Fabrication of new solid state phosphate selective electrodes for environmental monitoring

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ABSTRACT

A highly selective and sensitive phosphate sensor has been fabricated by constructing a crystal disk consisting of variable mixtures of aluminium powder (Al), aluminium phosphate ($AlPO_4$) and powdered copper (Cu). The membrane sensor exhibits linear potential response in the concentration range of 1.0×10^{-1} to 1.0×10^{-6} mol L^{-1}. The proposed sensor also exhibits a fast response time of <60 s. Its detection limit is lower than 1.0×10^{-6} mol L^{-1}. The electrode has a long lifetime and can be stored in air when not in use. The selectivity of the sensor with respect to other common ions is excellent.

1. Introduction

Phosphate levels in freshwaters have increased in the past 50 years, which may have a negative effect on aquatic ecology and water quality. Studies show that leaching of phosphate ions as small as $10 \, \mu g \, L^{-1}$ from agricultural land can contribute to eutrophication [1]. Thus, monitoring of phosphate ions is very important. The main methods for determination of phosphate ions in real samples are ion chromatography and spectrophotometric methods such as molybdenum blue and indirect lanthanum chloranilate methods [2].

The development of novel sensors for fast, accurate, sensitive and selective determination of phosphate species is of great interest due to its existence in clinical, environmental, agricultural and medical systems. Recently, a number of hydrogen phosphate membrane sensors based on different ion carriers such as dialkyl and diaryltin derivatives, uranyl salophen, vanadyl salen, vanadyl salophen, bis-thiourea and modified calixarene have been reported [3–6].

Ion sensitive electrodes provide a convenient and quick analytical technique for the estimation of specific ions in solutions. It makes them very attractive for applications where the sample may be turbid or colored as the case is in many environmental samples. The construction and use of ion sensitive electrodes is simple. They are usually cheap and produce results that are accurate and reproducible in short time [7,8]. Ion-selective electrodes (ISEs) are membrane-based electrodes that measure a specific ion in an aqueous solution. When the membrane of the electrode is in contact with a solution containing the specific ion, a voltage, dependent on the level of that ion in solution, develops at the membrane. The voltage develops in relation to an internal or external Ag/AgCl reference electrode. The ISEs measure for the specific ion concentrations directly. Ion-selective electrodes usually have two types of membranes:

i. Solid polymer membrane: The membrane is a porous plastic disk, permeable to the ion exchanger but impermeable to water. It allows the sensing cell to contact the sample solution.
ii. Solid state membrane: Consists of thin crystal disk which serves as an ionic conductor. The voltage developed between the sensing and reference electrodes is a measure of the concentration of the reactive ion being measured. As the concentration of the ion reacting at the sensing electrode varies, so does the voltage measured between the two electrodes.

As described in the Nernst equation, ISE response is a linear equation: $E = Eo + m(\ln a)$ where E is the measured voltage, Eo is the standard potential for the combination of the two half cells, m is the slope, ln is natural log, and a is the activity of the measured ion species. Assuming the ionic strength is fairly constant, the Nernst equation may be rewritten to describe the electrode response to the concentration, C, of the measured ionic species:

$E = Eo + m(\ln C)$. A graph of the natural log of concentration ($\ln C$) vs. potential (V) can be plotted which is linear. The method for determining the concentration of the phosphate anions using our solid state ISEs is based on the above principles. There are very few electrodes in the literature for the determination of phosphate ions. Most of them use polymer membrane technology. The electrodes shelf life and robustness to enable experimenters for use in environmental samples is found to be unsatisfactory. Hence we embarked on the production of solid state membrane disk that is selective to phosphate ions at ambient temperatures and environmental conditions. The electrodes are easy to prepare, easy to handle and have a long life time. The present paper describes the preparation and testing of a new potentiometric phosphate sensitive electrode as analytical tool for use in environmental monitoring.

2. Materials and methods

2.1. Apparatus and reagents

A Metrohm 781 pH/ion meter has been used for potential measurement and Ag/AgCl reference electrode was used as the external reference electrode. All reagents used were of analytical grade and were used without further purification. Measurements were made at ambient room temperature ($23 \pm 5\,^{\circ}C$).

Paul Weber 30 hydraulic press attached to Edward (EDM2) high vacuum pump was utilized in the preparation of pellets.

