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Full Paper

Development of a Differential Normal Pulse Voltammetric Method with a Plain Glassy Carbon Electrode for Determination of Phosphate in Water

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Abstract- This study aimed at developing a voltammetry-based method sensitive to interferences. Phosphate ion when reacted with molybdate forms an electroactive phosphomolybdate complex. Differential Normal Pulse Voltammetry (DNPV) and Cyclic Voltammetry (CV) techniques were used to assess the complex. Analysis by CV gave two redox centres with redox potentials of 0.167±0.02 V and 0.357±0.02 V, diffusion coefficients (D) of 1.408×10^{-4} cm^2 s^{-1} and 5.629×10^{-7} cm^2 s^{-1}. Analysis by DNPV also gave two responses with potentials of 0.02±0.001 V and 0.33±0.001 V. DNPV response increased with phosphate concentration. The Linear Concentration Range (LCR) was found to be 0 to 8 mg/L, Limit of Detection (LOD) of 0.06586 mg/L, Limit of Quantitation (LOQ) of 0.21952 mg/L. The method had an accuracy range of 89%-102% and a precision of 7.93%. The method was evaluated using fifty water samples randomly collected from Lake Naivasha, Kenya. The mean phosphate concentration was 0.6156±0.1046 mg/L (at 95% Confidence Level). The study, therefore, showed that the DNPV method developed could be applied to the determination of phosphates in water at low levels.

Keywords- Voltammetry; Differential Normal Pulse Voltammetry; Cyclic Voltammetry; Phosphate; Phosphomolybdate Complex

1. INTRODUCTION

Phosphate is an important macronutrient in water which strongly influences microorganism growth [1]. Phosphorus is an important element in biological systems and is mainly available to both animals and plants in form of phosphate. Over the past few decades, the amount of phosphorus in the environment has increased, due to intensified agriculture and industrial activities [2]. For crop farming purposes phosphate fertilizers are applied to increase the amount of phosphorus in soils in order to increase crop yield [3]. During heavy rainfall, large amounts of phosphorus end up in water sources such as rivers and lakes, resulting in algal bloom, and consequently eutrophication [4].

The standard method for determination of phosphates in water is based on UV-Vis spectrophotometry analysis of phosphomolybdate complex [5]. However this method suffers from matrix interferences since phosphate levels below 0.1 mg/L cannot be accurately determined [6]. Separation techniques such as ion chromatography has been used in analysis of different species of phosphorus that is, orthophosphates, condensed phosphates and organic phosphates [7]. Other separation based methods include: High Performance Liquid Chromatography, Capillary Electrophoresis and Liquid Waveguide Capillary Cell [8].

Electrochemical methods have also been employed for analysis of phosphates. The earliest attempt was potentiometric determination of phosphate ions by use of Lead as an Ion Selective Electrode [9]. So as to increase selectivity of potentiometric method, ion selective membranes were developed [10], however the major drawbacks were the small size and hydrophilic nature of phosphate molecule [11]. Phosphate is not a redox active ion and therefore its electrochemical study depends on its association with metal complexes, with the main complex being phosphomolybdate complex. Voltammetric methods for phosphate determination have so far been developed with great success. Analysis of phosphates in water using Linear Scan Voltammetry (LSV) and Cyclic Voltammetry have been done [12,13].

Pulse voltametric techniques have been reported to have higher sensitivity almost 10 times more than conventional techniques [14]. Differential Pulse Voltammetry technique was used to analyse phosphates at a glassy carbon electrode [15]. This technique offered greater sensitivity compared to LSV and CV [16]. This study aims to develop a voltammetric method based on Differential Normal Pulse Voltammetry (DNPV) for determination of phosphates in water.

2. EXPERIMENTAL

2.1. Chemicals and Solution

The chemicals used in this study were sourced from Loba Chemie Ltd Co. The chemicals used and their purity were as follows:

Sulphuric Acid (H_2SO_4) 98% (w/v) (Analytical Reagent), Ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$) 99.3% (w/w) (AR), Ascorbic Acid ($C_6H_8O_6$) 99% (w/w) (AR), Antimony potassium tartrate ($K_2Sb_2(C_4H_2O_6)_2$) 99% (w/w) (AR), Potassium dihydrogen orthophosphate anhydrous 99.5% (w/w) (AR).

2.2. Equipment and Apparatus

An analytical balance of a high degree of precision (± 0.0001g) was used to measure the mass of the chemicals. Volumetric flasks, measuring cylinders, pipettes, micropipette, beakers, filter funnel, filter papers etc., were used in preparation of reagents and samples.

