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Evaluation of Phosphate Ion-Selective Membranes for Real-time Soil Nutrient Sensing

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Abstract. *A real-time soil nutrient sensor would allow the efficient collection of data with a fine spatial resolution, to accurately characterize within-field variability for site-specific nutrient application. Our goal was to evaluate the applicability of a phosphate membrane to the measurement of phosphate levels in soil extractants and to determine how previously developed nitrate and potassium*

membranes would be affected by the presence of phosphate. A type of PVC-based phosphate membrane containing an organotin compound, bis(p-chlorobenzyl)tin dichloride, was evaluated, along with the nitrate and potassium membranes, in pH 7 Tris buffer solution and Kelowna soil extractant for sensitivity and long-term stability. The phosphate membranes in the Tris buffer solution of pH 7 exhibited a response over a range of 10^{-5} to 10^{-1} mol/L phosphate concentrations with an average slope of -28.2 ±1.5 mV per activity decade of dibasic phosphate. The response speed of tested electrodes containing phosphate, nitrate and potassium membranes was rapid, reaching an equilibrium response in less than 15 s. However, the phosphate membrane in the Kelowna solution of pH 8.5 was almost insensitive to different phosphate levels from 10^{-6} to 10^{-2} mol/L due to the presence of a high concentration of fluoride in the solution. In addition, the tin compound-based phosphate membranes had limited lifetimes of less than 14 days. It is not expected that the tested phosphate membranes could be used for phosphate detection in other soil extractants, such as Bray P1 and Mehlich III solutions, because they also contain high concentrations of fluoride.

Keywords. ion-selective membranes, ion-selective electrode (ISE), soil testing, phosphate, soil extractants, Kelowna, sensitivity, response time

Introduction

The soil macronutrients, nitrogen (N), phosphorus (P), and potassium (K), are the most important nutrients for crop growth. These nutrients in the soil solution are taken into plants in various ionic forms such as nitrate (NO_3^-), orthophosphates ($H_2PO_4^-$ or HPO_4^{2-}), and potassium (K^+) through a combination of root interception, mass flow and diffusion processes. Accurate measurement of soil macronutrients can be used to more accurately estimate needed fertilizer application rates, increasing the efficiency of soil fertility management, and improving the profitability of crop production.

Excessive use of commercial fertilizer has been cited as a source of contamination of surface and groundwater (Staver and Brinsfield, 1990; Mallarino, 1998). High levels of phosphorus in the soil may leach into water ecosystems and create an imbalance, resulting in excessive growth of algae in lakes and rivers. Optimum application rates can reduce the potential for environmental pollution created by excessive application of chemical fertilizers. Site-specific sensing of macronutrients would make it possible to characterize within-field variability, and lead to fertilizer application rates that are optimized for each sub-field area.

Monitoring phosphorus in soils is typically performed by compositing soil from a number of sampling sites into one sample for analysis using conventional soil laboratory testing methods. Various analytical methods have been used for the determination of phosphorus, mostly based on spectrophotometric techniques for detecting a colored complex formed by the reaction of phosphorus with a molybdate ion (Brown, 1998). However, sample collection and analysis methods are inherently costly and time consuming, thereby limiting the number of samples tested.

Recently, the majority of the research on methods for the determination of phosphorus has concentrated on the use of ion-selective electrodes (ISEs), which respond to monobasic ($H_2PO_4^-$) or dibasic (HPO_4^{2-}) phosphate forms, and flow injection analysis (FIA), because of advantages over spectrophotometric methods, such as fast response and low cost. Several researchers reported on the development of phosphate ISEs using PVC-based membranes to detect phosphates in biological samples (Glazier and Arnold, 1988; 1991; Carey and Riggan, 1994; Liu et al., 1997; Fibbioli et al., 2000; Wroblewski et al., 2001).

Among the PVC-based membranes, a cyclic polyamine ionophore (Carey and Riggan, 1994) provided good selectivity and favorable sensitivity with a detection limit of 10^{-5} mol/L dibasic phosphate in a solution with pH controlled at 7.2. Also, a tin compound ISE containing bis(p-chlorobenzyltin) dichloride as the ionophore was developed by Glazier and Arnold (1988 and 1991), and showed good selectivity for dibasic phosphate over nitrate and chloride.

Cobalt wire ISEs were useful in detecting monobasic phosphate in a potassium hydrogenphthalate solution of pH 5 (Chen et al., 1997; Marco et al., 1998). The solid-state ion-selective electrodes using cobalt wires have been used to monitor phosphates in waste waters and fertilizers (Xiao et al., 1995; Meruva and Meyerhoff, 1996; Chen et al., 1997; Engblom, 1998; Marco et al., 1998). In particular, Engblom (1998) studied the applicability of a metallic cobalt wire electrode to the measurement of phosphate in ammonium lactate-acetic acid (AL) extracts commonly used in Sweden. As a result, the cobalt electrodes were applicable to phosphate detection in soil extracts. However, the sensor was significantly affected by organic substances and pH in soil extracts, thereby resulting in reduced sensitivity.