2.2. Preparation of solid state electrodes

Aluminium powder (Al), aluminium phosphate ($AlPO_4$) and powdered copper (Cu) were mixed in various ratios so that the total weight was 0.5 g. The mixture was mixed well in mortar and pestle and transferred into a die and placed in the hydraulic press for 20 min at a pressure of 7000 atm. A 99% pure copper wire (1 mm in diameter) with a coil at the end was connected to the pellets using an epoxy resin. The pellets were 13.55 mm in diameter and were fixed to a glass tube with the same dimension. To obtain a good sealing the epoxy resin was applied to the edges of the tube from the inside and outside.

2.3. Conditioning of the electrode

Similar electrodes having the same composition were separately kept in air, in distilled water and in 1×10^{-3} mol L^{-1} solution of $Na_2HPO_4 \cdot 7H_2O$ and used to measure a standard phoshate solution at a pH of 7. The results are shown in Fig. 1. The electrode that was immersed in 1×10^{-3} mol L^{-1} solution of $Na_2HPO_4 \cdot 7H_2O$ for about 6 h showed quicker response and better regression for all the experiments conducted. Hence our protocol involves immersing the air stored electrodes in 1×10^{-3} mol L^{-1} solution of $Na_2HPO_4 \cdot 7H_2O$ for about 6 h prior to use. The electrodes have been in use for about 3–4 times a week and have not deviated from their regression value in the past 12 months. The surface of the electrodes was polished with a soft paper before conditioning.

3. Results and discussion

3.1. Effect of electrode composition

Membrane composition affects the sensitivity and selectivity of the phosphate sensitive electrode produced as above. Measurements were made in standard solutions comprising dihydrogen and monohydrogen phosphates in such a way that a buffer solution with the desired pH is obtained. For the purpose of this work several electrodes with varying compositions of Al, Cu and AlPO$_4$
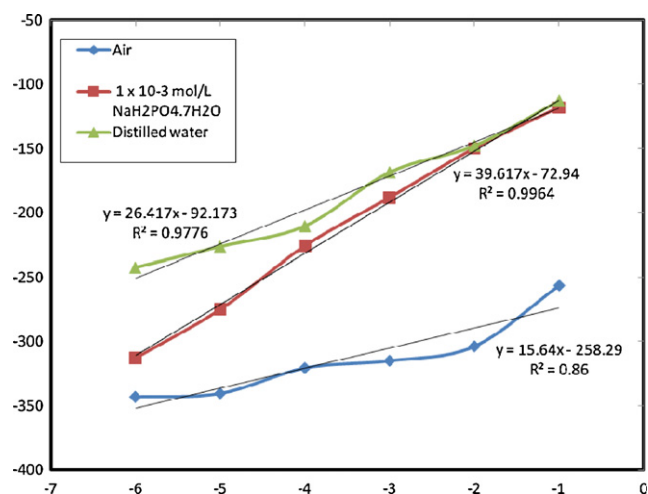

Fig. 1. The effect of media on the performance of the electrode.
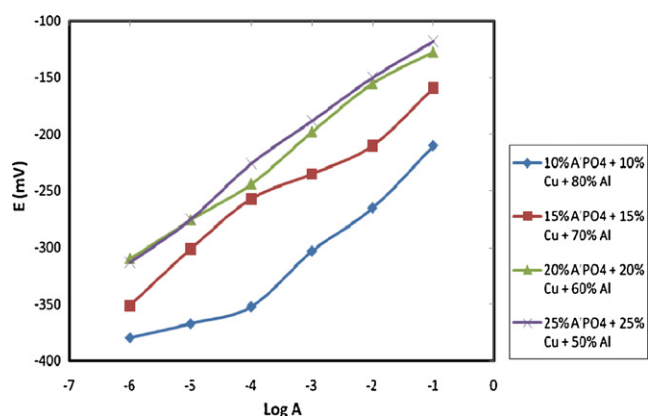

Fig. 2. Calibration curves for the phosphate sensitive electrodes of different compositions.

were made. The electrodes potential responses were measured in the Pi concentration ranges of 10^{-6} to 10^{-1} mol L^{-1}. The calibration curve was obtained by plotting the potential readings against log[Pi]. Fig. 2 and Table 1 summarize the calibration curve studies for some of the electodes fabricated. The electrode with the composition of 25% AlPO$_4$, 25% Cu and 50% Al was chosen for this study as it depicted analytical stability and better sensitivity in the phosphate concentration range under investigation. The Nernestian slope was found to be about 40 mV.