2.3. Preparation of Reagents

The reagents used in this study were prepared as follows:

Sulphuric Acid (H_2SO_4) 2.5 M: This solution was made by taking 68ml of concentrated sulphuric acid and 500 ml volumetric flask and diluting to the mark with distilled water. Ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$) 0.016 M: 20 g of ammonium heptamolybdate tetrahydrate was dissolved in distilled water and diluted to 500 ml. Ascorbic acid ($C_6H_8O_6$) 0.1 M: 1.76 g of ascorbic acid was dissolved in 100ml of distilled water. This solution was prepared as required (due to easily oxidizable nature of ascorbic acid). Potassium antimony tartrate ($K_2Sb_2(C_4H_2O_6)_2$) 0.0004 M: 0.2743 g of potassium antimony tartrate was dissolved in distilled water and diluted to 100 ml.

"Mixed reagent": 125 ml of 2.5 M sulphuric acid, 37.5 ml of ammonium molybdate, 75 ml of ascorbic acid solution and 12.5 ml of potassium antimony tartrate solution were then added and mixed thoroughly. This reagent is made up of 50% sulphuric acid, 15% ammonium molybdate, 30 % ascorbic acid and 5% potassium antimony tartrate.

Phosphate stock solution (1000 mg/L PO_4^{-3}): 0.1433 g of potassium dihydrogen phosphate (KH_2PO_4) was dissolved in 100 ml of distilled water to make 1000 mg/L phosphate (PO_4^{3-}) solution. Different standard concentrations of phosphates (100, 50, 25 mg/L) were prepared by dilution of the stock solution, then used to make calibration standards.

2.4. Electrochemical Instrument and Set Up Procedure

Cyclic Voltammetric (CV) and Differential Normal Pulse Voltammetric (DNPV) studies were done using CHI 123B Potentiostat model from CHI instruments company, USA. The reference electrode (RE) was made up of silver/silver chloride (Ag/AgCl (4 M KCl)) the counter electrode (CE) was made of platinum wire of a diameter 0.04 cm and the working electrode (WE) made up of glassy carbon of diameter 0.30 cm and a surface of 0.071 cm^2. The electrochemical cell used was designed to hold the three electrodes concurrently had a capacity

of 10 mL (100 µL). The electrodes were positioned in such a manner that the tips were close to the WE.

The RE, CE and WE were thoroughly cleaned and rinsed with deionized/distilled water. The working surface of the glassy carbon was polished using 0.3-micron alumina slurry on a polishing pad and then followed by 0.1-micron alumina slurry for about 2 minutes, to obtain a mirror finish of the glassy carbon. This was done before commencement of every experiment. Experiments were done in triplicates. CV and DNPV experiments were done at a temperature of 24±0.1 ºC.

The procedure for operating the potentiostat model CHI123 was used for both CV and DNPV studies. The instrument was switched on and given some time to initialize before running the CHI123 software installed in the computer. The potential window and the operating settings of CV and DNPV were selected using CHI123 software.

2.5. Analysis of Phosphomolybdate Complex

Phosphomolybdate complex is a Keggin ion with the formula $PMo_{12}O_{40}^{7-}$ [17]. This complex is formed by two reactions according to Equation 1 [13] and Equation 2 [18].

$$72H^{+} + 7PO_4^{3-} + 12Mo_7O_{24}^{6-} \rightarrow 7PMo_{12}O_{40}^{3-} + 36H_2O \quad (1)$$

The addition of ascorbic acid and antimony tartrate reduces $7PMo_{12}O_{40}^{3-}$ to $PMo_{12}O_{40}^{7-}$ through the following process[13].

$$PMo_{12}O_{40}^{3-} + 2e^{-} \rightarrow PMo_{12}O_{40}^{7-} \quad (2)$$

This reaction produces a complex $PMo_{12}O_{40}^{7-}$ in which Mo has an oxidation state of $+6$. Each of the above reactions involve 2 electrons [18].

In order to assess the redox behaviour of phosphomolybdate complex, phosphomolybdate complex 10 mg/L of the complex was prepared by pipetting 4.0 mL of phosphate solution from a 50 mg/L (prepared from 1000 mg/L) into a 25 mL volumetric flask, then 4 mL of mixed reagent was added and distilled water added to the mark.

10 mL of the phosphomolybdate complex prepared was then transferred into the quartz electrochemical cell for analysis. Cyclic voltammetry (CV) and Differential Normal Pulse Voltammetry (DNPV) techniques were used. Selection of electrochemical technique and input of electrochemical parameters and collection of data from the potentiostat was facilitated by a graphical software. Optimization of CV and DNPV techniques were done by selecting electrochemical parameters so as to obtain the best sensitivity. Optimization of the parameters was done through the graphical software of the potentiostat.

10 mL of phosphomolybdate complex prepared was transferred into an electrochemical cell. Prior to taking any measurements, the glassy carbon electrode (working electrode) was polished and rinsed with distilled water, then the electrode connections were made. The

complex was analysed by Cyclic Voltammetry and Differential Normal Pulse Voltammetry techniques.