Despite this continuing effort, few phosphate sensors have become commercially available, because the design of a carrier for selective recognition of orthophosphates is especially challenging (Tsagatakis et al., 1994; Fibbioli et al., 2000). According to Tsagatakis et al. (1994),

the free energy of the phosphate species is very small and the large size of orthophosphate prohibits the use of size-exclusion principles for increased selectivity. Another limitation is that the response of phosphate ISEs is dependent on the solution pH, since the ionic forms of phosphate in the solution vary as pH changes.

As we have previously evaluated nitrate and potassium membranes (Kim et al., 2003; 2004), the aim of this study was to investigate the applicability of a PVC-based phosphate membrane containing an organotin compound (Glazier and Arnold, 1988; 1991) to the determination of phosphates in soil extractants. For this purpose, the response characteristics of the phosphate membranes were evaluated, along with the nitrate and potassium membranes developed in previous studies, in terms of sensitivity and repeatability. In addition, the effects of base solution and membrane age on sensing performance were investigated.

Materials and Methods

Reagents

PVC-based phosphate ion-selective membranes were prepared using a tin compound, bis(p-chlorobenzyl)tin dichloride. The phosphate ionophore was synthesized according to the procedures outlined in Glazier (1988). Dibutyl sebacate as a plasticizer, N, N-dimethylformamide as a solvent for organic compounds, polyvinyl chloride (PVC), and tetrahydrofuran (THF) were purchased from Sigma-Aldrich Corp. (St. Louis, Mo.).

One nitrate ion-selective membrane reported in previous papers (Kim et al, 2003; 2004), was prepared using a quaternary ammonium compound, tetradodecylammonium nitrate (TDDA), and a plasticizer, nitrophenyl octyl ether (NPOE). Valinomycin, bis(2-ethylhexyl) sebacate (DOS) and potassium tetrakis (4-chlorophenyl) borate (KTpClPB) were used for the preparation of potassium ion-selective membranes. These chemicals also were purchased from Sigma-Aldrich Corp.

Two different base solutions, pH 7 Tris buffer solution and Kelowna soil extracting solution, were prepared using distilled and deionized water with a specific resistance of 18.0 MΩ cm^{-1} produced by a distilled water system (Model MP-6A, Corning). The pH 7 buffer solution consisted of 0.01 mol/L tris(hydroxymethyl) aminomethane (Tris, Fisher Scientific) with 0.0045 mol/L H_2SO_4 (sulfuric acid, Sigma-Aldrich) and the Kelowna extractant solution contained 0.25 mol/L CH_3COOH (acetic acid, Fisher Scientific) and 0.015 mol/L NH_4F(ammonium fluoride, Sigma-Aldrich).

All other chemicals used -- potassium dibasic phosphate (K_2HPO_4), sodium nitrate ($NaNO_3$), lithium acetate (LiAc), potassium chloride (KCl), and ammonium hydroxide (NH4OH), were of analytical reagent grade and purchased from Sigma-Aldrich Corp. (St. Louis, Mo.) and Fisher Scientific (Cincinnati, Ohio).

Preparation of Ion-Selective Membranes and Electrodes

The phosphate membrane-casting solution was prepared as reported in previous studies (Glazier and Arnold, 1991), and contained 70.2 mg (18% wt) of bis(p-chlorobenzyl)tin dichloride, 133.5 mg (34% wt) of PVC, 141.9 mg (36% wt) of dibutyl sebacate, and 48.3 mg (12% wt) of N, N-dimethylformamide in 3 mL of THF. Phosphate membranes were formed, as previously described by Glazier and Arnold (1988; 1991), by dipping the free ends of Hitachi ISE electrode bodies in the casting solution three times. Membranes were allowed to dry after the first two

dips and then they were stored overnight following the final dip. Phosphate ISEs were constructed by using 0.1mol/L KCl as an internal filling solution in the electrode body and inserting an Ag/AgCl reference electrode into the top. The electrodes were conditioned overnight in the Tris buffer solution. Prior to testing, the electrodes were immersed in 0.01M phosphate solution three times for a few minutes so that steady electrical potentials could be obtained in the presence of phosphate.

Ion-selective membranes for nitrate and potassium were prepared based on TDDA and valinomycin ionophores as reported in previous papers (Kim et al., 2003; 2004). The nitrate ion-selective membrane was obtained by casting a mixture of TDDA (30 mg, 15% wt), NPOE (80 mg, 40% wt), and PVC (90 mg, 45% wt) in 2 mL of THF. The composition of the potassium ion-selective membrane prepared was 4 mg (2% wt) of valinomycin, 1 mg (0.5% wt) of lipophilic additive (KTpClPB), 129.4 mg (64.70% wt) of DOS plasticizer, and 65.6 mg (32.80% wt) of PVC in 2 mL of THF. The casting solutions for both nitrate and potassium membranes were poured into 23-mm glass rings resting on polished glass plates, and allowed to evaporate for 24 h at room temperature. The membranes, formed as a film, were removed from the glass plate. Membrane disks, cut with a diameter of 2.5 mm from the membrane, were attached to the ends of the Hitachi ISE electrode bodies using THF solution. Each nitrate ISE electrode was filled with an internal solution consisting of 0.01mol/L $NaNO_3$ and 0.01mol/L NaCl. Potassium chloride (0.01mol/L) was employed as the internal reference solution of the potassium ISE electrodes. The nitrate and potassium ISE electrodes were stored overnight separately in 0.01 mol/L NaNO3 and 0.01 mol/L KCl solution, respectively.

