of this method include fresh sample and fast extraction process.

Phosphate in soil can be measured by potentiometric method if it was in solution form. Soil must be extracted with suitable extractant. The extraction of phosphate can be done with a liquid such as water, weak saline solution, or weak acid [7]. Extractants that has been used to extract phosphate in soil were NaHCO_3 [8], Kelowna [9], Morgan Wolf [10], K_2SO_4 [11], and H_2O [12]. These extractants mostly tested on standard methods (spectrometric). The aims of this research were to find the extractant that support for determining phosphate with

potentiometric method and evaluate the use of PEP method for determining phosphate in soil.

Methods

The experiment was conducted with several steps. It was started by constructing a working electrodes, electrode pre-treatment [13] and soil sampling in 4 areas namely Scaba, Keranjingan, Agrotechno Park Tegalboto, and Agrotechno Park Jubung. The next process determined the optimum extractant for phosphate in conventional potentiometric (CP) method. 20 grams of soil samples was extracted with variations of 200 mL extractants: Morgan Wolf, Kelowna, NaHCO_3 , K_2SO_4 and H_2O . The mixture was homogenised with a magnetic stirrer for 15 min and filtered. The filtrate was taken and added with 10 mL of 0.025 M KHP solution as ionic strength adjuster (ISA). The difference potential of solution (filtrate + ISA) is measured with cobalt electrodes and silver-silver chloride (Ag/AgCl) electrode until constant.

Determination of optimum extraction time was done by weighing 20 grams of soil samples and extracted with 200 mL optimum extractant. The mixture was homogenised with a magnetic stirrer at extraction time variation of the 5, 10, 15, 20 and 25 minutes. The extract obtained was analysis like optimum extractant method. After extractant and optimum extraction time was obtained, this condition is used for measuring phosphate by PEP and spectrometric methods. The difference of PEP method and PK method is the extraction process using glass bottles, 2.5 mL of the extract used and given absorbent (chamois). Phosphate measurement with spectrometric method using ascorbic acid method.

Evaluation of PEP method was done by comparing phosphate concentration obtain from PEP, CP and spectrometric method. Both PEP and CP method were tested of their characteristics included linear area, the detection limit, sensitivity, and repeatability.

Results and Discussion

Optimisation Extractant

A solution of extractant may be said to be optimum if it can extract in large amounts of phosphate which can be seen from the increasing negative potential difference in potentiometric measurement. In addition, the extractant doesn't interfere the measurement. It means when the extractant is added to the standard variation of concentration, extractant doesn't give effect to the potential difference.

According to Figure 1, the order of extractant that had negative different potential until less negatif was Olsen > K₂SO₄ > H₂O > Morgan Wolf > Kelowna. However, consideration based on Figure 1 and 2, Kelowna was selected as the optimum extractant although it didn't generate the most negative potential difference. Kelowna qualified the second requirement as the optimum extractant, it did not affect the measurement when it was added to standard solutions. Figure 2 showed that the shape of Kelowna's curve was not flat, the potential response was gradually change as the concentration change.

Perhaps the Kelowna solution could extract phosphate in soil due to presence fluoride ions in Kelowna which could replace phosphate bound to other compounds like Ca²⁺ in soil. This was evidenced by the low value of K_{sp} CaF₂ is 3.9 x 10⁻¹¹.

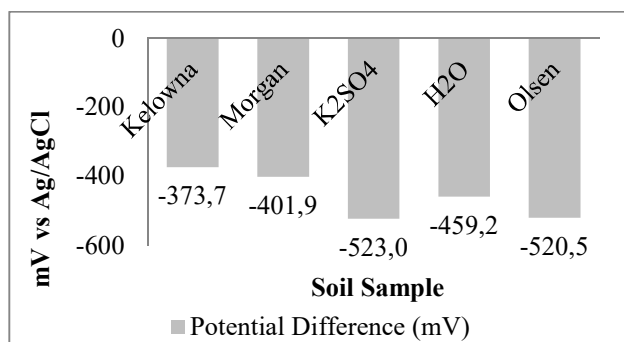


Figure 1. Optimum extractant for determining phosphate by potentiometric method used extractant: Kelowna, Morgan Wolf pH 4,8, K₂SO₄ 0,5 M, H₂O and Olsen (NaHCO₃) 0,5 M

