Evaluation of Nitrate and Potassium Ion-Selective Membranes for Soil Macronutrient Sensing

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Abstract. *On-the-go, real-time soil nutrient analysis would be useful in site-specific management of soil fertility. The rapid response and low sample volume associated with ion-selective field-effect transistors (ISFETs) make them good soil fertility sensor candidates. Ion-selective microelectrode technology requires an ion-selective membrane that responds selectively to one analyte in the presence of other ions in a solution. This article describes: (1) the evaluation of nitrate and potassium ion-selective membranes, and (2) the investigation of the interaction between the ion-selective membranes and soil extractants to identify membranes and extracting solutions that are compatible for use with a real-time ISFET sensor to measure nitrate and potassium ions in soil. The responses of the nitrate membranes with tetradodecylammonium nitrate (TDDA) or methlytridodecylammonium chloride (MTDA) and potassium membranes with valinomycin were affected by both membrane type and soil extractant. A TDDA-based nitrate membrane would be capable of detecting low concentrations in soils to about 10^{-5} mole/L NO_3^-. The valinomycin-based potassium membranes showed satisfactory selectivity performance in measuring potassium in the presence of interfering cations such as Na^+, Mg^{2+}, Ca^{2+}, Al^{3+}, and Li^+ as well as provided a consistent sensitivity when DI water, Kelowna, or Bray P_1 solutions were used as base solutions. The TDDA-based nitrate membrane and the valinomycin-based potassium membrane, used in conjunction with Kelowna extractant, would allow determination of nitrate and potassium levels, respectively, for site-specific control of fertilizer application.*

Keywords. *Ion-selective electrode (ISE), Ion-selective field-effect transistor (ISFET), Ion-selective membranes, Kelowna extractant, Nitrate, Potassium, Selectivity, Sensitivity, Soil extractant, Soil testing.*

Conventional soil testing methods, including soil sampling and chemical analysis, are costly and time consuming because they require complex processes for pre-treatment and expensive instruments for samples to be quantitatively analyzed. The high cost and long delays of such methods have limited their use in variable-rate fertility management systems. Accurate real-time sensors for measuring spatial variation in soil properties might be able to reduce the analysis time and cost associated with soil testing. An on-the-go soil nutrient sensor to monitor soil macronutrients, such as nitrogen, phosphorus, and potassium, would enhance the characterization of within-field variability and be useful in site-specific management of soil fertility.

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Ion-selective electrodes (ISEs), which are commercially used in the measurement of solution pH and blood electrolytes, were applied to the determination of nitrates in soil by many researchers in the 1970s and 1980s (Oien and Selmer-Olsen, 1969; Black and Waring, 1978; Li and Smith, 1984). Their research concentrated on the suitability of ISEs as an alternative to routine soil testing, and they reported that ISE technology was adaptable to soil nitrate analysis. However, no data were presented in support of using ISEs for rapid determination of soil nitrates as on-the-go sensors implemented on an agricultural vehicle.

Since the 1990s, ISE-based on-the-go measurement of soil properties (nitrate and pH) has been attempted by several researchers (Adamchuck et al., 1999; Adsett et al., 1999; Adamchuk, 2002). Despite advances in ISE-based sensors that have led to the development of a prototype soil pH sensor (Collings et al., 2003), research is still being conducted to overcome several limitations, including the durability of the ion-selective electrode in contact with soil particles, as well as potential drift during continuous operation.

Recently, as an alternative to the ISE-based sensing method, the application of an ISFET chip combined with flow injection analysis (FIA) to soil analysis was reported (Birrell and Hummel, 2000; Artigas et al., 2001; Birrell and Hummel, 2001). ISFETs have the same theoretical basis as ion-selective electrodes, i.e., both ISEs and ISFETs respond to the activity of the ions in the sample, and the response is linearly related to the logarithm of the ion concentration. ISFET technology offers inherent features such as fast response, small dimensions, low output impedance, high signal-to-noise ratio, low sample volumes, and the potential for mass production, all of which are required for a real-time

sensor. One problem that exists with ISFETs is long-term drift (Bergveld, 1991), which can be overcome with FIA. FIA (Ruzicka and Hansen, 1988) operates by pulsing a sample solution and carrier (base) solution to the sensor. This pulsing action allows a differential measurement between the two solutions, providing a baseline for each sample. The electrical responses of nitrate ISFETs tested by Birrell and Hummel (2001) were consistent and predictable when used with an FIA system to minimize long-term output drift. Precision and accuracy of the system were dependent on maintaining precise, repeatable injection times and constant flow parameters during the calibration and testing cycle.

An important component of both ISEs and ISFETs 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 soil nutrients, including NO_3^-, K^+, and Na^+ (Nielson and Hansen, 1976; Tsukada et al., 1989; Knoll et al., 1994). Furthermore, for the determination of phosphorus, several researchers reported the development of phosphate ion-selective membranes ($H_2PO_4^-$ or HPO_4^{2-}) with acceptable sensitivity and good selectivity (Glazier and Arnold, 1991; Carey and Riggan, 1994).

In standard soil testing methods to determine soil macronutrient content, various extractants (soil extracting solutions) are used, depending on the nutrient to be extracted. For example, distilled water, 2M KCl, and 0.01M $CuSO_4$ extractants are used for nitrate (Oien and Selmer-Olsen, 1969; Van Lierop, 1986) and in the Midwest, available soil potassium and phosphorus levels are usually determined with 1M NH_4OAc and Bray P_1 (0.025M HCl + 0.03M NH_4F) solutions (Brown, 1998), respectively. The Mehlich III extractant (0.2M CH_3COOH + 0.015M NH_4F + 0.25M NH_4NO_3 + 0.013M HNO_3 + 0.001M EDTA) is being used to extract phosphorus, potassium, and other cations in soil (Mehlich, 1984). Van Lierop (1986, 1988) and Van Lierop and Gough (1989) reported that the Kelowna multiple-ion extractant (0.25M CH_3COOH + 0.015M NH_4F) could be used when determining soil nitrate concentrations, as well as when extracting phosphorus and potassium.

Technological advances, particularly in the biomedical fields, have increased the availability of ion-selective membranes, but their application to soil nutrient sensing might be limited by the presence of ions in soil solutions that are not present in biomedical solutions. The use of a single extractant that does not adversely affect the response of ion-selective membranes and that can extract representative amounts of soil macronutrients for ISFET analysis is needed for our automated, on-the-go sensing approach.