Cyclic voltammograms of backgrounds (reagents) and phosphomolybdate complex were recorded at 0.2 V/s scan rate. So as to determine the diffusion coefficient, D, of phosphomolybdate complex, voltammograms at scan rate 0.2, 0.4, 0.6, 0.8 and 1 V/s were obtained.

In order to validate the DNPV method in terms of Linear Concentration Range (LCR), Limit of Detection (LOD), Limit of Quantitation (LOQ), calibration standards containing 0, 2, 4, 6, 8, and 10 mg/L of phosphomolybdate complex were prepared by pipetting 0, 1.0, 2.0, 3.0, 4.0, and 5.0 mL from 50 mg/L of PO_4^{3-} solution into 25 ml volumetric flasks, 4 mL of "mixed reagent" was then added to each flask and made to volume with distilled water.

Fifty water samples were randomly collected from L. Naivasha. The samples were collected in 50 mL precleaned plastic water bottles then transported to Chiromo Campus, University of Nairobi. The water was then stored in a freezer for subsequent analysis.

20 mL of collected water sample were filtered and then transferred into 25 mL volumetric flask, 4 mL of mixed reagent was then added, and finally made to the mark by distilled water. After 10 minutes, 10 mL of the sample was transferred into an electrochemical cell and analysed using DNPV method. The output data from the electrochemical analyses was recorded in comma separated values (csv) files. Voltammograms were prepared using LaTeX document preparation software and data analysed using Microsoft Excel Version 2021.

3. RESULTS AND DISCUSSION

3.1. Optimization of DNPV Variables

The variables: 1st amplitude and 2nd pulse widths, sampling width, pulse period and quite time were optimized by using the graphical software of the potentiostat. The optimized variables were then used for DNPV analysis of the phosphomolybdate complex. The optimized values are presented in Table 1.

Table 1. Differential Normal Pulse Voltammetry Variables

Parameter	**Value**
Init E (V)	-0.6
Final E (V)	2.4
Increment E (V)	0.001
Amplitude (V)	0.05
1st Pulse Width (sec)	0.01
2nd Pulse Width (sec)	0.01
Sample Width (sec)	0.001
Pulse Period (sec)	0.01
Quiet Time (sec)	1
Sensitivity (A/V)	0.01

The purpose of optimization was to achieve the best variables for use in the determination of the phosphates.

3.2. Redox Behaviour of Phosphomolybdate Complex using DNPV

DNPV scans were done oxidatively between a potential window of -0.6 to 2.4 V. The voltammograms of the reactants: ascorbic acid, potassium antimony tartrate and ammonium molybdate did not show any peaks, however sulphuric acid showed several peaks, these peaks were attributed to electrolysis of water see Figure 1.

When phosphate was added to the reactants, phosphomolybdate complex was formed and a peak was observed at potential 0.33 V.

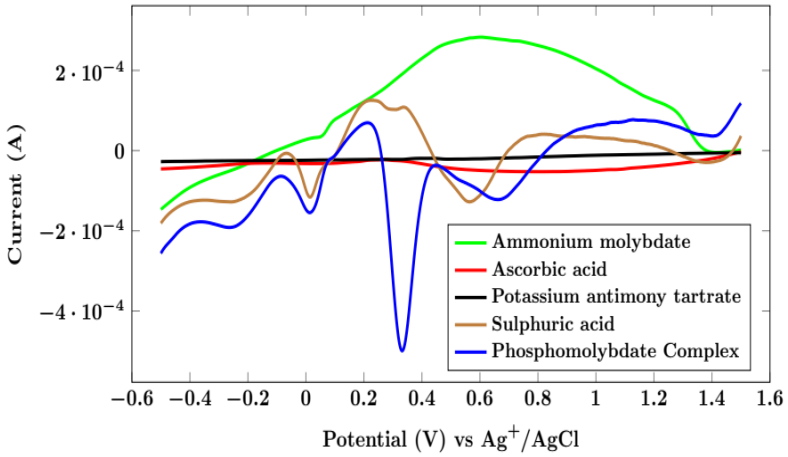

Figure 1. DNPV Voltammograms of reactants and phosphomolybdate complex; Phosphomolybdate complex formed by 50% sulphuric acid, 15% ammonium molybdate, 30% ascorbic acid and 5% potassium antimony tartrate versus Ag/AgCl/(4 M KCl) RE