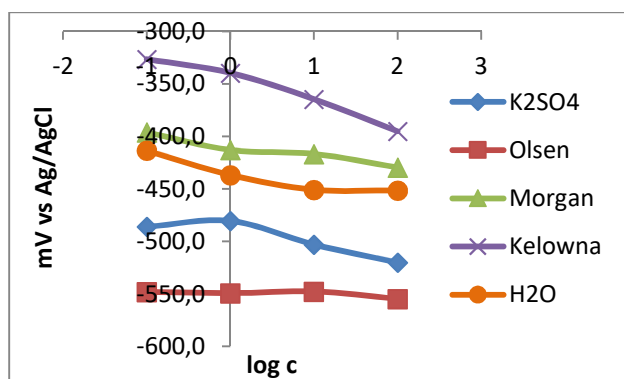


Figure 2. The effect of variation of standard concentration to response electrode in various extractants

Optimisation of Extraction Time

Investigation of extraction time is presented in Figure 3, that showing a variation of potential difference obtained when the variation of the extraction time was applied. Extraction time of 10 min showed the most

negative value. It meant that Kelowna extractant was estimated to be able to extract maximum phosphate at the time. In addition, 10 minutes was considered to be efficient for extracting phosphate. So, 10 minutes was selected as the optimum extraction time. This results would be applied for time shaking in PEP method.

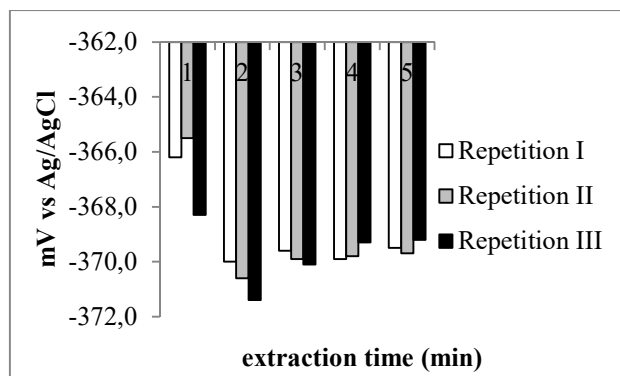


Figure 3. Optimum of extraction time phosphate in soil

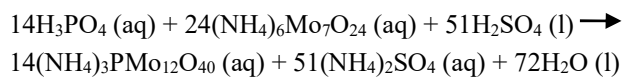
Evaluation of PEP Method

Evaluation of the performance of PEP method was done by comparing this method with CP method and standard spectrometric (SS) method. Comparison were performed using the average value of the phosphate concentration obtained from the three methods. Phosphate analysis with potentiometric method based on the formation of thin layers of Co₃(PO₄)₂ in cobalt electrode that caused a potential difference. The differences of PEP and CP method were the extraction process and used of absorbent (chamois).

Based on Figure 4, there were differences of phosphate concentration obtained from three methods. The difference of phosphate concentration was in PEP method and CP method due to the movement of phosphate in sample and the difference of cobalt electrode surface area in contact with the phosphate. Phosphate can be easier to move in solution (CP method) than when absorbed in the pores of the *chamois* (PEP method). It made the chance of cobalt phosphate formation in CP method bigger than in PEP method. In addition, cobalt electrode immersed with sample well in CP method than PEP method because cobalt electrode tip is in contact with the sample. It also made the chance of formation cobalt phosphate in CP method bigger than PEP method. Thus, the concentration of phosphate in CP method obtained would be higher than the PEP method.