The overall objective of this research was to investigate the suitability of different ion-selective membranes for sensing important soil macronutrients such as NO_3^-, $H_2PO_4^-$, and K^+ in order to develop a multi-ISFET chip integrated with an automatic soil extraction system for real-time soil analysis. This article describes the evaluation of nitrate- and potassium-selective membranes and the investigation of the interaction between ion-selective membranes and standard soil extractants. Specific objectives were:

- To characterize the capabilities of ion-selective membranes for soil nitrate and potassium sensing with respect to their sensitivity, lower detection limits, and selectivity against interferences of other ions.
- To investigate the effect of soil extractants on the response characteristics of ion-selective membranes when measuring typical ranges of nitrate and potassium concentrations in soils.
- To identify a combination of ion-selective membranes that is suitable for use with a real-time ISFET sensor for sensing nitrate and potassium ions in soil.

Methods and Procedure

Reagents

PVC-based nitrate ion-selective membranes were prepared using quaternary ammonium compounds as ligands based on previous studies (Nielson and Hansen, 1976; Tsukada et al., 1989; Birrell and Hummel, 2000). The ligands, tetradodecylammonium nitrate (TDDA) and methyltridodecylammonium chloride (MTDA), and the plasticizers, nitrophenyl octyl ether (NPOE) and tri-(2-ethylhexyl) trimellitate (TOTM), were obtained from Sigma-Aldrich Corp. (St. Louis, Mo.).

Potassium ion-selective membranes based on valinomycin as an ionophore were prepared using techniques developed in previous studies (Moody et al., 1988; Knoll et al., 1994; Bae and Cho, 2002). The valinomycin as an ionophore; NPOE, bis(2-ethylhexyl) sebacate (DOS), and bis(2-ethylhexyl) adipate (DOA) as plasticizers; and potassium tetrakis (4-chlorophenyl) borate (KTpClPB) as a lipophilic additive were purchased from Sigma-Aldrich Corp.(St. Louis, Mo.).

Preparation of Ion-Selective Membranes and Electrodes

Two chemical compositions for nitrate and potassium membranes were used according to the procedures described in previous studies (Knoll et al., 1994; Birrell and Hummel, 2000). The nitrate ion-selective membranes were prepared with a mixture of 30 mg (15% wt) of ligand (TDDA or MTDA), 80 mg (40% wt) of plasticizer (NPOE or TOTM), and 90 mg (45% wt) of high-molecular-weight polyvinyl chloride (PVC). The composition of the potassium ion-selective membrane prepared was 4 mg (2% wt) of ligand (valinomycin), 1 mg (0.5% wt) of lipophilic additive (KTpClPB), 129.4 mg (64.70% wt) of plasticizer (DOS, NPOE, or DOA), and 65.6 mg (32.80% wt) of PVC.

The membranes were produced by dissolving the mixture in 2 mL of tetrahydrofuran (THF). The mixture was stirred until the membrane components were completely dissolved, poured into a 23 mm glass ring resting on a polished glass plate, and allowed to evaporate for 24 h at room temperature. The membrane, formed as a film, was removed from the glass plate, and three disks with a diameter of 2.5 mm were cut from each membrane. The membrane disks were attached to the ends of Hitachi ISE electrode bodies (PVC) using the THF solvent. Prior to testing, the ion-selective electrodes (ISEs) with the nitrate and potassium membranes were conditioned in 0.01M $NaNO_3$ and 0.01M KCl solutions, respectively, for at least 6 h, so that steady electrical potentials could be obtained.

Each nitrate ISE electrode was filled with an internal solution consisting of 0.01M $NaNO_3$ and 0.01M NaCl. Potassium chloride (0.01M) was employed as the internal reference solution of the potassium electrodes. An Ag/AgCl electrode was immersed as the inner reference electrode. 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^- from the reference electrode, 1M LiOAc was used as the outer reference solution in the reference electrode.

EMF Measurements

An automated test apparatus was designed for the simultaneous measurement of the electromotive forces (EMFs) of 16 ISE electrodes (fig. 1) generated by the change in membrane potential at different ionic concentrations. To control the system and record values obtained from the ISE electrodes, a program was developed with Microsoft Access 2000 and Visual Basic 6.0 (Microsoft Corp., Seattle, Wash.). A Daqbook 200 (IOTech, Cleveland, Ohio) portable PC-based data acquisition system and a 400 MHz Pentium II computer were used to collect and store ISE voltage outputs. To minimize current leakage and capacitive loading, and to reduce signal noise, the electrode outputs were conditioned using a 16-channel buffering circuit module equipped with LF 356N operational amplifiers (10^{12} Ω input impedance, 3 pF input capacitance, <8 nA bias current; National Semiconductor, Santa Clara, Cal.).

Various test solutions were contained in eight Teflon-coated 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 (fig. 1). 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 kHz data, were obtained on a 3 s interval by the A/D board. With this data sampling protocol, a check for steady-state output could be made while maintaining manageable data file size. The three electrode readings were averaged to represent a single EMF output response at each concentration level. For sensitivity testing, solutions were arranged and tested in a sequence from lowest to highest concentration of the test ion. For selectivity testing, the test solutions were arranged and tested in a sequence from lowest to highest selectivity for the primary ion over the interference ion. In each instance, three iterations of each sequence were conducted.

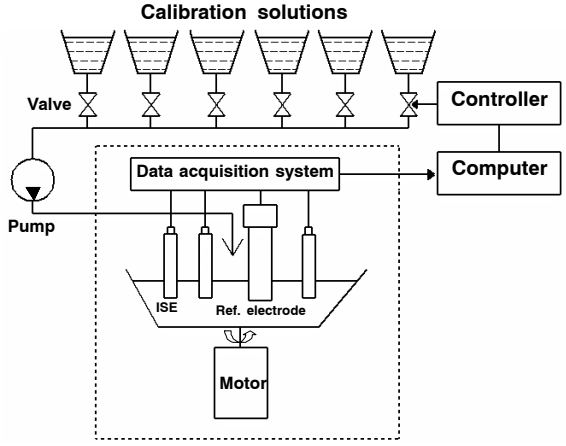

Figure 1. Schematic representation of the automated test stand (only three of the fifteen ISEs are shown).