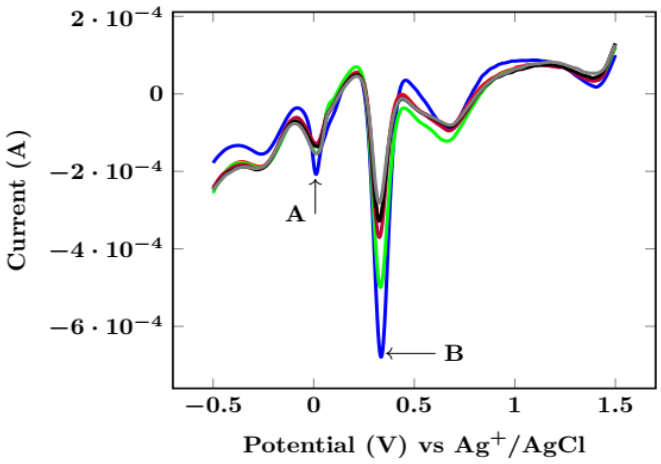

Figure 2. DNPV Voltammograms of phosphomolybdate complex at different concentrations. Peaks A and B were observed at redox potentials of 0.02V and 0.33V respectively

When the concentration of phosphomolybdate complex was altered by increasing the complex concentration through spiking with phosphate solution, there was a change in voltammogram peak heights which varied as the complex concentration see Figure 2.

The other peaks did not show any increase in peak height as phosphate concentration increased, hence they were not due to the formation of the complex. Both peaks were observed between 0 to 0.5V potential, peak A at 0.02 V and peak B at 0.33V. Potentials 0.02 V and 0.33 V provided DNPV redox potentials for phosphomolybdate complex.

3.3. Redox behaviour of Phosphomolybdate Complex when assessed using CV

The Cyclic Voltammograms of reactants; ammonium molybdate, ascorbic acid, potassium antimony tartrate and sulphuric acid were recorded (Figure 3). It was observed that voltammograms of ammonium molybdate, potassium antimony tartrate and sulphuric acid did not show any peak. However, the CV for ascorbic acid showed a single broad reduction peak between potentials 0.2 and 0.4 V, this observation is in agreement with previous observation [19], this peak is attributed to oxidation of ascorbic acid at the working electrode.

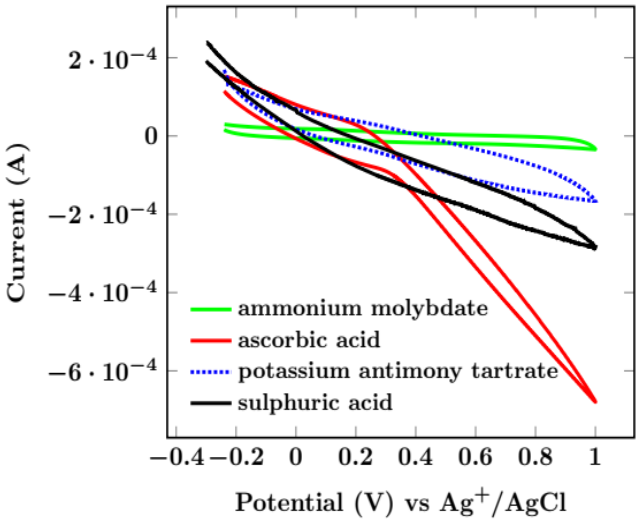

Figure 3. Cyclic voltammograms of reactants on glassy carbon electrode; ammonium molybdate (0.016M), ascorbic acid (0.1M), potassium antimony tartrate (0.0004M) and sulphuric acid (2.5M) at 0.2V/s scan rate versus Ag/AgCl/(4 M KCl) reference electrode

The cyclic voltammogram of Phosphomolybdate complex ($PMo_{12}O_{40}^{7-}$) showed two reduction peaks and two oxidation peaks see Figure 4. The reduction peaks were observed at potentials E1 = 0.43 V and E2 = 0.21 V and oxidation peaks at E1′ = 0.28 V and E2′ = 0.13 V. The two peaks observed during both cycles indicated that phosphomolybdate complex has two redox centres. These redox centres are due to oxidation of phosphomolybdate complex at the working electrode (WE). The oxidation process takes place at the molybdenum metal ion. The

peaks observed were due to oxidation of $PMo_{12}O_{40}^{7-}$ complex, and reduction process that occurs in two stages. In the first peak Mo (VI) is reduced to Mo (IV) while the second peak is due to the reduction of Mo(IV) to Mo(II) [20].

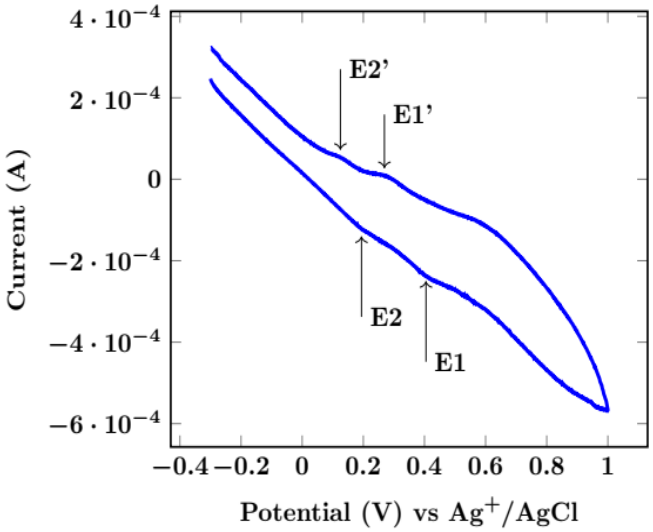

Figure 4. Cyclic Voltammograms of phosphomolybdate complex formed by 10 mg/L phosphate reaction with 50% sulphuric acid, 15% ammonium molybdate, 30% ascorbic acid and 5% potassium antimony tartrate at 0.2 V/s scan rate versus Ag/AgCl/(4 M KCl) reference electrode