The difference of phosphate concentration obtained from spectrometric and potentiometric methods (PEP method or method PK) due to difference way for detecting phosphate. Potentiometric method detects phosphate in form of H₂PO₄⁻ while spectrometric method detect phosphate in form of a phosphate complex compound. Based on Figure 4, the concentration of phosphate measured on spectrometric method was smaller than the potentiometric method both PEP and PK methods. It was caused by complex compound (fosfomolibdenum) that can be reduced by ascorbic acid about 20-25% when two electrons involved in this reaction. As a result, a small measured phosphate concentration. Thus, it was known that the concentration of phosphate in soil followed this order: CP method > PEP method > method Spectrometric.

The formation reaction of the complex had been proposed by Murphy and Riley [14] following this reaction:



Furthermore, the complex is reduced by the presence of ascorbic acid. It followed this reaction:

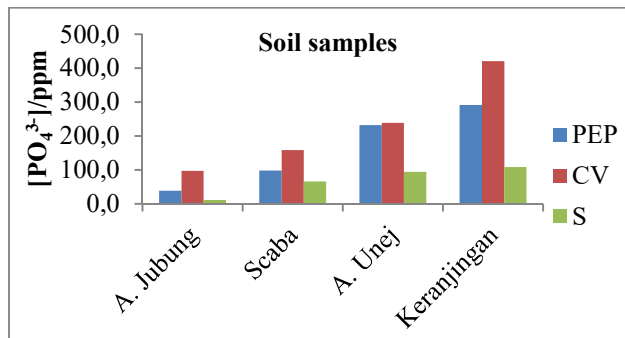
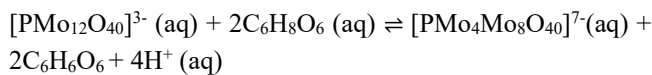


Figure 4. Comparison of phosphate concentration in soil with portabel extractor-potentiometric (PEP) method, conventional potentiometric (CP) and spectrometric (S) method

This complex $[\text{PMo}_4\text{Mo}_8\text{O}_{40}]^{7-}$ is measured in by visible spectrophotometer at a wavelength of 712 nm. The complex was stable in room temperature. According to Van Wazar [14], reduction of compound $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ into the compound $[\text{PMo}_4\text{Mo}_8\text{O}_{40}]^{7-}$ was likely to occur around 20-25% and its reduction was a reversible reaction.

Evaluation of PEP method was undertaken by giving a correlation. If the correlation value (R^2) is high, it will mean that PEP method could be used for determining phosphate in soil. The correlation value was said to be high enough correlation if it's more than 0,8.

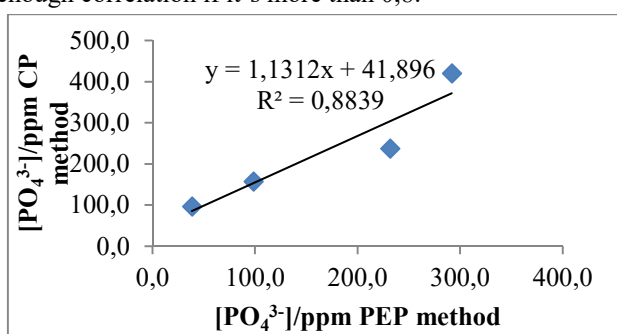


Figure 5. Correlation of portable extractor-potentiometric (PEP) method and conventional potentiometric (CP) for determining phosphate in soil

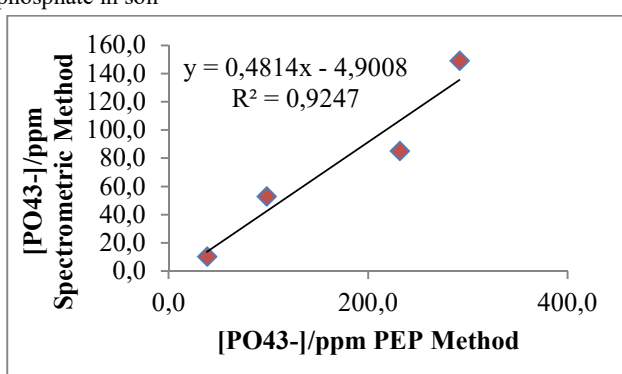


Figure 6. Correlation of portable extractor-potentiometric (PEP) method and spectrometric (S) method for determining phosphate in soil