Sensitivity Tests

For nitrate sensing, two membranes (I, II) of each ligand-plasticizer combination were prepared on two different dates and used to investigate membrane variation in sensitivity within each membrane type. Three membrane disks were cut from each membrane, and the initial test included six disks from two TDDA-NPOE membranes, six disks from two MTDA-NPOE membranes, and three disks from one MTDA-TOTM membrane. For the second test, six disks from two TDDA-NPOE membranes, three disks from one MTDA-NPOE membrane, and six disks from two MTDA-TOTM membranes were selected. Thus, 15 electrodes with three different types of membranes were simultaneously tested using each test run of the automated test stand.

For the potassium tests, three different types of potassium membranes (valinomycin-DOS, valinomycin-NPOE, and valinomycin-DOA) were tested. Two nitrate membranes (TDDA-NPOE and MTDA-NPOE) were also included in the potassium test set to investigate whether their response would be affected by the presence of other cations and anions.

Various soil extractants were used as base solutions: deionized (DI) water, 0.01M $CuSO_4$, and Kelowna solutions for nitrate testing; and DI water, Bray P_1, Mehlich III, and Kelowna solutions for potassium testing. According to standard laboratory procedures (Van Lierop, 1986; Brown, 1998), each base solution was prepared using double-distilled water (18.1 MΩ cm^{-1}) and chemicals of laboratory grade. By using the base solutions, two sets of six calibration solutions in the concentration range of 10^{-6} to 10^{-1} mole/L $NaNO_3$ and KCl, respectively, were prepared by successive 10:1 dilutions of the 0.1 mole/L concentration standard.

The effects of membrane composition and extractant on sensitivity were investigated by comparing the Nernstian slopes obtained from the linear relationship between the logarithm of the ionic activities of nitrate and potassium, respectively, and EMFs of the corresponding ISEs.

The Nernst equation was used to calculate the sensitivity:

$$\text{EMF} = E_o + E_J + S \log a_i \qquad (1)$$

where

EMF = electromotive force generated by the difference of membrane potential
E_o = standard potential (mV)
E_J = liquid-junction potential (mV)
S = Nernstian slope (59.16/z_i mV/decade change in concentration for H_2O at 25°C)
z_i = charge number of ion i
a_i = activity of ion i in the sample solution (mole/L).

The molar concentration can be converted to activities using single-ion activity coefficients:

$$a_i = \gamma_i c_i \quad (2)$$

where

a_i = single-ion activity (mole/L)
γ_i = single-ion activity coefficient
c_i = ionic molar concentration (mole/L).

The single-ion coefficients are determined from the mean activity coefficients of the electrolyte, which are estimated using the Debye-Hückel formula (Ammann, 1986; Eggins, 2002). The Debye-Hückel equation is given as follows:

$$\log \gamma_i = \frac{-Az_i^2\sqrt{I}}{1 + B\mathbf{a}\sqrt{I}} \quad (3)$$

where A and B are constants with values of 0.5108 (mole^{-1} L$^{1/2}$) and 0.328 (mole^{-1} L$^{1/2}$ Å^{-1}), respectively, at 25°C, **a** is the ion size parameter (Å), and z is the charge on the ion. The ionic strength (I) is a measure of the total ions in solution (mole/L), weighted according to their charges and concentrations, as in the following equation:

$$I = \frac{1}{2}\sum_i c_i z_i^2 \quad (4)$$

where c_i is concentration of any ion in the sample solution (mole/L), and z_i is charge of any ion in the sample solution.

Liquid-junction potentials are always generated when electrolytic solutions of different ionic compositions are in contact (Ammann, 1986). A typical reference electrode has a liquid-junction potential at the junction of the reference electrode with the sample solution. For this experiment, the potential was assumed to be constant.

Selectivity Tests

The Nernst equation used in the sensitivity tests assumes that the membrane is ideally specific to the ion of interest. However, in most cases, the membrane responds to other interfering ions and the measured EMF is the sum of the membrane potentials. The extent of interference is expressed in the Nikolski-Eiseman equation (eq. 5) in terms of the electrode potential and a selectivity coefficient, as follows:

$$\text{EMF} = E_o + E_J + S\log\left[a_i + \sum K_{ij}(a_j)^{Z_i/Z_j}\right] \quad (5)$$

where

E_o = standard potential
E_J = liquid-junction potential
S = Nernstian slope (theoretically, $59.16/z_i$)
a_i = activity of primary ion
a_j = activity of interference ion
Z_i = charge of primary ion
Z_j = charge of interference ion
K_{ij} = selectivity coefficients.

The selectivity factor (K_{ij}) is a measure of the preference by the sensor for the interfering ion (j) relative to the ion (i) to be detected (Ammann, 1986). Obviously, for ideally selective membranes, all of the K_{ij} values should be zero. A selectivity factor <1 indicates a preference for the primary ion (i) relative to the interference ion (j). Selectivity factors are determined experimentally using several techniques: the separate solution method (SSM), the fixed interference method (FIM), and the fixed primary ion method (FPM) (Ammann, 1986; IUPAC, 1994).

In this test, the selectivity factors 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) in the following way:

$$K_{i,j} = 10^{(E_j - E_i)/S}\frac{a_i}{a_j^{Z_i/Z_j}} \quad (6)$$

where

a_i = activity of 0.01M primary ion
a_j = activity of 0.1M interfering ion
E_i = EMF measured with solution of 0.01M primary ion
E_j = EMF measured with solution of 0.1M interfering ion
S = Nernstian slope obtained with 0.01M and 0.1M primary ion solutions.

The selectivity tests were conducted with the same sets of membranes as those used in the sensitivity tests. The selectivity of each membrane in different base solutions for nitrate and potassium over interference ions was investigated in the following order: bicarbonate ($NaHCO_3$), chloride (NaCl), and bromide (NaBr) for nitrate membrane selectivity; and magnesium ($Mg(NO_3)_2$), calcium ($Ca(NO_3)_2$, sodium ($NaNO_3$), lithium ($LiNO_3$), aluminum ($Al(NO_3)_3$), and ammonium (NH_4NO_3) for potassium membrane selectivity using sodium salts and nitrate salts, respectively.