The formal redox potential of the complex was calculated using Equation 3:

$$E^0 = \frac{E_{pa} + E_{pc}}{2} \quad (3)$$

where E_{pa} is the anodic peak current and E_{pc} is cathodic peak current. The formal redox potential for the two redox centers were found to be 0.357 V and 0.167 V

Using Linear Scan Voltammetry [12] reported two reduction peaks of the complex at 0.25 V and at 0.15 V corresponding to reduction of Mo (VI) →Mo (IV) and Mo(IV) → Mo(II) respectively. Analysis of the complex by [13] using Cyclic Voltammetry showed that reduction peaks were observed at 0.27 V and 0.13 V while oxidation peaks were observed at 0.16V for oxidation of Mo(II) → Mo(IV) and 0.30V for oxidation of Mo(IV) → Mo(VI). In this study, the reduction potential was observed at 0.28V and 0.13V for Mo(VI) →Mo (IV) and Mo(IV) → Mo(II) respectively. The results compared well with reported reduction potentials [12,13]. This was an affirmation that the peaks produced by CV was indeed that of the phosphomolybdate complex.

Equilibrium constant for the reaction was also calculated using Nernst Equation:

$$E^0 = \frac{0.0592}{n} \log K_{eq} \quad (4)$$

K_{eq} values for formal redox potentials E^0, 0.357V and 0.167 V, were calculated and found to be 1.15×10^{12} and 4.36×10^{5} respectively.

Diffusion coefficient D of the complex was determined by applying CV at scan rates of 0.2, 04, 0.6, 0.8 and 1.0 V/s. The voltammograms are presented in Figure 5.

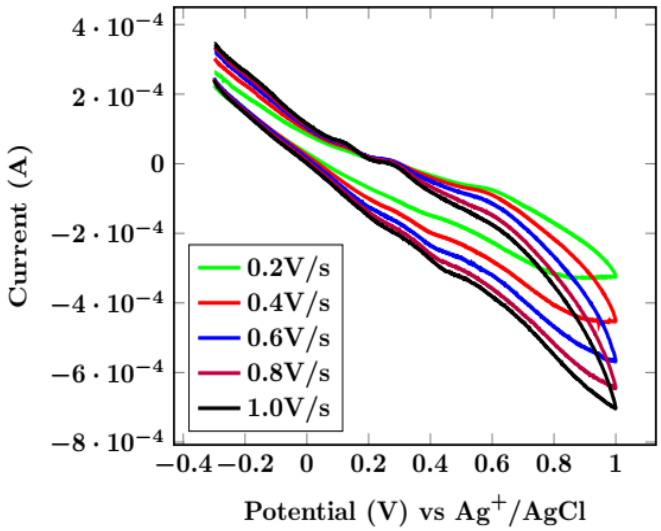

Figure 5. Cyclic Voltammograms of phosphomolybdate complex at varying scan rates formed by 10mg/L phosphate solution with 50% sulphuric acid, 15% ammonium molybdate, 30% ascorbic acid and 5% potassium antimony tartrate solution on glassy carbon electrode versus Ag/AgCl/(4 M KCl) reference electrode

By using Randles-Sevcik equation (Equation 5), which describes a linear relationship between the increasing peak current (i_p) and the square root of the scan rate (Vs^{-1}) [21,22].

$$i_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} C v^{1/2} \quad (5)$$

Diffusion coefficients D, of the two redox centres were determined as $1.408 \times 10^{-4}\ cm^2 s^{-1}$ for Mo(VI) to Mo(IV) and $5.271 \times 10^{-7} cm^2 s^{-1}$for Mo (IV) to Mo(II). When compared to diffusion coefficient of a smaller molecule (low molecular weight) such as potassium ferric cyanide which has a D of $6.35 \times 10^{-6} cm^2 s^{-1}$ [23], the D value of $1.408 \times 10^{-4}\ cm^2 s^{-1}$ was found to be large, but the D value of $5.271 \times 10^{-7} cm^2 s^{-1}$ was found to be small. For the D value of $1.408 \times 10^{-4}\ cm^2 s^{-1}$ this was attributed to changes in experimental conditions such as temperature.