3.2. Response time of the electrode

The conventional IUPAC definition of response time for ISE is the time which elapses between the instant when an ISE and a reference electrode are brought into contact with the sample solution [9]. The response time obviously is dependent on concentration change. In this study, the dipping method that gives static response was employed. The potential values were measured for each concen-

Table 1
Average Nernstian slopes for different phosphate sensitive electrodes.

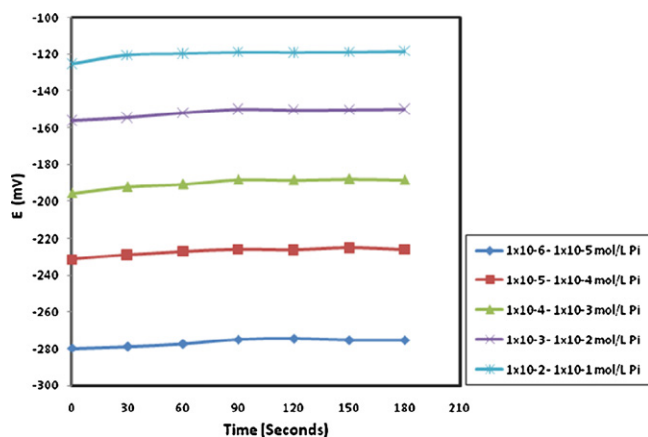| Composition	Average slope (10^{-6} to 10^{-1} mol L^{-1})	R^2
10% AlPO$_4$ + 10% Cu + 80% Al	34.4 ± 1.8	0.9447
15% AlPO$_4$ + 15% Cu + 70% Al	35.8 ± 1.2	0.9814
20% AlPO$_4$ + 20% Cu + 60% Al	37.6 ± 1.1	0.9956
25% AlPO$_4$ + 25% Cu + 50% Al	39.6 ± 1.4	0.9964

Fig. 3. The dependence of response time with concentration.

tration change after 0 (point of electrode immersion in solution), 30, 60, 90, 120, 150 and 180 s when Pi concentration was changed ranging from 1×10^{-6} to 1×10^{-1} mol L^{-1}. The response was found to be stable in about 60 s. The dependence of response time with change of concentration of phosphate species is depicted in Fig. 3.

3.3. Effect of pH and ionic strength

In dilute aqueous solution, phosphate exists in four forms. In strongly basic conditions, the phosphate ion (PO_4^{-3}) predominates, whereas in weakly basic conditions, the hydrogen phosphate ion (HPO_4^{-2}) is prevalent. In weakly acid conditions, the dihydrogen phosphate ion ($H_2PO_4^-$) is most common. In strongly acid conditions, aqueous phosphoric acid (H_3PO_4) is the main form. For a neutral pH (pH 7.0), only $H_2PO_4^-$ and HPO_4^{-2} ions are present in approximately equal amounts. Our standard phosphate solutions at specific pH were prepared by mixing the monohydrogen and dihydrogen phosphates applying the Henderson–Hasselbalch equation: $pH = pK_a + \log([HPO_4^{2-}]/[H_2PO_4^-])$. The speciation diagram of phosphates with respect to pH is shown below [10].

Ion selective electrodes measure the concentration of ions in equilibrium at the membrane surface. In dilute solutions this is directly related to the total number of ions in the solution but at higher concentrations, inter-ionic interactions between all ions in the solution (both positive and negative) tend to reduce the mobility and thus there are relatively fewer of the measured ions in the vicinity of the membrane than in the bulk solution. Thus the measured voltage is less than it would be if it reflected the total number in the solution and this causes an erroneously low estimate of the concentration in samples with a high concentration and/or a complex matrix. The activity coefficient is always less than one and becomes smaller as the ionic strength increases; thus the difference between the measured activity and the actual concentration becomes higher at higher concentrations. This effect causes two main problems in ISE measurement. Firstly, when constructing a calibration graph using concentration units, the line is seen to curve away from linearity as the concentration increases (it remains straight, up to the highest concentrations if activity units are used). Thus, if concentration units are used, it is necessary to measure many more calibration points in order to define the curve more precisely and permit accurate interpolation of sample results. Secondly, it is most likely that the sample solutions will contain other ions in addition to the ion being measured and the ionic strength of the samples may be significantly higher than that of the standards. Thus there will be an incompatibility between the calibration line and the measured samples leading to errors in the interpolated results [11]. The complete Nernst equation is composed of