At the beginning of the test sequence, the EMFs in 0.1M and 0.01M primary ion solutions were measured to determine Nernstian slopes for each membrane. The responses of the 0.01M primary ion and 0.1M interfering ion solutions were then measured so that the selectivity coefficients of each interfering ion, based on the separate solution method, could be calculated using equation 6. The SAS General Linear Model (GLM) procedure was used to determine whether the selectivity factors of the membranes in the presence of different extractants were significantly different, using Duncan's multiple range test at a significance level of 5%.

Results and Discussion

Evaluation of Nitrate Ion-Selective Membranes

Sensitivity

The responses of the ion-selective electrodes having three different nitrate membranes (TDDA-NPOE, MTDA-NPOE, and MTDA-NPOE) tested in different base solutions are shown in figure 2 when nitrate concentrations ranged from 10^{-6} to 10^{-1} mole/L. All membrane potentials of six individual electrodes of each membrane type (I and II) were normalized by offsetting all the electrode readings to force the measured level in 0.1 mole/L nitrate solution for the first replication to be 100 mV. Each curve was obtained by averaging the normalized EMF values.

As shown in figure 2a, in the DI extractant, the EMF values generated from all of the tested membranes were linearly proportional to the logarithm of the nitrate concentration (ionic activity) in the range 10^{-1} to 10^{-5} mole/L. However, there was little change in voltage readings in the range of 10^{-6} to 10^{-5} mole/L nitrate concentrations. All of the electrodes exhibited a linear response over a range of 10^{-5} to 10^{-1} mole/L nitrate concentrations, and their lower detection limits, calculated by the IUPAC method (IUPAC, 1994), were determined to be 9.2×10^{-6} to 1.1×10^{-5} mole/L. The results are different from those shown in previous experiments

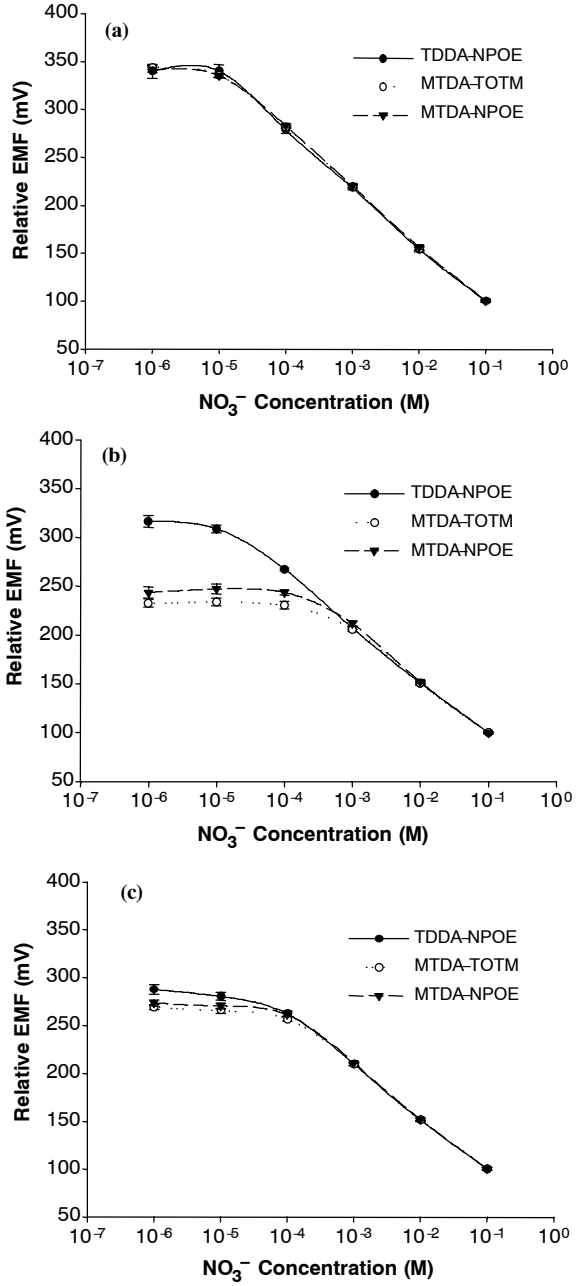

Figure 2. Electrode relative EMF vs. nitrate concentration for different nitrate membranes: (a) in DI water, (b) in 0.01M $CuSO_4$, and (c) in Kelowna extractants.

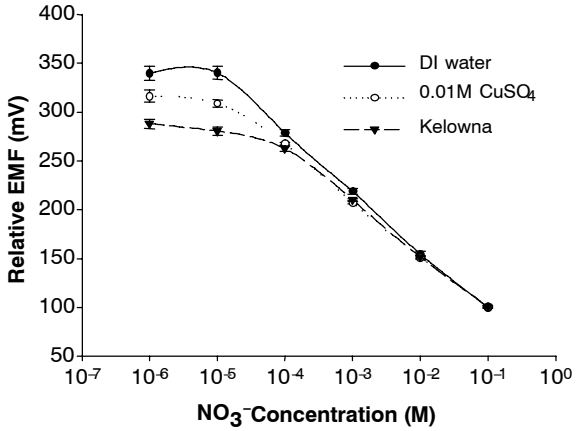

Figure 3. Effect of soil extractant on the sensitivity response of TDDA-NPOE nitrate membranes.

(Birrell and Hummel, 2000), where at low nitrate concentrations of 10^{-5} mole/L, on the average, the TDDA membranes (−58.3 mV/decade) showed slightly lower sensitivities than did the MTDA membranes (−61.5 mV/decade).

When the electrodes were tested in the 0.01M $CuSO_4$ solution (fig. 2b), a decrease in sensitivity occurred at nitrate concentrations below 10^{-4} mole/L across all membranes. However, the TDDA membranes showed higher sensitivity at low concentrations than did the MTDA membranes. The linear response range of the TDDA-NPOE membrane seemed to be ~10^{-5} to 10^{-1} mole/L, whereas that of the MTDA membranes existed in the range of 10^{-4} to 10^{-1} mole/L nitrate concentrations.

In the Kelowna solution (fig. 2c), the responses of the tested nitrate membranes were decreased considerably as compared to those obtained in the DI water and 0.01M $CuSO_4$ solutions. The EMFs were considerably decreased at low concentrations (<10^{-4} mole/L), thereby resulting in the higher detection limits of 3.7 to 6.2 × 10^{-5} mole/L nitrate concentrations. The results indicate that two anions, acetate (CH_3COO^-) and fluoride (F^-), present in the Kelowna solution might have an effect on the sensitivity of the three nitrate membranes.