3.4. Validation of DNPV Method

3.4.1. Linearity

Validation of DNPV method was done by determining: linear concentration range (LCR), limit of detection (LOD), limit of quantitation (LOQ), accuracy and precision. Voltammograms for validation of LCR, LOD and LOQ were obtained at varying concentrations of phosphomolybdate complex see Figure 6.

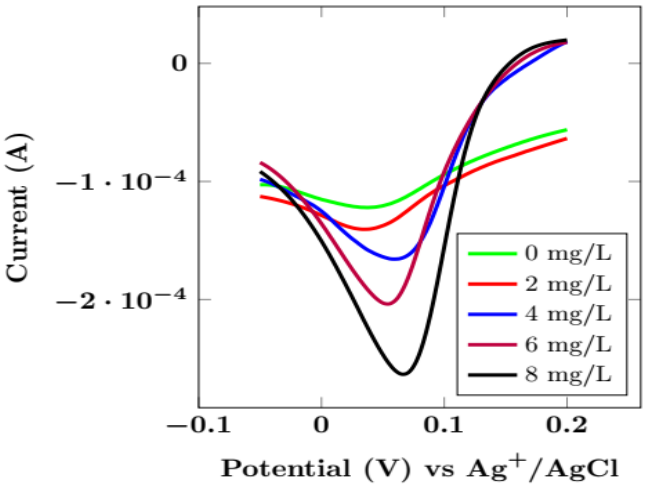

Figure 6. DNPV Voltammograms of 0, 2, 4, 6, and 8 mg/L phosphate concentration

The DNPV voltammograms were obtained between 0.0 and 0.2 V potential. The phosphomolybdate peak chosen for validation of the method was a peak between 0.0 V and 0.2 V, this is because this peak was well defined, the peak height could be easily be determined and at low concentration the peaks of the standards were well resolved.

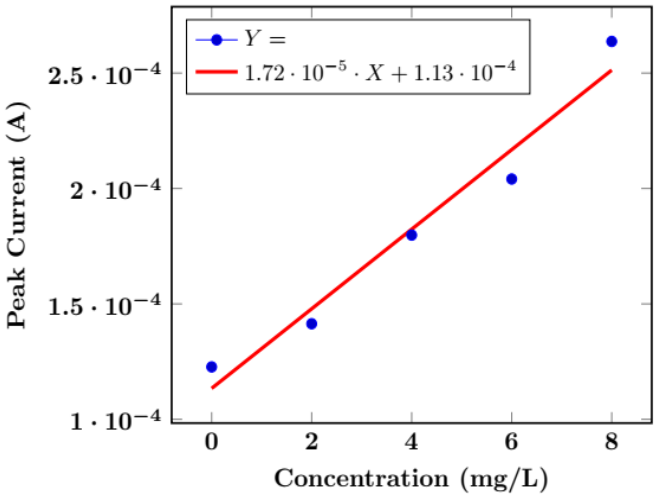

Figure 7. Standard calibration curve of peak current against phosphate concentration, the linear equation is $Y=1.7235 \cdot 10^{-5} X + 0.0001134$, and $r=0.9816$

The peak currents of the standards were used to plot a scatter plot of peak current versus concentration, and a linear regression equation was obtained, see Figure 7. From the calibration curve plotted, LOD and LOQ could be determined. There was a strong linear correlation coefficient or r=0.9816 between the peak current and concentration. From the linear relationship, the slope, the y-intercept and the linear regression equation were determined. The standard calibration curve was then used to determine phosphate concentration of collected water samples.

From the standard calibration curve, a linear concentration range was observed from 0 to 8 mg/L, with the largest peak current corresponding to 8 mg/L phosphate. It was noted that the curve was not linear for phosphate concentration of 10 mg/L and greater. The linear regression equation of y on x i.e., was found to be $y = 1.7235 \cdot 10^{-5} X + 0.0001134$. The random errors of the regression equation $s_{y/x}$ was evaluated to be $1.2256 \cdot 10^{-5}$. The confidence limits for y intercept, a were found to be $0.0001134 \pm 3.0212 \cdot 10^{-5}$ and the confidence limits for the slope b were evaluated and found to be $1.7235 \cdot 10^{-5} \pm 6.1669 \cdot 10^{-6}$.

3.4.2. Limit of Detection and Limit of Quantitation

Limit of Detection (LOD) of an analytical method is the smallest amount of an analyte in a sample which can be detected. LOD was calculated using Equation 6:

$$L.O.D = \frac{3s_B}{b} \tag{6}$$

where b, is the slope of the calibration curve and s_B is the standard deviation of the blank. LOD of the method was found to be $0.06586 mg/L$.

Similarly, Limit of quantitation (LOQ) was also determined. LOQ is regarded as the lower limit for precise quantitative measurements, LOQ was calculated using Equation 7.

$$L.O.D = \frac{10s_B}{b} \tag{7}$$

LOQ was found to be $0.21952\ mg/L$.

