LABORATORY EVALUATION OF ION-SELECTIVE ELECTRODES FOR SIMULTANEOUS ANALYSIS OF MACRONUTRIENTS IN HYDROPONIC SOLUTION

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ABSTRACT

Automated sensing of macronutrients in hydroponic solution would allow more efficient management of nutrients for crop growth in closed hydroponic systems. Ion-selective microelectrode technology requires an ion-selective membrane or a solid metal material that responds selectively to one analyte in the presence of other ions in a solution. This study reports on the evaluation of a sensor array consisting of five different ion selective electrodes (ISEs) for simultaneous determination of NO_3^--N, $H_2PO_4^-$, K^+, Ca^{2+} and Mg^{2+} in hydroponic solution. Ion-selective membranes for nitrate, potassium, calcium, and magnesium and a cobalt-rod metal for phosphate were evaluated using an automated test stand by comparing the sensing elements with respect to their sensitivity and selectivity in standard solutions. The feasibility of using the sensor array for simultaneous determination of N-P-K-Ca-Mg over the typical range of macronutrient concentrations in hydroponic solutions was examined. The sensitivity and selectivity of PVC membrane-based ion-selective electrodes with TDDA-NPOE, valinomycin, and calcium ionophore II for NO_3^--N, K^+ and Ca^{2+} respectively, and of a cobalt rod-based ion-selective electrode for $H_2PO_4^-$ were satisfactory for measuring macronutrients over typical ranges of hydroponic concentrations. However, the use of potassium hydrogen phthalate (KHP) buffer solution was needed to measure phosphorus ions with acceptable sensitivity. Further studies to identify a magnesium ion-selective membrane that shows a sensitive response to magnesium in the presence of calcium are needed.

INTRODUCTION

Hydroponics, known as a soilless farming, is a method of growing plants using mineral nutrient solutions in water, without soil. The macronutrients, nitrogen (N), phosphorus (P), potassium (K), calcium (Ca) and magnesium (Mg) in the hydroponic solution are essential elements for crop growth. These nutrients are generally taken into plants in various ionic forms, such as nitrate (NO_3^-), orthophosphates ($H_2PO_4^-$ or HPO_4^{2-}), potassium (K^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}) through a combination of root interception, mass flow and diffusion processes (Havlin et al., 1999). Current nutrient management practices generally require that samples of the recirculation water be sent to a laboratory in order to determine available nutrient status of hydroponic solutions, both for efficient use of fertilizers as well as for reduction of environmental impact. However, these laboratory methods are cumbersome and time consuming, resulting in relatively slow response times when changes in nutrient management are indicated. Responsiveness could be increased through the use of fast on-site measurements of macronutrients using sensor technology.

The need for such fast on-site monitoring has led to the application of ion-selective electrode (ISE) technology for measurement of hydroponic macronutrients, because of advantages over analytical methods (i.e., spectroscopic techniques). Advantages of ISE technology include: simple methodology; direct measurement of analyte; sensitivity over a wide concentration range; low cost; and portability. An important component of ISEs is an ion-selective membrane that responds selectively to one analyte in the presence of other ions in a solution. Significant progress has been made in recent years in the development of various ion-selective membranes in the area of analytical chemistry. There are currently ion-selective membranes available for most of the important hydroponic nutrients, including NO_3^-, K^+, Ca^{2+}, Mg^{2+}, and Cl^- (Nielson and Hansen, 1976; Tsukada et al., 1989; Knoll et al., 1994; Gallardo et al., 2004). However, disadvantages of ion-selective electrodes, as compared to the analytical methods, include possible chemical interferences by other ions and a possible limitation of the accuracy of the measurement due to electrode response drift (Carey and Riggan, 1994). Therefore, the application of the ion sensors based on ion-selective membranes to hydroponic nutrient sensing might be limited by high concentrations of various interfering ions, such as nitrate, ammonium, phosphorus, potassium, calcium, magnesium, and sulfur, in hydroponic solutions.

The objective of this study was to characterize the capabilities of various ion-selective membranes for hydroponic nutrient sensing with respect to their sensitivity to target ions and selectivity against interferences of other ions. Specifically, we wanted to identify a combination of ion-selective membranes suitable for use with a real-time ISE sensor that could measure the concentrations of NO_3^--N, $H_2PO_4^-$, K^+, Ca^{2+} and Mg^{2+} ions in hydroponic solutions.