A comparison of the sensitivity results for one membrane (TDDA-NPOE) across the DI, 0.01M $CuSO_4$, and Kelowna extractants (fig. 3) indicates that the sensitivity of nitrate membranes at low nitrate concentrations (<10^{-4} mole/L) is affected by soil extractant. However, the usable portion of the nitrate concentration:EMF curve appears to be from 10^{-1} to 10^{-5} mole/L NO_3, which encompasses the range of interest (7.14 × 10^{-5} to 2.14 × 10^{-4} mole/L NO_3). This corresponds to 1 to 3 mg/L NO_3-N at a dilution ratio (solution: soil) of 10:1 for soil nitrate sensing.

The SAS TTEST procedure was used to investigate differences in sensitivity between membranes of the same

Table 1. Means and standard deviations of sensitivity slopes (mV/decade) of nitrate membranes of the same composition in Kelowna solution.

Membrane Composition	ID	Date (2003)	Nitrate Concentration Range[a]		
			10^{-1} M to 10^{-5} M	10^{-1} M to 10^{-4} M	10^{-1} M to 10^{-3} M
MTDA-TOTM	I	21 Jan.	−43.73 ±0.66	−53.03 ±0.66	−55.00 ±0.91 a
	II	24 May	−43.32 ±0.61	−52.94 ±0.68	−55.96 ±0.49 b
MTDA-NPOE	I	27 Feb.	−45.31 ±0.31	−54.67 ±0.25	−55.68 ±0.31
	II	24 May	−44.94 ±0.76	−54.38 ±0.57	−55.90 ±0.48
TDDA-NPOE	I	20 Mar.	−47.13 ±1.47	−54.83 ±1.43	−55.96 ±2.23
	II	17 Apr.	−47.33 ±1.21	−55.03 ±1.00	−55.36 ±0.92

[a] Mean membrane sensitivities followed by the same letter within a nitrate concentration range are not significantly different at the 5% level, based on the t-test. Letters are omitted when differences are not significant.

Table 2. Means and standard deviations of sensitivity slopes (mV/decade) of nitrate membranes by extractant type.

Membrane Composition	Nitrate Concentration Range[a]		
	10^{-1} M to 10^{-5} M	10^{-1} M to 10^{-4} M	10^{-1} M to 10^{-3} M
DI water			
MTDA-TOTM	−61.27 ±0.26 b	−63.00 ±0.30 b	−62.54 ±0.46 b
MTDA-NPOE	−61.40 ±0.49 b	−63.71 ±0.78 a	−63.52 ±1.11 a
TDDA-NPOE	−62.23 ±1.55 a	−62.44 ±1.16 c	−62.68 ±1.34 b
Kelowna solution			
MTDA-TOTM	−43.63 ±0.66 c	−53.01 ±0.65 b	−55.24 ±0.92
MTDA-NPOE	−45.06 ±0.66 b	−54.48 ±0.50 a	−55.70 ±1.78
TDDA-NPOE	−47.17 ±1.38 a	−54.92 ±1.28 a	−55.83 ±0.44
0.01M $CuSO_4$ solution			
MTDA-TOTM	−35.17 ±1.06 c	−45.46 ±1.24 c	−54.57 ±1.16 b
MTDA-NPOE	−39.00 ±1.35 b	−49.78 ±0.76 b	−57.36 ±1.54 a
TDDA-NPOE	−54.00 ±0.78 a	−56.80 ±0.45 a	−55.03 ±0.81 b

[a] Mean membrane sensitivities followed by the same letter within a nitrate concentration and within an extractant comparison are not significantly different at the 5% level, based on Duncan's multiple range test. Letters are omitted when differences are not significant.

composition (I and II) but prepared on different dates. The results (table 1) showed that there was no significant difference in sensitivity between membranes of the same composition in Kelowna solution.

SAS GLM comparisons of the sensitivity of the nitrate membranes for different nitrate concentration ranges by each extractant (table 2) show that the sensitivity of the membranes varied considerably depending on soil extractant type. The low standard deviations of the means, ranging from 0.26 to 1.78 mV/decade across the various nitrate concentration levels, indicate stable EMF response of the membranes across the tests. In general, the sensitivity slopes obtained in DI water were higher than those measured with $CuSO_4$ and Kelowna solutions. In the range of 10^{-4} to 10^{-1} mole/L nitrate concentrations, the averaged sensitivity slopes were −62 to −63 mV/decade for DI water, −53 to −54 mV/decade for the Kelowna solution, and −45 to −56 mV/decade for the 0.01M $CuSO_4$ solution. According to Duncan's multiple range test, in the 0.01M $CuSO_4$ solution, the sensitivity responses of the TDDA-NPOE membranes were higher than those of the MTDA-NPOE and MTDA-TOTM membranes. However, in the Kelowna solution, in the range of 10^{-4} to 10^{-1} mole/L nitrate concentrations, there was no significant difference in sensitivity between the TDDA-NPOE and MTDA-NPOE membranes.

Selectivity

Potentiometric selectivity coefficients with respect to the interference anions, bicarbonate (HCO_3^-), chloride (Cl^-), and bromide (Br^-), in different extracting solutions and obtained by the separate solution method, are summarized in table 3. In the tests using the $CuSO_4$ solution, results for the bicarbonate ion were not obtained because the bicarbonate chemical did not completely dissolve and formed a precipitate in the 0.01M $CuSO_4$ solution.

The results obtained from the SAS GLM analysis showed that the selectivity responses of the membranes were affected considerably by both membrane type and extracting solution type. As obtained in previous experiments (Birrell and Hummel, 2000), the TDDA-NPOE membrane displayed greater selectivity for nitrate against the three tested interfering species than did the MTDA membranes. In addition, in DI water, the mean selectivity coefficients for chloride obtained with the three different membranes were comparable to those reported by Birrell and Hummel (2000):

Table 3. Comparison of selectivity coefficients (log *K*) of nitrate membranes by extractant type.