A double junction Ag/AgCl electrode (Model PHE 3211, Omega Engineering, Stamford, Conn.) was used as the reference electrode. To dissuade contamination of sample analyte ions such as K^+ and NO_3^- by the reference electrode, 1mol/L LiAc was used as the outer reference solution in the reference electrode.

EMF Measurements

A test apparatus (fig. 1) was used for automatically controlling the system based on user-defined parameters and simultaneously recording EMF (electromotive force) values of 16 electrodes. Details of this equipment were described previously (Kim et al., 2003; 2004).

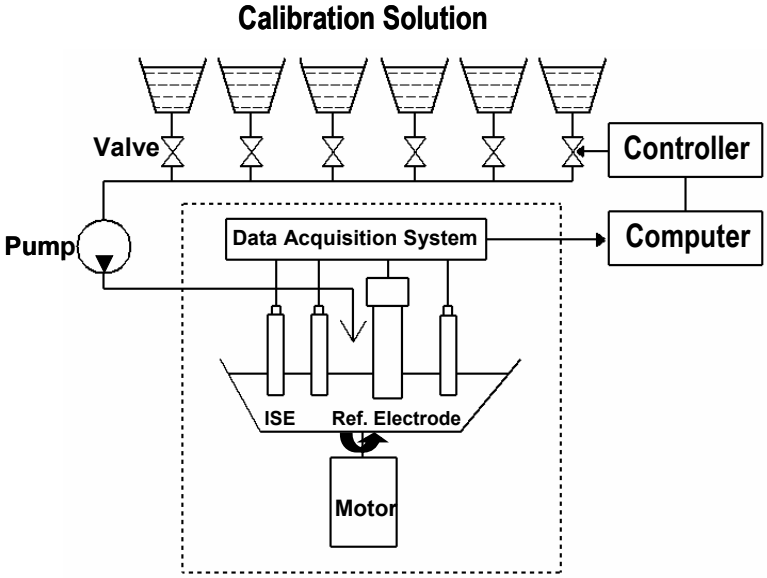

Figure 1. Schematic representation of the automated test apparatus.

Data collection was conducted at 15 s and 60 s after the injection of each test solution into the test stand. At each of the two data collection times, three measurements, each consisting of the mean of a 0.1-s burst of 1 kHz data, were obtained on a 3-s interval and averaged.

Sensitivity Tests

The response characteristics of the electrodes were examined by measuring the EMFs of each ISE in six standard solutions of K_2HPO_4 containing from 10^{-6} to 10^{-1} mol/L concentrations. The standard solutions were prepared by successive 10:1 dilutions of the 0.1 mol/L concentration using each of two different base solutions (the Tris buffer and the Kelowna solution).

Each test included phosphate, nitrate, and potassium ISEs. A set of test phosphate ISEs included four different ages, i.e., time between membrane preparation and test: six electrodes of age 4 days, and one each of 14, 20, and 33 days, in order to determine how the responses of the ISEs to phosphate changed as the membranes aged. The electrodes with potassium and nitrate membranes were also tested to investigate how those membranes would be affected by the presence of phosphate and potassium. As a result, nine phosphate ISEs, two potassium ISEs, and two nitrate ISEs were included in the test set.

Since the phosphate species in solution is a function of pH (Lindsay, 1979), fig. 2a), the pHs of all tested Tris buffer standards containing different phosphate concentrations were adjusted to 7.00±0.01, as measured with a combination pH electrode (Model 81-72, Orion, Cambridge, Mass.) and a pH meter (Model SA-720, Orion, Cambridge, Mass.), through the addition of sulfuric acid. Duplicating this pH level used by Glazier and Arnold (1991) allowed a comparison with those results, even though, at this pH level, a portion of the phosphate is not in the dibasic form detected by the ISE. When using the Kelowna extractant as the base solution, the pHs of the standard solutions were readjusted to 8.5±0.01, where the predominant form is dibasic phosphate. Another advantage was that pH 8.5 was above the range of pH where small additions of a base solution produce rapid pH changes (fig. 2b).

The sensitivity tests were repeated three times. The EMF values of the all ISEs at different K_2HPO_4 concentrations (10^{-6}, 10^{-5}, 10^{-4}, 10^{-3}, 10^{-2}, and 10^{-1} mol/L K_2HPO_4) were determined in each test sequence with the automated test stand.