Based on Figure 5, the correlation between PEP and CP method in determining phosphate concentration in soil was quite good with the R^2 value was 0.883. It showed that phosphate concentrations obtained from PEP method was quite comparable to CP method even though the phosphate concentration obtained in PEP method was smaller than the CP method.

Based on Figure 6, the correlation spectrometric method and PEP method was good and equal to 0.924. This indicated that the value of phosphate concentration in soil with PEP method could be said to be proportional to the phosphate concentration in the spectrometric method.

Characteristics of Potentiometric Method

The characteristic of potentiometric method for determining phosphate in soil included linear range, sensitivity, detection limit and repeatability. Linear area is an area where the electrode can sensitively response potential difference in some variations in the concentration of the standard solution. Linear area can be obtained from the calibration curve prepared by plotting the x-axis (log concentration) and y-axis (potential difference).

Based on Figure 7, the linear range for the PEP method for determination of phosphate in soil is between 1 to 100 ppm concentration with the linear regression equation $y = -28,47x - 359,5$ and correlation (R^2) 0.959. It means that 96% phosphate measurements usnig PEP method was affected by the concentration and 4%, was affected by interfere ion.

Based on Figure 8, the linear range for the CP method in determining phosphate in soil was between 1 to 100 ppm concentration. The linear regression equation was $y = -23,67x - 342,8$ and correlation value (R^2) 0.951. it means that 95% measurement of phosphate potential difference using CP method was affected by the concentration whereas 5% measurement was affected by interfere ion.

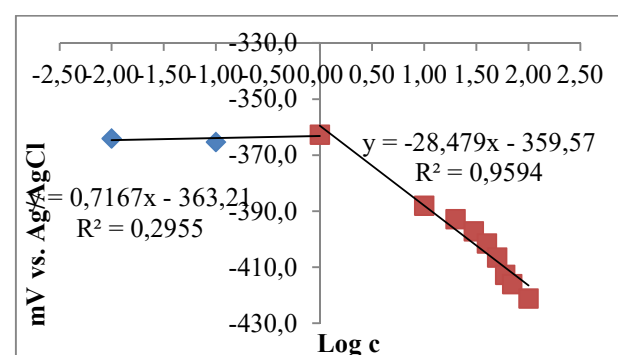


Figure 7. Curve for determining the linear range using portable extractor-potentiometric (PEP) method

The detection limit is the smallest concentration of an analyte that can be measured by the instrument. Based on calculations, the detection limit for cobalt electrodes using PEP method of 0.83 ppm and 0.72 ppm for the CP method. It showed that the smallest concentration of phosphate which can be measured well by cobalt electrodes

was 0.83 ppm and 0.72 ppm. When they compared with the sample measurement, the tool is able to detect samples for phosphate concentrations because sample were measured in the range of 1-30 ppm for both methods of PEP and PK methods.

Sensitivity is a measure of the ability of the instrument or method to detect differences in the concentration of the analyte or standard solution. Sensitivity is expressed by the slope of the calibration curve. Sensitivity of cobalt electrode in phosphate analysis by PEP method was 28.47 mV per decade and by CP method was 23.67 mV per decade. Large slope value means that a small change in analyte concentration could provide meaningful responses.