MATERIALS AND METHODS

Preparation of N-P-K-Ca-Mg Ion-Selective Electrodes

Following detailed procedures reported in previous research (Maj-Zurawsk et al., 1989; Muller et al., 1988; Schefer et al., 1986, Kim et al, 2006), five different PVC-based ion-selective membranes were prepared with different mixtures of chemicals for sensing nitrate, potassium, calcium, and magnesium ions (Table 1 & Fig. 1). The chemical compositions of the nitrate and potassium ion-selective membranes were the same as those reported in Kim et al. (2006). One and two chemical compositions for calcium and magnesium membranes, respectively, were prepared according to the procedures described in several previous studies (Maj-Zurawsk et al., 1989; Muller et al., 1988; Schefer et al., 1986). For sensing phosphate, cobalt electrodes with a purity of 99.95% were prepared, according to procedures reported in Kim et al. (2007).

Table 1. Chemical composition of nitrate, potassium, calcium, and magnesium ion-selective membranes used in the study.

| Target Ion	Chemicals used	Composition
NO_3^-	TDDA(Tetradodecylammonium nitrate)	15% wt (30mg)
	NPOE (2-Nitrophenyl octylether)	40% wt (80mg)
	PVC (Polyvinyl chloride high molecular weight)	45% wt (90mg)
K^+	Valinomycin	2% wt (4mg)
	KTpClPB (Potassium tetrakis(4-chloropheny)borate)	0.5% wt (1mg)
	DOS (Bis(2-ethyhexyl) sebacate)	64.7% wt (129.4mg)
	PVC	32.8% wt (65.6mg)
Ca^{++}	Calcium Ionophore Ⅱ (Schefer et al., 1986)	1.0% wt (2mg)
	KTpClPB	0.6% wt (1.2mg)
	NPOE	65.60% wt (131.2mg)
	PVC	32.80% wt (65.6mg)
Mg^{++}(I)	Magnesium Ionophore Ⅰ (Muller et al., 1988)	1.4% wt (2.8mg)
	KTpClPB	1.0% wt (2mg)
	NPOE	64.5% wt (129mg)
	PVC	33.1% wt (66.2mg)
Mg^{++}(III)	Magnesium IonophoreⅢ(Maj-Zurawsk et al., 1989)	0.99% wt (1.98mg)
	KTpClPB	0.64% wt (1.28mg)
	Chloroparafin	65.58% wt (131.16mg)
	PVC	32.79% wt (65.58mg)

Fig. 1. Ion-selective membranes for N, K, Ca, and Mg (left) and cobalt electrode for P (right).

The membrane disks with a diameter of 2.5 mm were attached to the ends of PVC electrode bodies using tetrahydrofuran (THF) solvent. Each ISE electrode was filled with an internal solution consisting of 0.01M $NaNO_3$ + 0.01M NaCl, 0.01M KCl, 0.01M $CaCl_2$, and 0.01M $MgCl_2$, for N, K, Ca, and Mg ions, respectively. An Ag/AgCl electrode was immersed as the inner reference electrode. The P electrode was prepared by pressing a 6-mm-long segment of cobalt rod into the hole of the PVC electrode body. The gap between the electrode body and the rod was filled with silicone and allowed to dry overnight. A glass junction Ag/AgCl electrode (BAS, USA) was used as the reference electrode.