Membrane Composition	Interference Ion[a]		
	HCO_3^-	Cl^-	Br^-
DI water			
MTDA-TOTM	−2.42 c	−1.67 c	−0.62 c
MTDA-NPOE	−2.62 b	−1.77 b	−0.66 b
TDDA-NPOE	−3.47 a	−2.30 a	−0.92 a
Kelowna solution			
MTDA-TOTM	−2.73 c	−1.72 c	−0.73 c
MTDA-NPOE	−2.89 b	−1.81 b	−0.77 b
TDDA-NPOE	−3.22 a	−2.07 a	−1.03 a
0.01M $CuSO_4$ solution			
MTDA-TOTM	−−[b]	−2.02 c	−0.79 c
MTDA-NPOE	−−	−2.13 b	−0.86 b
TDDA-NPOE	−−	−2.78 a	−1.15 a

[a] Membrane selectivity coefficients followed by the same letter within a nitrate concentration and within an extractant comparison are not significantly different at the 5% level, based on Duncan's multiple range test.
[b] Precipitation during test solution preparation precluded collection of these data.

−1.67, −1.70, and −2.40 for MTDA-TOTM, MTDA-NPOE, and TDDA-NPOE, respectively. The highest selectivity for nitrate over the two anions, chloride and bromide, was obtained when using the 0.01M $CuSO_4$ extracting solution. The selectivity factors (log K_{ij}) for chloride ranged from −1.67 to −2.78, indicating that the membranes were 47 to 603 times more sensitive to nitrate than to chloride. Bromide was included in the selectivity tests as a check ion, since the literature shows little or no selectivity for nitrate over bromide. The selectivity of the membranes for nitrate over bromide was lowest, i.e., the largest selectivity factor (log K_{ij}), and approximately −1 for all membranes and extracting solutions.

Figure 4 shows the effect of chloride ion on the response of the TDDA-NPOE nitrate ion-selective membrane when tested in various soil extractants including DI water, Mehlich III, Bray P_1, and Kelowna solutions. In the DI water, in the chloride concentration range of 10^{-5} to 10^{-1} mole/L, the nitrate membrane was sensitive enough to show almost Nernstian slopes (59 mV/decade). However, if a small amount of nitrate were added to the DI water, it would show apparent sensitivity for nitrate because the TDDA membrane is about 200 times (log K = −2.30, table 3) more sensitive to

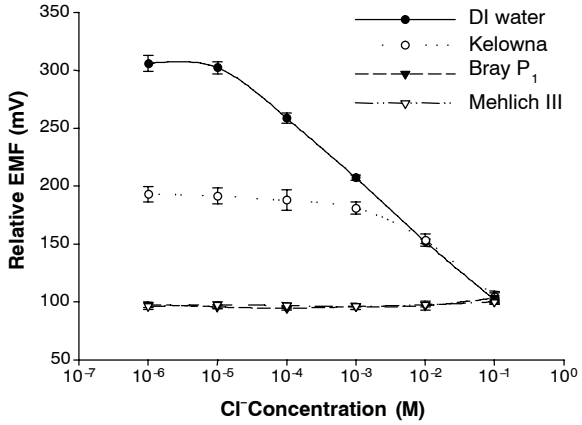

Figure 4. Effect of chloride on the sensitivity response of TDDA-NPOE nitrate membranes for various soil extractants.

nitrate than to chloride. In the other solutions, at low chloride concentrations below 10^{-3} mole/L, the EMF values measured with the nitrate-selective membranes were almost constant, regardless of chloride concentration. It seemed that soil extractants play a role in suppressing chloride interference in the range of 10^{-6} to 10^{-3} mole/L chloride concentrations.

Evaluation of Potassium Ion-Selective Membranes

Sensitivity

The responses of three valinomycin membranes with different plasticizers (DOS, NPOE, and DOA) to varying potassium concentration were evaluated (fig. 5) when four different soil extractants (DI water, Kelowna, Bray P_1, and Mehlich III) were used as base solutions. In general, as found in the nitrate membrane tests, the EMF values obtained with tested potassium membranes were linearly proportional to changes in potassium concentration ranging from 10^{-3} to 10^{-1} mole/L.

All of the tested potassium membranes in DI water (fig. 5a) showed a linear Nernstian response, with typical slopes of 54.6 to 58.2 mV per decade change in activity of potassium ion when the KCl concentrations were above 10^{-5} mole/L. As potassium concentration was decreased to 10^{-6} mole/L, the response slope was reduced, but some response to potassium ion concentration was still exhibited. Therefore, it was expected that the lower detection limits of the tested potassium membranes in DI water might be below 10^{-6} M. Such results are comparable to those measured with standard PVC potassium membranes described by Oh et al. (1998).

When the potassium membranes were tested in the Kelowna and Bray P_1 solutions (figs. 5b and 5c, respectively), at low potassium concentrations (<10^{-4} mole/L), the response slopes were considerably reduced as compared to those measured in DI water (fig. 5a). Eventually, there was little response of any of the three membranes in the potassium concentration range of 10^{-6} to 10^{-4} mole/L. Based on the regression analysis using the EMF values in the range of 10^{-1} to 10^{-3} mole/L, the lower detection limits for potassium were 1.7 to 2.7 × 10^{-4} mole/L and 2.6 to 3.1 × 10^{-4} mole/L in the Kelowna and Bray P_1 solutions, respectively.

The response ranges of three potassium membranes in the Mehlich III solution (fig. 5d) were considerably reduced, thereby resulting in decreased sensitivity (<40 mV/decade) at higher potassium concentrations (10^{-3} to 10^{-1} mole/L). In addition, the lower detection limits for potassium were much higher (10^{-3} mole/L) for the Mehlich III solution than for the other solutions. This poor detection limit is related to the fact that the Mehlich III solution contains high concentrations of