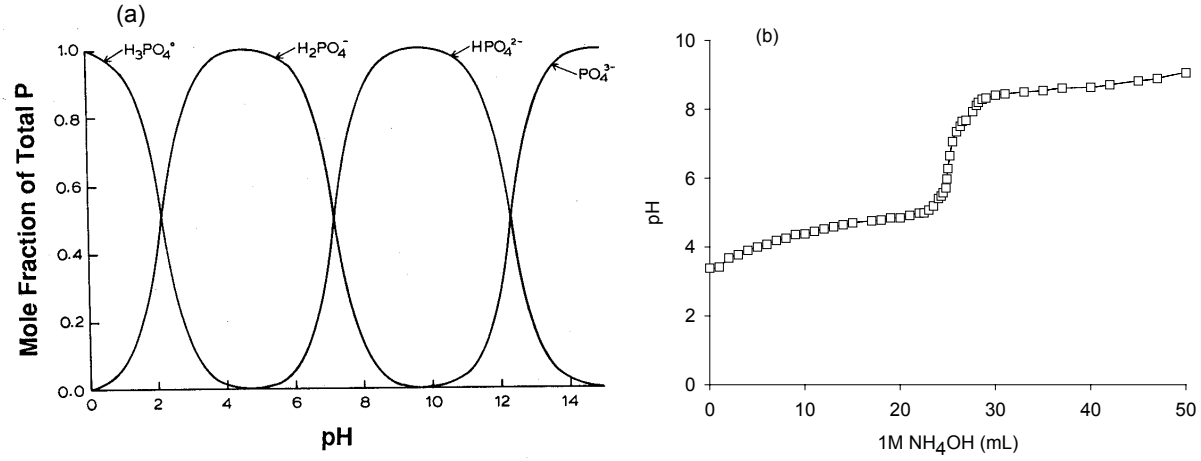

Figure 2. Distribution of orthophosphate ions depending on pH level (a, Lindsay (1979)) and titration curve for 90mL of Kelowna solution (b).

Since standard potentials among electrodes normally vary due to difference in internal resistance and thickness of the membrane (Carey and Riggan, 1994), the electric potential was normalized by setting the EMF values obtained at 10^{-6}M phosphate concentration in the third replication to 0 mV. This procedure removed variability between electrodes in terms of standard potential, while allowing differences between replications to be evaluated.

To calculate sensitivity slopes for phosphate ISEs in tested concentration ranges, each activity of dibasic and monobasic phosphate species in solution was calculated using an iterative method. The approach considers change in ionic strength and uses known equilibrium constants for the reaction of phosphates in solution, because the ionic strength is a function of the solution pH due to phosphate species equilibria with the hydrogen ion activity (Lindsay, 1979; Carey and Riggan, 1994).

The total phosphate concentration in the pH range of 4~10 can be calculated:

$$[PO_4]_{total} = [H_2PO_4^-] + [HPO_4^{2-}] \quad (1)$$

where $[PO_4]$ is total phosphate concentration, and $[H_2PO_4]$ and $[HPO_4]$ are concentrations of monobasic and dibasic phosphates, respectively.

The equilibrium constant between monobasic and dibasic phosphates can be represented:

$$\log\frac{[H_2PO_4^-]}{[HPO_4^{2-}]} = 7.20 - pH \quad (2)$$

The ionic strength was calculated using the estimated concentrations, and the activity coefficients for the dibasic phosphate species were then estimated using the Debye-Hückel formula (Lindsay, 1979; Eggins, 2002).

Results and Discussion

Response Characteristics in Tris Buffer and Kelowna Solutions

The response (EMF) curves of the six newest phosphate ISEs (4 days old at the time of testing), two nitrate and two potassium ISEs to different potassium phosphate (K_2HPO_4) concentrations ranging from 10^{-6} mol/L to 10^{-1} mol/L in pH 7 Tris buffer and Kelowna solutions are shown in figure 3. In each of the three replicates of the test sequence, successively more concentrated test solutions were presented to the ISEs. It is evident that the phosphate electrodes in the Tris buffer solution (fig. 3a) were sensitive to different phosphate concentrations and the responses were repeatable during three replicate measurements. Similarly, the potassium ISEs responded to potassium with consistent sensitivity (fig. 3b). The nitrate ISEs had a slight sensitivity to phosphate (fig. 3b) with a decrease in EMF (<15 mV) at 10^{-1} mol/L phosphate concentration.

The use of Kelowna solution influenced the responses of all ISEs significantly. In particular, as shown in figure 3c, the responses of the phosphate ISEs in the Kelowna solution were decreased considerably, thereby resulting in little change in EMF in the range of 10^{-6} to 10^{-2} mol/L phosphate concentration. Similarly, at low potassium concentrations below 10^{-3} mol/L, there appeared to be little change in response for the potassium membranes (fig. 3d). However, the potassium ISEs exhibited a linear response over a range of 10^{-3} to 10^{-1} mol/L potassium concentrations.