Nernst factor, sensitivity factor and selectivity factor. If one does not consider the sensitivity and selectivity factors (i.e. assuming 100% sensitivity and selectivity), the Nernst equation can be written as: $E = E_0 + RT/nF$. R/F can be replaced by 0.198 called the Nernst factor. The factor $0.198T/n$ will ideally give a value of 59 mV for a monovalent ion. The Nernst equation can be modified by the sensitivity of the electrode $S/100\%$. Similarly the selectivity of an electrode is never 100%. Other ions may interfere. Hence selectivity factor has to be included to account for the interfering ions. Our ISE is able to detect both the monohydrogen and dihydrogen phosphate ions which exist in the solution in accordance with the speciation diagram given above. Hence the value of n in the Nernst equation may be calculated by considering the concentration of the two species. For example at a pH of 7.0, 62% of the dihydrogen phosphate and 38% of the monohydrogen phosphate anions are presumed to exist in the solution giving rise to a calculated n value of about 1.4. Hence the ideal Nernstian slope is expected to be $0.198T/1.4$ which produces a value of 42 mV. The effect of pH on the response of the electrode in the calibration curve studies was undertaken by varying the pH from 4 to 9. The results showed no change in potential for the electrode under consideration. Since the solutions contain different compositions of the monohydrogen and dihydrogen phosphate anions in the different pH's, it is indicative of the fact that the electrode is sensitive to both anions without any particular preference. Hence the measurement obtained correlates to the total phosphate species in the solution. If activity was directly proportional to concentration, the ISE response would be linear. If there is no ionic strength buffer, increasing the concentration changes the ionic strength, which changes the activity coefficient, which drives the activity away from the concentration, and, therefore, the ISE response becomes non-linear with concentration. Previous investigators have employed the use of 0.1 M $NaNO_3$ in order to keep the ionic strength constant [8]. The effect of a change in ionic strength brought about by the concentrations of phosphate species in our working solution is evident. However the effect of this change on the total electrode potential was found to be less important at solution concentration less than 10^{-2} mol L^{-1}. Hence in this study no attempt was necessitated to keep the ionic strength constant as the main aim of our investigation is to produce robust phosphate sensitive electrodes that may be used in environmental samples without the need for ionic strength control.

3.4. Interference studies for various cations and anions

All ion sensitive electrodes are sensitive to some other ions to some extent. For many applications these interferences are insignificant (unless there is a high ratio of interfering ion to primary ion) and can often be ignored. In some extreme cases, however, the electrode is far more sensitive to the interfering ion than to the primary ion and can only be used if the interfering ion is only present in trace quantities or even completely absent. Hence it is important to study the effects of all other ions in the medium. The response of an ion selective electrode is the potential developed as a function of the ionic activity of the species in solution. Hence when activity increases the electrode potential is expected to become more positive if the electrode is sensing a cation and more negative if it is sensing an anion. As can be seen from Table 2, no appreciable interference was observed for most of the ions studied. The electrode is found to be sensitive to chloride and hydroxide ions appreciably. Further study in the use of the electrode to monitor chloride is under investigation. Determination of both chloride and phosphate ions simultaneously using our electrode for environmental samples is also under investigation. It is generally accepted that the slope of ion sensitive electrodes increase by about 2 mV/decade with each 10 °C rise in temperature [12,13].

Table 2
The effect of interfering ions on the electrode response (the standard phosphate solution is 1×10^{-2} mol L^{-1} constituted from 62% monohydrogen and 38% dihydrogen phosphates. The interferent species were also 1×10^{-2} mol L^{-1} before mixing).