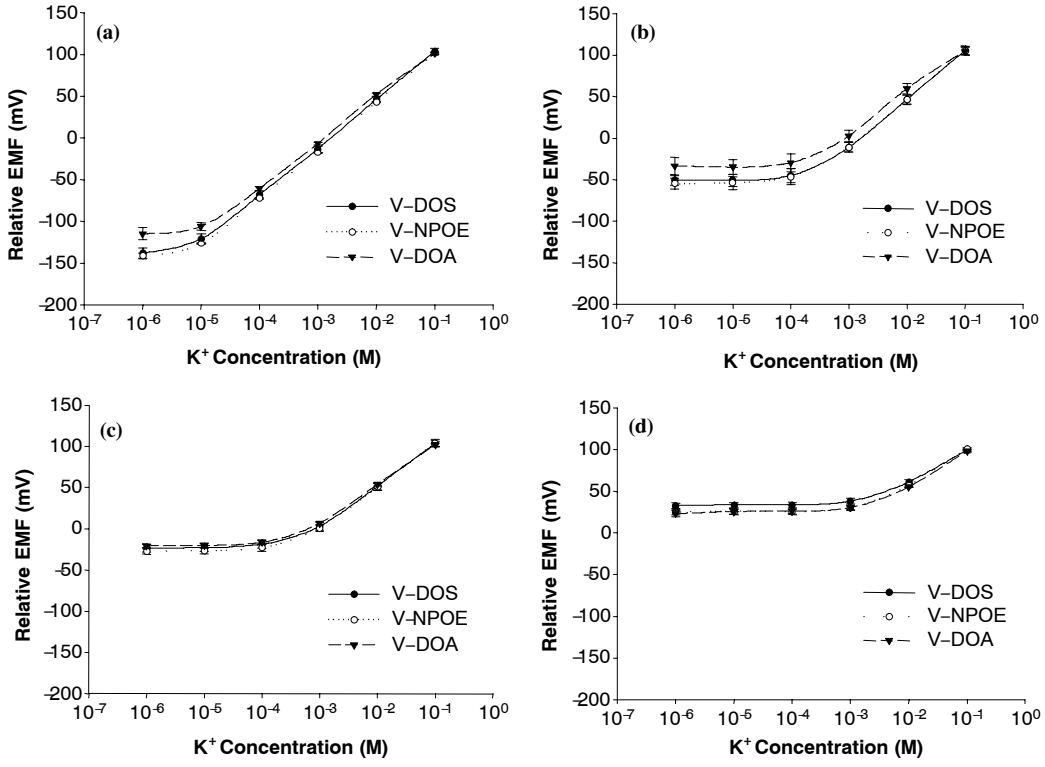

Figure 5. Electrode relative EMF vs. potassium concentration for potassium membranes: (a) in DI water, (b) in Kelowna, (c) in Bray P_1, and (d) in Mehlich III extractants.

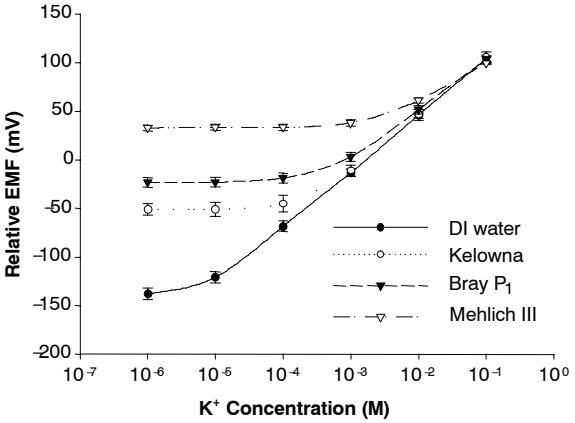

Figure 6. Effect of soil extractant on sensitivity response of valinomycin-DOS potassium membranes.

various cations such as NH_4^+ and H^+ that interfere with potassium measurement.

Figure 6 compares the response curves of a valinomycin-DOS potassium membrane in different extractants. At potassium concentrations below 10^{-3} mole/L, the responses of the potassium membrane were dramatically diminished when tested in the three soil extractants, as compared to those obtained in DI water. However, in Kelowna and Bray P_1 solutions, even though the responses were non-linear, the usable range of the KCl concentration:EMF relationship (10^{-1} to ~10^{-4}) still encompassed the range of interest (1.28×10^{-4} to 3.85×10^{-4} mole/L K). This corresponds to 5 to 15 mg/L K at a dilution ratio (solution: soil) of 10:1 for soil potassium sensing.

Table 4 shows the mean membrane sensitivity and the standard deviation of the membrane sensitivity of three replicate measurements for different potassium concentrations when various soil extractants were used as base solutions. The effects of extractant and plasticizer type on sensitivity of the three potassium membranes are apparent. In the range of 10^{-4} to 10^{-1} mole/L potassium concentrations, the average sensitivity slopes were 56 to 60 mV/decade for DI water and 46 to 52 mV/decade for the Kelowna, 41 to 44 mV/decade for the Bray P_1, and 22 to 25 mV/decade for the Mehlich III solutions. According to Duncan's multiple range test, the DOA-based membrane was significantly less sensitive to potassium than the other two tested membranes. There were no significant differences in sensitivity between the NPOE- and DOS-based membranes in either DI water or the Kelowna extractant. Similar to the standard deviations of sensitivity slopes exhibited by the nitrate membranes, the potassium membranes showed a high level of repeatability (i.e., standard deviations of 0.1 to 2.3 mV/decade).

Table 4. Means and standard deviations of sensitivity slopes (mV/decade) of potassium membranes by extractant type.

Membrane Composition	Potassium Concentration Range[a]		
	10^{-1} M to 10^{-5} M	10^{-1} M to 10^{-4} M	10^{-1} M to 10^{-3} M
DI water			
V-DOS	57.96 ±0.83 a	59.87 ±0.84 a	61.94 ±1.02 a
V-NPOE	58.59 ±0.32 a	60.21 ±0.46 a	62.65 ±0.69 a
V-DOA	54.20 ±1.30 b	56.57 ±1.18 b	57.12 ±0.88 b
Kelowna solution			
V-DOS	40.55 ±0.88 a	51.20 ±1.10 a	58.84 ±0.62 a
V-NPOE	41.30 ±0.93 a	51.50 ±1.41 a	58.63 ±0.79 a
V-DOA	36.94 ±1.59 b	46.20 ±2.25 b	51.48 ±2.04 b
Bray P_1 solution			
V-DOS	32.47 ±0.46 b	41.95 ±0.60 b	51.16 ±0.67 b
V-NPOE	33.81 ±0.58 a	43.73 ±0.63 a	52.89 ±0.96 a
V-DOA	31.73 ±0.53 c	40.79 ±0.52 c	48.73 ±0.11 c
Mehlich III solution			
V-DOS	15.96 ±0.56 b	22.15 ±0.84 b	30.86 ±1.18 b
V-NPOE	18.16 ±0.59a	25.36 ±0.77 a	35.39 ±1.19 a
V-DOA	17.46 ±1.11 a	24.20 ±1.08 a	34.06 ±0.61 a

[a] Mean membrane sensitivities followed by the same letter within a potassium concentration range and within an extractant comparison are not significantly different at the 5% level, based on Duncan's multiple range test.