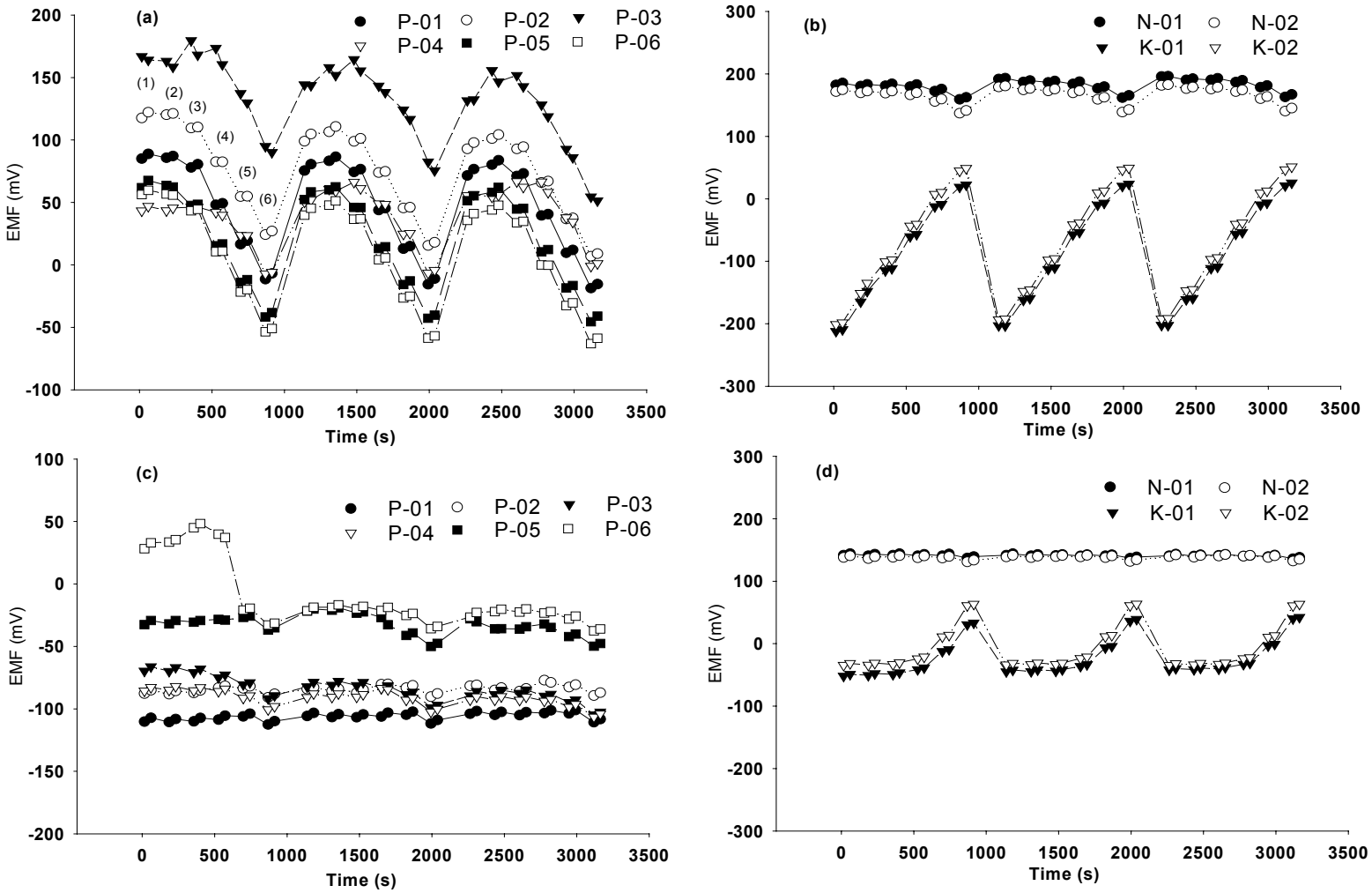

Figure 3. Response test profiles for different K_2HPO_4 concentrations: (a) phosphate membrane response in Tris buffer, (b) nitrate and potassium membrane response in Tris buffer, (c) phosphate membrane response in Kelowna extracting solution, and (d) nitrate and potassium membrane response in Kelowna extracting solution. The numbers in (a) identify the different K_2HPO_4 concentrations: (1) 10^{-6}; (2) 10^{-5}; (3) 10^{-4}; (4) 10^{-3}; (5) 10^{-2}; and (6) 10^{-1} mol/L.

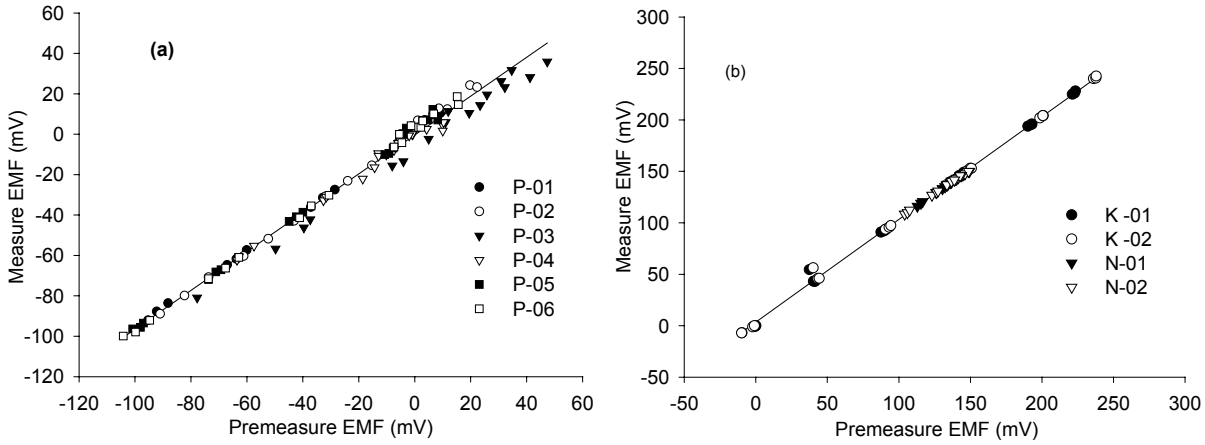

Figure 4. Relationship between EMF values measured 15s and 60s after the injection of test solutions for phosphate (a) and nitrate and potassium membranes (b).