Limit of detection of the standard method (UV-Vis spectrophotometry) for analysis of phosphates in water has been reported to be $0.010\ mg/L$ [24]. Linear Scan Voltammetry (LSV) has been used to determine phosphates with a limit of detection of $4.0\ \mu g/L$ [12], the method employs a gold working electrode, Ag/AgCl reference electrode and a platinum counter electrode. Cyclic Voltammetry has also been applied in analysis of phosphate with a detection limit of $0.3\ \mu g/L$, [13], this method used screen-printed graphite electrode, screen printed $Ag/AgCl$ paste and a screen-printed counter electrode. These methods have a lower limit of detection compared to the DNPV method developed. The difference in limit of detection between LSV, CV and the developed method could be attributed to different working electrodes employed, modified reagents and experimental conditions.

3.4.3. Accuracy and Precision

Voltammograms of an original 2 mg/L phosphate, 50%, 100% and 150% addition of the original phosphate concentration were recorded Figure 8.

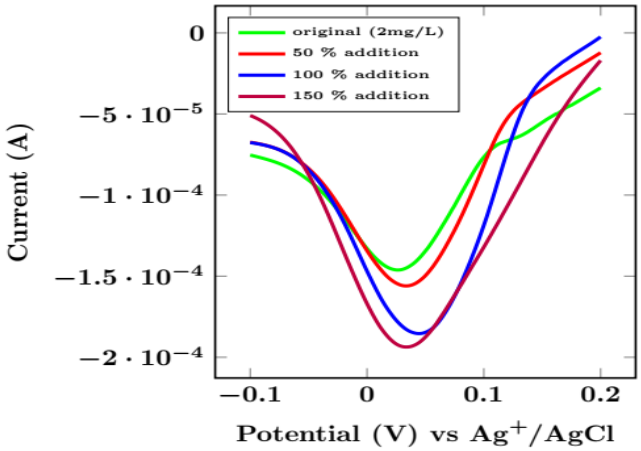

Figure 8. DNPV Voltammograms of original 2 mg/L phosphate solution spiked with 50%, 100% and 150% of original phosphate concentration.

The peak current increased as the % spiking increased due to increase in the amount of phosphomolybdate complex formed as phosphate was adeed. Accuracy was calculated as percentage recovery using Equation 8.

$$\% \text{ Recovery} = \frac{\text{Observed Result}}{\text{Expected Result}} \times 100 \qquad (8)$$

The expected result (expected peak current) was calculated using the calibration equation. Table 2. shows the percentage recoveries obtained.

Table 2. Percentage Recovery at 50%, 100% and 150% of original phosphate concentration

Concentration	**Observed Current (A)**	**Expected Current(A)**	**% Recovery**
Original (2mg/L)	0.0001464	0.0001479	99.0 %
50% addition (3mg/L)	0.0001566	0.0001651	94.9 %
100% addition (4mg/L)	0.0001865	0.0001823	102.3 %
150% addition (6mg/L)	0.0001939	0.0002168	89.4 %

The percentage recovery was found to range from 89% to 102% which was within the recommended limit of 90% to 110% [25].

Precision was determined by taking 10 replicate measurements of 4 mg/L of phosphate concentration. Precision was calculated using Equation 9:

$$\% \, RSD = \frac{s}{\bar{x}} \times 100 \tag{9}$$

%RSD was then found to be 7.93%.

Precision provides how well replicate measurements agree with one another and is usually expressed as a standard deviation [26] or the relative standard deviation [25]. The lower the %RSD the precise the method of analysis i.e., the closer in agreement the obtained results are. For electroanalysis method a %RSD of 7.93% is within acceptable limit (usually less 10%) for electroanalysis methods [27].

3.5. Evaluation of DNPV Method for Determination of Phosphates in Selected Waters

The Differential Normal Pulse Voltametric method was then used to analyse phosphate in natural water obtained from Lake Naivasha, Kenya. Lake Naivasha was chosen because of its eutrophication status which has been monitored over the decades [28,29].

Analyses were done on fifty water samples which had been randomly sampled from the lake. The sample size of fifty was chosen so as to cover a large lake surface. The analysis was done in triplicates and the voltammograms recorded so as to obtain peak currents of each water sample. Figure 9 below shows a voltammogram of phosphomolybdate complex from analysing a water sample using DNPV technique.