Interferent solution	10 mL standard + 90 mL H$_2$O	10 mL standard + 10 mL interferent + 80 mL H$_2$O	10 mL standard + 20 mL interferent + 70 mL H$_2$O	10 mL standard + 30 mL interferent + 60 mL H$_2$O	10 mL standard + 40 mL interferent + 50 mL H$_2$O
KBr	−287.9	−296.7	−303.1	−310.2	−315.8
KCl	−280.1	−434.1	−459.2	−475.4	−483.5
KI	−296.5	−299.3	−309.5	−306.7	−303.5
KCN	−261.0	−357.7	−424.3	−466.1	−491.2
KOH	−253.0	−258.8	−273.1	−480.1	−579.2
KNO$_3$	−210.4	−234.8	−218.0	−213.1	−206.5
NaCl	−282.6	−451.1	−483.0	−503.2	−521.2
NaOH	−263.2	−266.4	−293.0	−535.4	−644.2
NaF	−231.5	−253.5	−252.3	−231.4	−265.0
NaI	−236.4	−251.2	−264.1	−266.4	−265.1
Na$_2$SO$_4$	−226.5	−218.0	−209.1	−209.4	−208.5
Na$_2$CO$_3$	−213.7	−232.1	−216.0	−202.7	−217.8
CaCl$_2$	−268.1	−401.0	−454.9	−473.7	−480.1
Ca(NO$_3$)$_2$	−267.7	−273.7	−266.2	−279.8	−288.5
Ca(OH)$_2$	−214.3	−306.3	−386.2	−570.8	−1061.2
CaCO$_3$	−236.0	−252.0	−271.9	−248.0	−238.0
MgSO$_4$·7H$_2$O	−254.2	−242.0	−208.9	−200.6	−203.9
MgCl$_2$·6H$_2$O	−245.4	−490.4	−526.5	−553.8	−563.3
Mg(NO$_3$)$_2$·6H$_2$O	−287.7	−216.5	−202.6	−198.7	−191.8
Zn(CN)$_2$	−256.0	−253.6	−254.6	−255.2	−259.8
ZnSO$_4$·7H$_2$O	−203.1	−181.7	−186.6	−186.9	−188.4
Zn(NO$_3$)$_2$·4H$_2$O	−189.9	−166.4	−168.0	−170.8	−171.8
CuSO$_4$	−195.0	−86.8	−19.5	−10.1	−2.5
Cu(NO$_3$)$_2$	−221.7	−119.5	−89.4	82.4	89.5
CuCl$_2$·2H$_2$O	−210.6	−321.7	−389.0	−461.0	−479.7
CoCO$_3$·xH$_2$O	−230.4	−278.4	−260.5	−240.0	−243.8
Co(NO$_3$)$_2$·6H$_2$O	−234.9	−200.2	−216.8	−234.7	−248.9
CoCl$_2$·6H$_2$O	−212.6	−429.1	−474.4	−493.5	−510.0
Ni(NO$_3$)$_2$·6H$_2$O	−243.0	−250.1	−244.9	−249.8	−258.1
NiCl$_2$·6H$_2$O	−251.0	−415.8	−445.9	−477.7	−491.2
NaNO$_3$	−215.1	−212.8	−208.2	−219.1	−225.4
Pb(NO$_3$)$_2$	−206.2	−113.5	−135.5	−143.2	−177.3
AgNO$_3$	−241.0	−127.0	35.2	161.4	182.4
V$_2$O$_5$	−237.6	−216.4	−186.7	−125.1	−53.6
BaCl$_2$·2H$_2$O	−235.8	−381.0	−455.9	−492.8	−519.2
HgCl$_2$	−211.5	−391.2	−453.0	−457.9	−460.8
NH$_4$Br	−308.0	−296.8	−299.6	−303.8	−311.7
NH$_4$Cl	−261.4	−334.9	−410.7	−433.2	−465.5
NH$_4$ClO$_4$	−260.9	−282.4	−286.6	−295.1	−298.0
KClO$_3$	−230.8	−245.3	−280.1	−299.8	−329.1
Na$_4$P$_2$O$_7$·10H$_2$O	−192.0	−191.3	−187.7	−184.7	−182.4

4. Conclusion

Phosphorus (P) loss from agricultural soils has been shown to be a major contributor to anthropogenic eutrophication of surface waters [14]. Among the strategies which have been investigated to counter this problem are source measures which decrease the risk of P being mobilised and transported from the source [15,16]. These source measures have included various soil amendments to increase the soil's capacity to retain P, mostly due to their Fe, Al or Ca content [17]. More precise knowledge on the available phosphorous is mandatory to counteract the ill effects of excess phosphorous in the aquatic environment. Ideally a hand held device that can easily estimate the amount of phosphates in the effluents is required for quick monitoring of the phosphates. Measurement of phosphate has been of tremendous interest in recent decades. Phosphate is an essential nutrient for plants, and its measurement has been used to control fertilizers applied to maximize crop yield and quality in hydroponics and agriculture, or to control undesired growth of the algae and other aquatic vegetation to prevent the eutrophication of natural water bodies. Thus, due to the importance of phosphate and the protection of the global environment, there is a need in the development of simple and compact phosphate sensor. Our work tries to address the problems outlined above.

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