EMF Measurements

An automated test apparatus (Fig. 2) was designed for the simultaneous measurement of the electromotive forces (EMFs) of 8 ISE electrodes generated by the change in membrane potential at different ionic concentrations. To control the system and record values obtained from the ISE electrodes, a control program was developed with Labview CVI. A National Instruments data acquisition board (NI PCI-6221) and a computer were used to collect and store ISE voltage outputs. Various test solutions were contained in eight stainless steel buckets, and were transferred to the sample solution holder by a multi-channel peristaltic pump. The program automatically activated valves to control solution flow into the sample holder. The program also controlled the rotational speed of the sample holder at 37 rpm to stir the test solutions during data collection. Three rinses were used at each solution exchange to completely remove any residues of the previous solution. To expel solutions from the holder between tests and rinses, the rotational speed was increased to 290 rpm. Each individual test began when the desired volume of test solution had been delivered to the solution holder, which was rotating at 37 rpm. After 60 s, three EMF measurements, each consisting of the mean of a 0.1 s burst of 1,000 Hz data, were obtained on a 3 s interval by the A/D board. The three electrode readings were averaged to represent a single EMF output response at each concentration level.
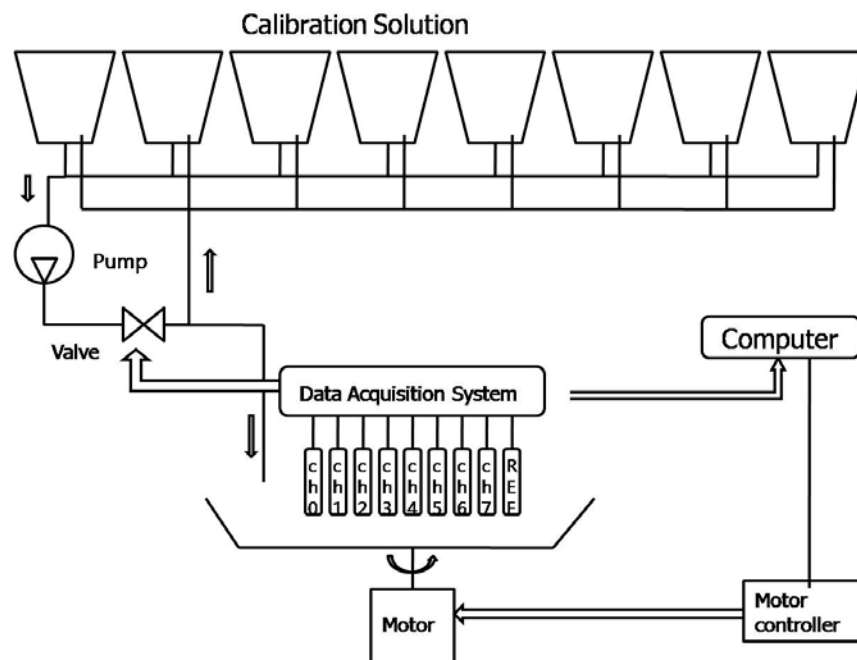
Fig. 2. Automated test stand for N-P-K-Ca-Mg selective electrodes (top) and functional diagram of the automated test stand (bottom).

Sensitivity and Selectivity Tests

The sensitivity responses of all electrodes were characterized by measuring the EMFs of each ISE in six standard solutions of single ion concentrations ranging from 10^{-6} to 10^{-1} M. In accordance with the methods prescribed by Kim et al. (2006), the selectivity factors (Kij) were determined using the separate solution

method (SSM), in which the selectivity factors are calculated based on EMF values obtained with pure single electrolyte solutions of the primary ion (0.01M) and interference ion (0.1M). The selectivity factor (Kij) is a measure of the preference by the sensor for the interfering ion (j) relative to the ion (i) to be detected. Obviously, for ideally selective membranes, all of the Kij values should be zero. A selectivity factor <1 indicates a preference for the primary ion (i) relative to the interference ion (j).

RESULTS AND DISCUSSION

The responses of the nitrate and potassium ion-selective electrodes based on TDDA-NPOE and valinomycin, respectively, are shown in Figure 3 (left) when single ion concentrations of nitrate (top) and potassium (bottom) ranged from 10^{-6} to 10^{-1} M. The EMF values obtained with the nitrate and potassium membranes were nearly linearly proportional to the logarithm of nitrate and potassium concentrations, respectively, in the range of 10^{-5} to 10^{-1} M. However, there was little change in EMF readings for concentrations in the range of 10^{-6} to 10^{-5} M. The results are comparable to those reported by Kim et al. (2006). Clearly, the ranges of interest would be measurable with the electrodes when target NO_3-N and K concentrations in hydroponic solutions for paprika were considered to be 178.5 ppm NO_3-N and 225 ppm K (1.27×10^{-2} M and 5.7×10^{-3} M for NO_3-N and K, respectively). Paprika is one of the most commonly cultivated hydroponic crops in Korea. Table 2 shows the typical concentrations of macronutrients in solutions prepared for hydroponic paprika.

The mean selectivity coefficients for chloride, sulphate, and monobasic phosphate, obtained with the TDDA-NPOE-based nitrate ion-selective membrane were -2.49, -3.30, and -4.48, showing that chloride held the highest potential for interference. However, the membrane was still 309 times more sensitive to nitrate than to chloride. The selectivity of the valinomycin-based potassium ISE was in the order: $NH_4^+ \ll Na^+ < Mg^{++} \sim Ca^{++}$. When considering typical ranges of cation concentrations in hydroponic solutions, it was expected that the valinomycin-based potassium membrane would determine potassium concentrations with acceptable selectivity levels.