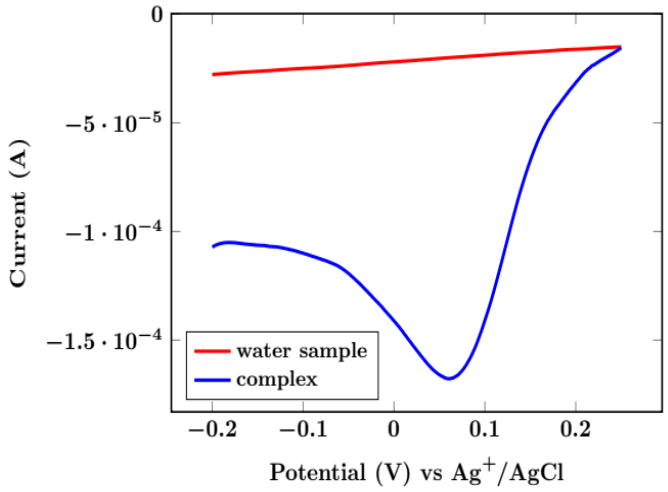

Figure 9. Water sample and the phosphomolybdate complex formed after introducing the mixed reagent to the sample

The scan for the natural water alone from the lake water did not show any peak; however, a peak was observed when the lake water sample was scanned after adding the reagents, the observed peak was attributed to the formation of the phosphomolybdate complex. The appearance of the blue colour which is a characteristic of the phosphomolybdate complex

further confirmed that the developed method was able to detect phosphomolybdate complex in water samples. The peak observed appeared between 0 and 0.2 V which confirmed a phosphomolybdate complex peak. The peak appearing between 0–0.2 V was chosen for analyses since it provided a well-defined peak and the peak current could easily be determined.

In order to determine the amount of Phosphate in the samples, phosphate standards of 0, 2, 4, 6 and 8 mg/L were used to prepare a standard calibration curve and the linear equation obtained used to find the unknown concentrations. The mean, $\bar{x}$ of the phosphate concentration of the water samples were determined to be 0.6156 ± 0.1056 mg/L (at 95% confidence level) and standard deviation s of 0.3811 mg/L. The statistics obtained for the phosphate concentration are summarised and presented in Table 3.

Table 3. Statistical summary of the phosphate concentration of L. Naivasha water samples

Statistic	**Value**
Number of samples	50
Minimum	0.0187 mg/L
Maximum	1.7398 mg/L
Mean	0.6156 mg/L
Median	0.5121 mg/L
Variance	0.1452 mg/L
Standard deviation	0.3811 mg/L
95 % confidence interval for the mean	0.510 to 0.7212 mg/L

According to [30], the concentration of dissolved phosphorus in lake Naivasha water ranged from $0.3 - 2\ mg/L$). A review by [31] on the state of the lake Naivasha with regard to phosphorus input showed that there was an annual load of $1.4\ g/m^2$ on the lake surface during wet season and $0.2\ g/m^2$ in normal wet season. A more recent study reported that the average phosphate concentration was $0.33\ mg/L$ [29]. These studies were based on the phosphomolybdate blue absorbance method.

When the developed method (DNPV) was applied, the average phosphate concentration was found to be $0.615\ mg/L$, with a range of 0.51 to 0.72 mg/L, indicating that the method was able to determine the phosphate level within the same range that had been reported [30].The increased phosphate levels in the lake Naivasha water could be attributed to the increased human activities especially agricultural activities going on around the lake region.

4. CONCLUSION

A highly sensitive Differential Normal Pulse Voltammetric (DNPV) method for determination of phosphates in water that was developed could also be used to assess the redox behaviour of phosphomolybdate complex. The DNPV method showed two peaks of the complex which appeared between 0 to 0.5 V potential (one peak at 0.02 V and another peak at

0.33 V). Using cyclic voltammetry, the formal redox potentials for the complex were recorded at 0.167 V and 0.357 V and the diffusion coefficients of the redox centers of the complex ware found to be $1.408 \times 10^{-4}\ cm^2 s^{-1}$ and $5.629 \times 10^{-7}\ cm^2 s^{-1}$. DNPV method required that the variables be optimized as follows: amplitude: 0.05V; first and second pulse width; 0.01 seconds, a sampling width; 0.001 seconds; pulse period; 0.001 seconds and a quiet time:1 second. The developed method was validated to work in the following parameters: Linear concentration range (LCR): 0 to 8 mg/L of phosphate concentration with a linear correlation coefficient $r = 0.9816$; Limit of detection (LOD) of the method: 0.06586 mg/L and the limit of quantitation (LOQ): 0.21952 mg/L. The accuracy of the method in terms of the percentage recovery was in the range of 89% to 102% while the precision in terms percentage relative standard deviation (%RSD) of ten replicate measurements of a single concentration was 7.93%. The accuracy and precision were within acceptable limits. Using the natural water from L. Naivasha, the method was able to detect phosphate concentration at 0.6156 ± 0.1046 mg/L. This study has therefore shown that the differential normal pulse voltammetry (DNPV) technique is sensitive enough to analyse phosphate levels in water.

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Declarations of interest

The authors declare no conflict of interest in this reported work.

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