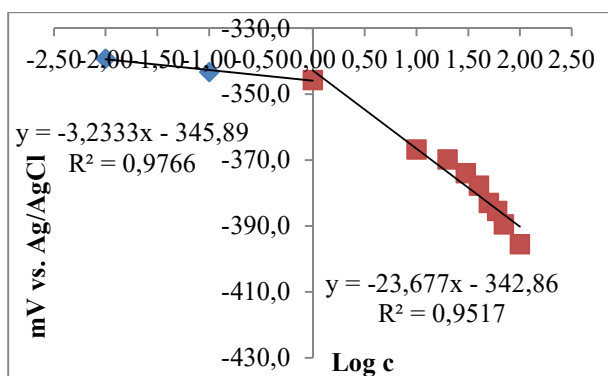


Figure 8. Curve for determining the linear range using conventional potentiometric (CP) method

Repeatability is a measure of the ability of a device to produce output (potential difference) as same as the input (concentration) that was measured by the same instrument. Repeatability is expressed as the coefficient of variation (Kv) which shows the degree of measurement error due to repetition. Repeatability of the electrode to detect the sample said to be good if the value of Kv (coefficient of variation) of less than 5%.

Based on Figure 9, the lowest value of the coefficient of variation was 0.02% at 30 ppm concentration, while the highest value of the coefficient of variation was 1.36% at 60 ppm concentration. The data indicated that the repeatability of the cobalt electrode in phosphate analysis using PEP method was good because the value less than 5%.

Based on Figure 10, the lowest value of the coefficient of variation was 0.08% at 1, 60 and 100 ppm concentrations while the highest value of the coefficient of variation was 0.16% at 60 ppm concentration. The data indicated that the repeatability of the cobalt electrode in phosphate analyses using CP method was good because the Kv's value less than 5%.

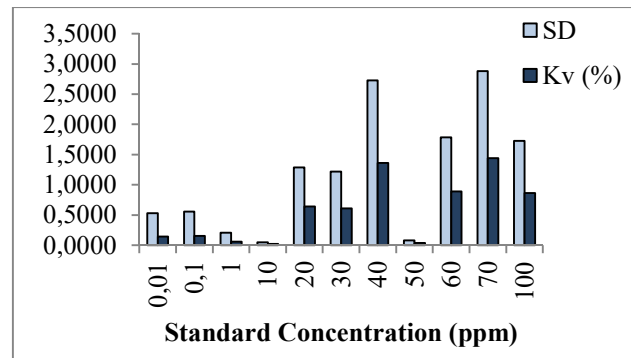


Figure 9. The coefficient of variation (Kv) of portable extractor-potentiometric (PEP) method in phosphate analysis

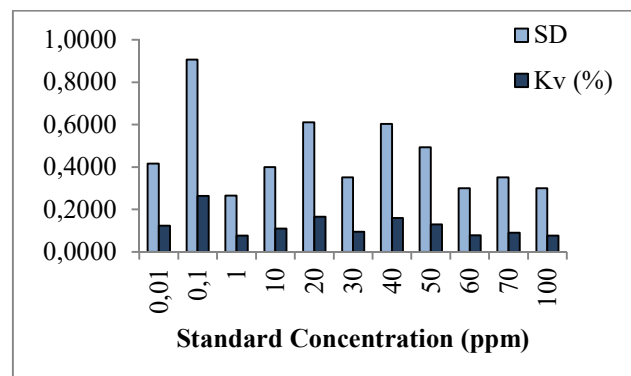


Figure 10. The coefficient of variation (Kv) of conventional potentiometric (CP) method in phosphate analysis

Conclusions

The optimum extractant for soil phosphate measurement with potentiometric method is Kelowna. The optimum extraction time for the measurement of phosphate in the soil is 10 minutes. PEP method could be used for determining phosphate in soil because it had a good correlation with CP and spectrometric method. Characteristic of portable extractor-potentiometric method included linear response with slope -28,47 mV per decade and detection limit was 0,72 ppm. Conventional potentiometric method was obtained linear response with slope -24,67 mV per decade and detection limit was 0,83 ppm. Repeatability for both portable extractor-potentiometric and conventional potentiometric method were less than 5%.

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