Table 2. Typical target concentrations of macronutrients in hydroponic solution prepared for paprika.

| Nutrient	Concentration, ppm
NO_3-N	178.5
NH_4-N	17.5
P	30
K	225
Ca	130
Mg	27
S	32
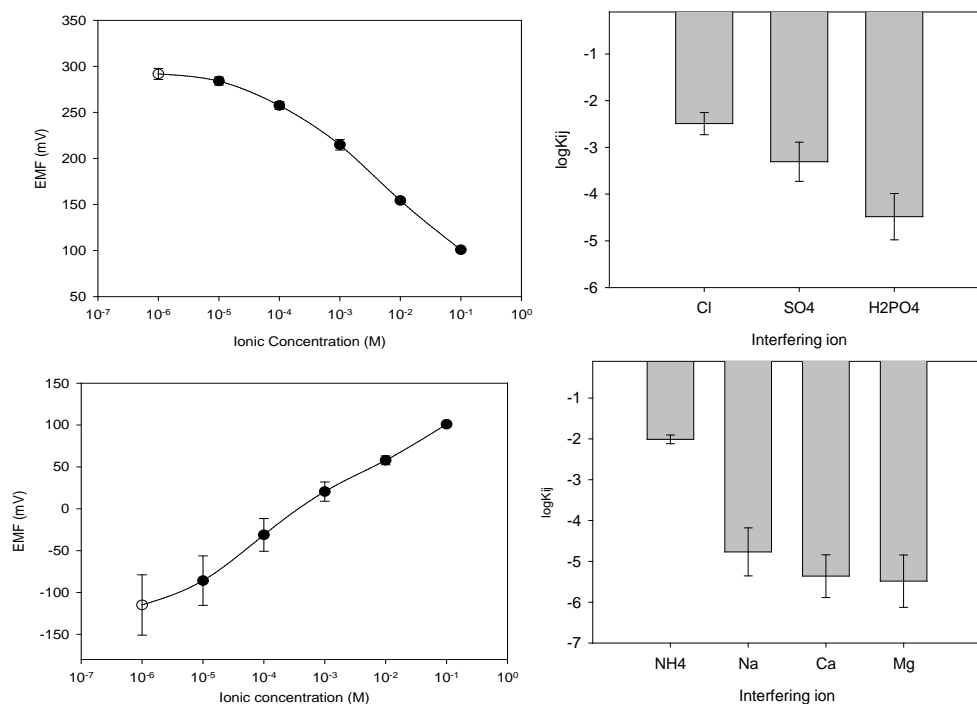
Fig. 3. Response curves of TDDA-NPOE-based nitrate ion-selective membrane and valinomycin-based potassium ion-selective membrane to different nitrate and potassium concentrations, respectively (left) and selectivity coefficients of the two electrodes (right), all using DI water as a base solution.

Figure 4 shows the EMF responses for the cobalt electrode to six varying KH_2PO_4 concentrations ranging from 10^{-6} to 10^{-1} M in the 0.025M KHP buffer. As shown in the figure, the cobalt electrode showed sensitive responses to phosphate over a range of 10^{-5} to 10^{-1} M total phosphate concentration, with a detection limit of about 10^{-5} M total phosphate concentration. This encompasses the range of interest around 10^{-3} M (31 ppm) for P levels in hydroponic solution for paprika (Table 2). Nevertheless, separate use of the KHP buffer was needed to determine P because the cobalt electrode did not show consistent and sensitive responses to P in DI water (data not shown). The selectivity levels for phosphate over other anions, chloride, nitrate, and sulphate were acceptable, showing absolute mean selectivity coefficients > 2.