A study of the response speed of each membrane type was conducted by relating the EMF values taken at 15 s (premeasure) to those obtained at 60 s (measure) after each test solution was introduced. As shown in fig. 4, the measure EMF (Y) values were highly correlated with the premeasure EMFs (X), showing an almost 1:1 relationship between the two values: Y= 0.96X - 0.41 (R^2=0.99**) for phosphate and Y= 0.99X + 3.39 (R^2=0.99**) for nitrate and potassium ISEs. Therefore, it was evident that the ISEs could reach an equilibrium response in less than 15 s.

Variability of response between membranes

The variability of response among the six tested phosphate ISEs was examined by comparing the standard deviations in EMF measured with the ISEs for three replicate measurements of phosphates and average sensitivity of each ISE (fig. 5). One electrode, P-03, showed relatively poor repeatability (fig. 5a) with a standard deviation in EMF of >10 mV. Comparing sensitivity slopes in the concentration ranges of 10^{-5} to 10^{-1}, and 10^{-4} to 10^{-1} mol/L phosphate (fig. 5b), one electrode, P-04, showed less sensitivity than did the other electrodes. Obviously, these two electrodes (P-03 and P-04) were producing questionable data. Based on data obtained with the other four electrodes (P-01, P-02, P-05, and P-06), phosphate ISEs responded to phosphate

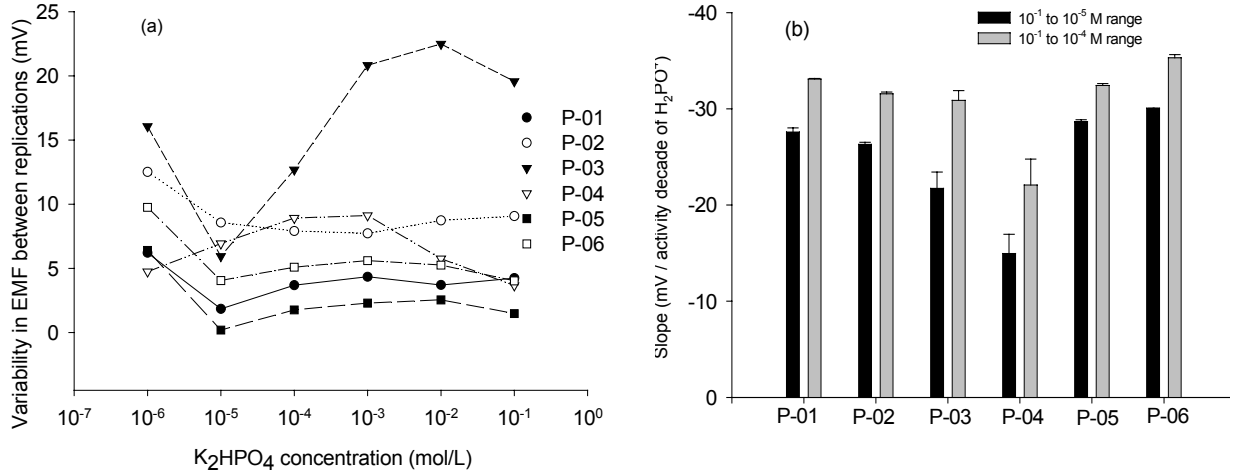

Figure 5. Comparison of phosphate ISEs in terms of standard deviation of EMF values (a) and sensitivity slope (b).

over a range of 10^{-5} to 10^{-1} mol/L with an average slope of -28.2 mV per activity decade of HPO_4^{2-}, yielding a standard deviation in EMFs of 5.3 ± 3.0 mV for three replicate measurements.

Sensitivity of membranes in Tris buffer and Kelowna solutions

Sensitivity of each membrane type to varying phosphate concentrations was calculated when using the Tris buffer and the Kelowna solution as base solutions (fig. 6). In general, in the Tris buffer solution (pH = 7.00±0.01), the EMF values obtained with the phosphate membranes (fig. 6a) were almost linearly proportional to the logarithm of phosphate concentration in the range of 10^{-4} to 10^{-1} mol/L with a sensitivity slope of -33.1 ± 1.5 mV per activity decade of HPO_4^{2-}, which is comparable to the sensitivities reported in previous studies (Glazier and Arnold, 1988). In contrast, in the Kelowna solution (pH = 8.5 ± 0.01), the four phosphate membranes were almost insensitive to phosphate (fig. 6c), regardless of the level of phosphate in the tested solutions.