The tested calcium ion-selective membrane showed sensitive responses to calcium concentrations ranging from 10^{-6} to 10^{-1} M (Fig. 5). However, relatively high standard deviations in EMF values were observed as compared to those measured with the nitrate and potassium electrodes. Selectivity levels for calcium over four interfering cations, Na^+, NH_4^+, K^+, and Mg^{++}, were satisfactory, indicated by the fact that the mean selectivity factors for sodium, ammonium, potassium and magnesium were -5.56, -5.79, -6.97, and -3.5, respectively.
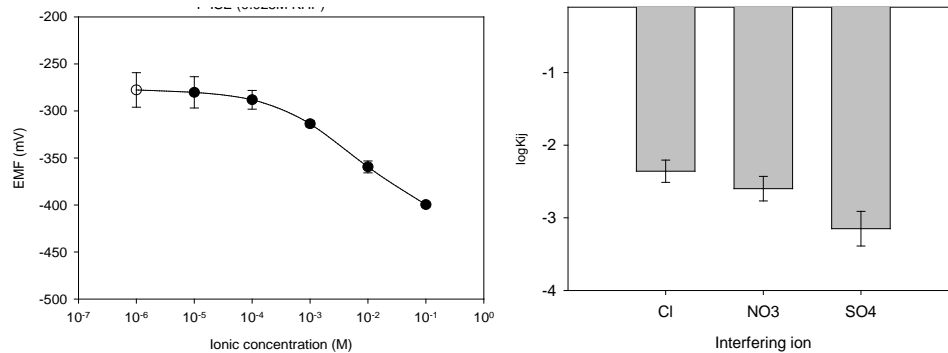
Fig. 4. Response curves of cobalt-based P electrode to different phosphate concentrations (left) and selectivity coefficients of the P electrode for phosphate over interfering anions (right), all with KHP as a base solution.
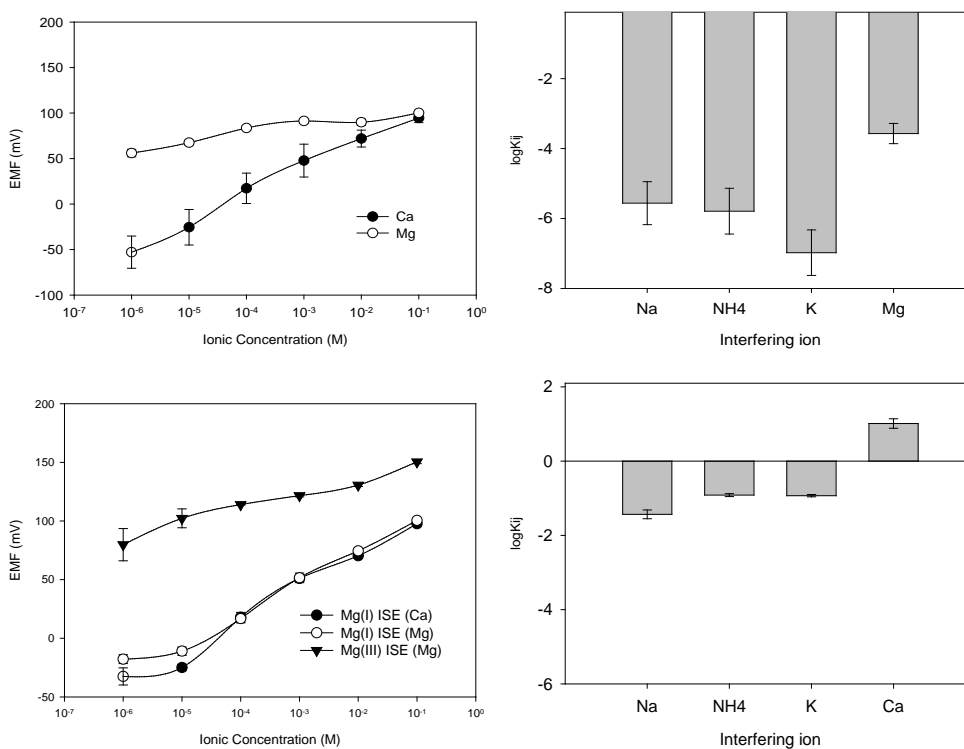
Fig. 5. Response curves of a calcium ion-selective membrane (upper-left) and two different magnesium ion-selective membranes (bottom-left) to different calcium and magnesium concentrations and selectivity coefficients of the Ca (upper-right) and Mg (bottom-right) electrodes over interfering cations, all measured using DI water as a base solution.

The two magnesium electrodes gave good responses to varying magnesium concentrations in the range of 10^{-6} to 10^{-1} M. The magnesium electrode based on ionophore I showed greater sensitivity for magnesium than did the electrode based on ionophore III. However, as shown in the selectivity tests, the magnesium ion-selective membrane (I) was more sensitive to calcium than to magnesium, given that the mean selectivity factor for calcium was 1.01. Obviously, a new magnesium ion-selective membrane is needed that can determine the

concentrations of magnesium ion in the presence of calcium with acceptable sensitivity and good selectivity.

CONCLUSIONS

In this study, various PVC-based ion-selective membranes were evaluated to determine concentrations of macronutrients, i.e., NO_3-N, P, K, Ca, and Mg, in hydroponic nutrient solutions. An automated test apparatus was used for simultaneous measurement of EMFs of 8 ISE electrodes generated by the change in membrane potential at different ionic concentrations. The sensitivity and selectivity of PVC membrane-based ion-selective electrodes with TDDA-NPOE, valinomycin, and calcium ionophore II for sensing nitrate, potassium, and calcium, respectively, and of cobalt rod-based phosphate ion-selective electrodes were satisfactory for measuring N, P, K, and Ca ions over typical ranges of hydroponic concentrations. However, the use of KHP buffer solution was needed to measure phosphorus ions with acceptable sensitivity. Further studies are needed to identify a magnesium ion-selective membrane that shows a sensitive response to magnesium in the presence of calcium.

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