The potassium membranes in the Tris buffer solution (fig. 6b) showed a slope of 50.3 ± 1.3 mV per activity decade of K^+. In the Kelowna solution (fig. 6d), at low potassium concentrations below 10^{-3} mol/L, the sensitivity of potassium membranes was considerably decreased, thereby

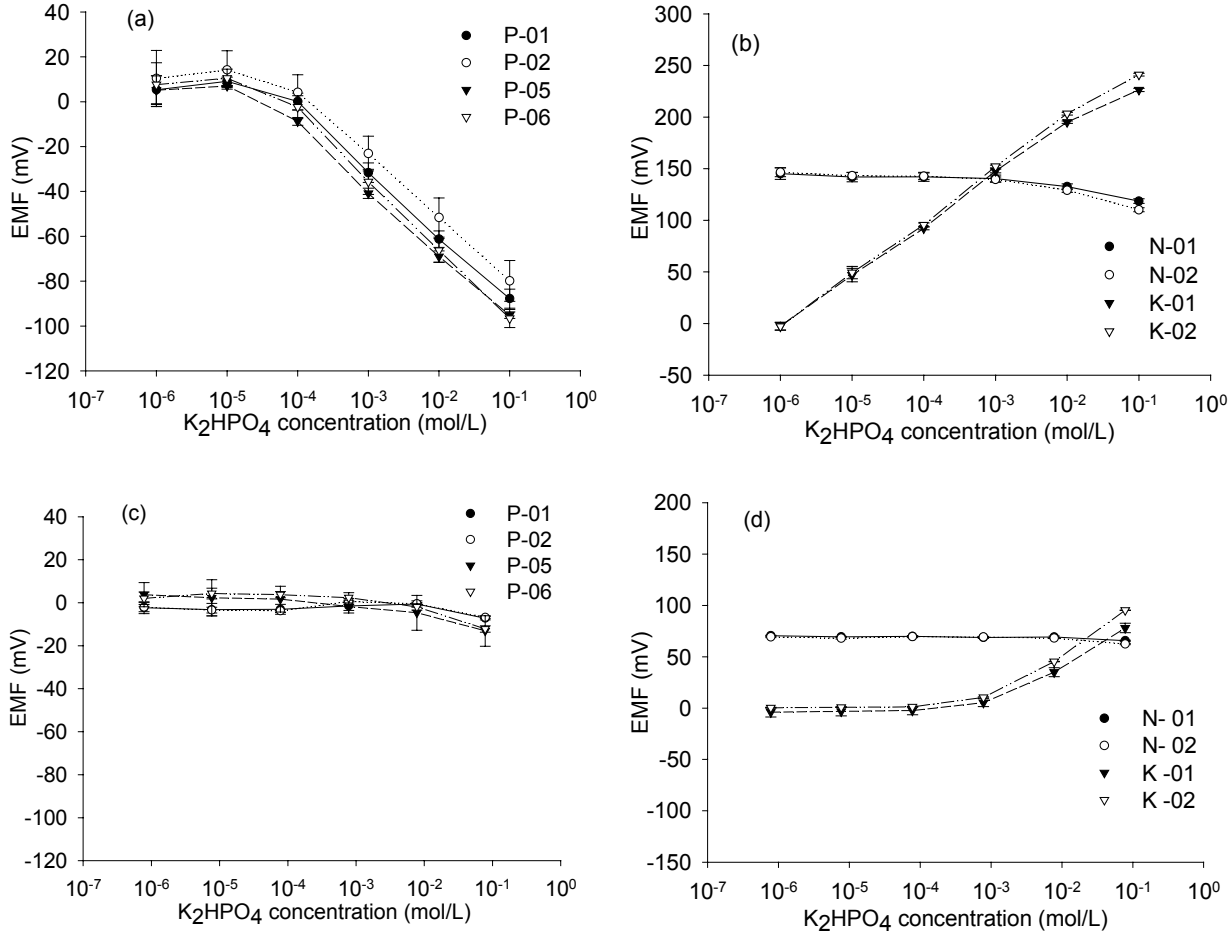

Figure 6. Response of each membrane to different K_2HPO_4 concentrations: (a) phosphate membrane response in Tris buffer, (b) nitrate and potassium membrane response in Tris buffer, (c) phosphate membrane response in Kelowna extracting solution, and (d) nitrate and potassium membrane response in Kelowna extracting solution.

resulting in a detection limit of about 10^{-3} mol/L, which is higher than that (10^{-4} mol/L) obtained in previous studies (Kim et al., 2004). Such a decrease in sensitivity for the potassium membranes, as compared to that in previous tests, occurred because of the presence of a high concentration (about 0.2 mol/L) of ammonium (NH_4^+), which was introduced when ammonium hydroxide was added to adjust the pH of the Kelowna solution.

Effects of base solution type and membrane age on sensitivity

As observed from a plot (fig. 7a) comparing responses of the phosphate membranes in different base solutions, the average EMF value of the phosphate ISEs in the Tris buffer solution decreased by about 100 mV as the phosphate concentration increased from 10^{-6} mol/L to 10^{-1} mol/L, whereas the decrease over the same concentration range obtained in the Kelowna solution was only about 13 ~18 mV.

Such a significant decrease in sensitivity for the phosphate membranes may be associated with the presence of a high concentration of fluoride (0.015 mol/L) in the Kelowna solution. Previous studies by Glazier and Arnold (1991) show that the selectivity coefficient of the membrane for fluoride is 0.279, which means that the tin compound phosphate membrane is only about 3.58 times more sensitive to dibasic phosphate than to fluoride. When fluoride and dibasic phosphate having the same concentration are dissolved in solution, the ionic activities for fluoride are larger than those for dibasic phosphate, since there is a greater decrease in ionic activity for dibasic phosphate than for fluoride. For example, at 0.1 mol/L total phosphate concentration, the ionic activity of dibasic phosphate in the pH 8.5 Kelowna solution was approximately 0.01, which is nearly the same as that of 0.015 mol/L fluoride concentration. This means the sensitivity in the 0.1 mol/L phosphate standard may be reduced by about 8 mV (27.9% of 28.2 mV/decade in a range of 10^{-5} to 10^{-1} mol/L) due to interference by the fluoride ion. The reduced sensitivity of about 20 mV for the phosphate concentration change from 0.01 mol/L to 0.1 mol/L is of similar magnitude to the sensitivity of -15 ~ -18 mV/decade obtained in this experiment.

The changes in response to phosphate when electrodes having different ages were simultaneously tested are shown in figure 7b. The electrodes were stored in the pH 7 Tris buffer at room temperature (22.5 to 23.5 °C) between measurements. As shown in figure 7b, the responses of the electrodes dramatically deteriorated as the electrodes aged. After 14 days of use, an increase in detection limit from 10^{-5} to 10^{-4} ~10^{-3} mol/L total phosphate concentration and a much shorter linear range were observed. Possible causes of the deterioration of electrode response are rapid leaching of the tin compound ionophore from the membrane or a rapid breakdown of the tin compound structure.

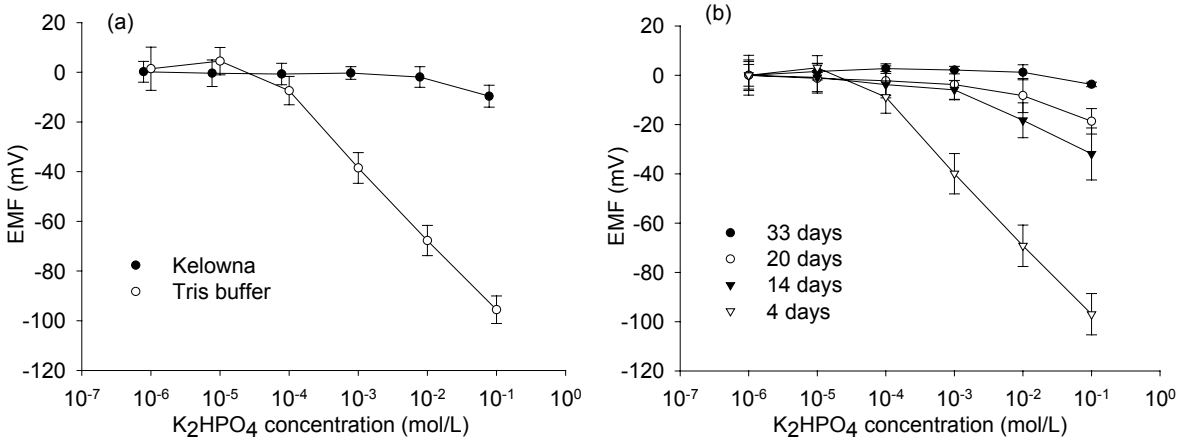

Figure 7. Effects of base solutions (a) and membrane ages (b) on change in electrode response.

Summary and Conclusions

The sensitivity and long-term stability of a PVC-based phosphate membrane containing an organotin compound as an ionophore were evaluated in pH 7 Tris buffer solution and Kelowna soil extractant to find out whether the phosphate membranes could be of use in the determination of phosphate in soil extractants. PVC-based nitrate and potassium membranes developed in previous studies (Kim et al, 2003; 2004) were also included in the test set to investigate the sensitivity of the nitrate and potassium membranes to phosphate and potassium.

The PVC-based phosphate membrane containing an organotin compound exhibited a linear response over a range of 10^{-4} to 10^{-1} mol/L phosphate concentrations in the Tris buffer of pH 7 with an average slope of -33.1 $\pm$1.5 mV per activity decade of dibasic phosphate, which is comparable to results obtained in previous studies (Glazier and Arnold, 1988; 1991), The response speed of tested electrodes containing phosphate, nitrate and potassium membranes was rapid enough to reach an equilibrium response in less than 15 s. The tested potassium membranes responded to potassium with consistent sensitivity and good repeatability, consistent with results of previous tests (Kim et al., 2004). Nitrate membranes showed little response, as expected, to phosphate even though there was a slight decrease in EMF at 10^{-1} mol/L phosphate concentration in the Tris buffer solution.

The phosphate membrane in the Kelowna solution, which had been adjusted to a pH of 8.5, was almost insensitive to different phosphate levels from 10^{-6} to 10^{-2} mol/L due to the presence of a high concentration of fluoride in the Kelowna solution. Regrettably, it is not expected that the responses of the tested phosphate membranes would be different in other common phosphorus soil extractants, such as Bray P1 and Mehlich III solutions, because they also contain high concentrations of fluoride. Modification of the composition of the extractant solution to reduce the level of fluoride may be an area for future work. However, this approach does not appear promising, because fluoride plays a significant role in preventing the re-adsorption of solubilized P by soil colloids during extraction.

The limited functional lifetime of less than 14 days exhibited by the phosphate membrane was less than had been expected. Additional research will be needed to determine if modifications to storage conditions can extend membrane life.

For future work, evaluation of other types of phosphate membranes is planned, with the goal of identifying a sensitive membrane composition that is minimally affected by the various ions present in soil extractants.

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