When the three potassium membranes were tested at 0.1 and 0.01 mole/L potassium concentrations in the presence or absence of NO_3^- (table 5), the DOS- and DOA-based potassium membranes showed consistent sensitivity slopes regardless of the presence of NO_3^-, whereas the NPOE-based potassium membrane gave unacceptable response slopes (<7 mV/decade) when NO_3^- was present in the test solutions, which results from the insensitive response of the NPOE-based membrane in the presence of nitrate ions of 0.1 mole/L concentration. These results are identical to those obtained by Cuin et al. (1999), who reported that the presence of high concentrations of nitrate (0.2 mole/L) affected the response of a potassium sensor fabricated with a valinomycin membrane containing NPOE as plasticizer. From these results, we conclude that the valinomycin-NPOE potassium membrane cannot be used with nitrate membranes for simultaneous measurement of nitrate and potassium concentrations due to nitrate interference with the potassium membrane.

Selectivity

A comparison of the mean selectivity coefficients (log K_{ij}) of the DOS- and DOA-based potassium membranes, obtained by the separate solution method, for the six cations in the four different solutions is shown in table 6. Selectivity data for the NPOE-based potassium membrane are not presented since, as shown in table 5, the response of NPOE-based membrane was affected by high nitrate concentration

Table 5. The effect of nitrate on the sensitivity response (mV/decade) of potassium membranes.

	Plasticizer Type[a]					
	DOS		NPOE		DOA	
Extractant	– NO_3^-	+ NO_3^-	– NO_3^-	+ NO_3^-	– NO_3^-	+ NO_3^-
DI water	62.6 ±1.52	58.6 ±0.92	62.6 ±1.72	–4.3 ±1.73	53.4 ±2.96	57.5 ±1.05
Kelowna solution	59.8 ±1.69	54.7 ±1.67	59.7 ±1.27	–6.9 ±3.75	59.8 ±1.98	54.1 ±1.73
Bray P_1 solution	53.6 ±1.27	55.6 ±2.75	55.8 ±1.07	0.67 ±2.95	50.1 ±0.91	53.7 ±3.12
Mehlich III solution	38.7 ±1.72	47.5 ±1.46	44.2 ±2.04	3.9 ±3.42	43.1 ±1.09	45.5 ±1.95

[a] – NO_3^- and + NO_3^- indicate the absence or presence of nitrate ion, respectively.

Table 6. Comparison of selectivity coefficients (log *K*) of potassium membranes by extractant type.

Membrane Composition[a]	Interference Ion[b]					
	Al^{+3}	Mg^{+2}	Ca^{+2}	Li^{+}	Na^{+}	NH_4^{+}
DI water						
V-DOS	−4.05 b	−3.98 b	−4.00 b	−3.60 b	−3.54 b	−1.64 b
V-DOA	−4.45 a	−4.40 a	−4.41 a	−3.87 a	−3.95 a	−1.77 a
Kelowna solution						
V-DOS	−2.93 b	−2.94 b	−2.88 b	−2.61 b	−2.57 b	−1.63 b
V-DOA	−3.12 a	−3.13 a	−3.07 a	−2.79 a	−2.75 a	−1.82 a
Bray P_1 solution						
V-DOS	−2.55 b	−2.53 b	−2.54 b	−2.18 b	−2.19 b	−1.69 b
V-DOA	−2.76 a	−2.71 a	−2.72 a	−2.34 a	−2.39 a	−1.79 a
Mehlich III solution						
V-DOS	−1.99 b	−1.97 b	−1.90 b	−1.62 b	−1.57 a	−1.42 a
V-DOA	−2.13 a	−2.06 a	−1.89 a	−1.72 a	−1.38 b	−1.47 a

[a] Selectivity coefficients were not calculated for the V-NPOE membrane, since the sensitivities of the membrane were affected by nitrate concentration (table 5).

[b] Membrane selectivity coefficients followed by the same letter within a nitrate concentration and within an extractant comparison are not significantly different at the 5% level, based on Duncan's multiple range test

of 0.1M contained in KNO_3 solutions, thereby resulting in unacceptable selectivity coefficients, which were determined by the separate solution method using equation 6.

The SAS multiple comparison analysis indicated that selectivity for potassium over other cations was enhanced when the DOA-based membrane was used (table 6). The DOA- and DOS-based membranes showed the same order in selectivity magnitude for potassium: $NH_4^+ << Na^+ \sim Li^+ < Mg^{2+} \sim Ca^{2+} \sim Al^{3+}$. In general, the selectivity coefficients for potassium over most of the tested cations (except NH_4^+) were high enough to detect potassium in the tested extracting solutions (except Mehlich III), which is consistent with the results reported by other researchers (Knoll et al., 1994; Oh et al., 1998; Bae and Cho, 2002).

Using only the data for the DOS-based potassium membrane (fig. 7), the effect of base solution on membrane selectivity is illustrated. Obviously, the selectivity for potassium over the tested interfering cations was affected by soil extractant. However, the selectivity for potassium in the presence of ammonium was nearly constant regardless of base solution type, with logarithmic selectivity coefficients ($\log K_{ij}$) of −1.42 to −1.82, which corresponds to 26 ~ 66 times more sensitivity to potassium than to ammonium. In DI water, the highest selectivity towards potassium was observed. As poor sensitivity for potassium was observed in the Mehlich III solution, the selectivity performance for potassium over other cations was decreased. This phenomenon is probably due to kinetic limitations in the transfer of potassium ions by various other cations and anions present in the Mehlich III solution (Oh et al., 1998).

Conclusions

The responses of nitrate membranes with tetradodecylammonium nitrate (TDDA) or methlytridodecylammonium chloride (MTDA) and potassium membranes with valinomycin as sensing materials were significantly affected by soil extractants. However, the TDDA-based nitrate and valinomycin-based potassium membranes, used in conjunction with the Kelowna solution as a base solution, were sensitive

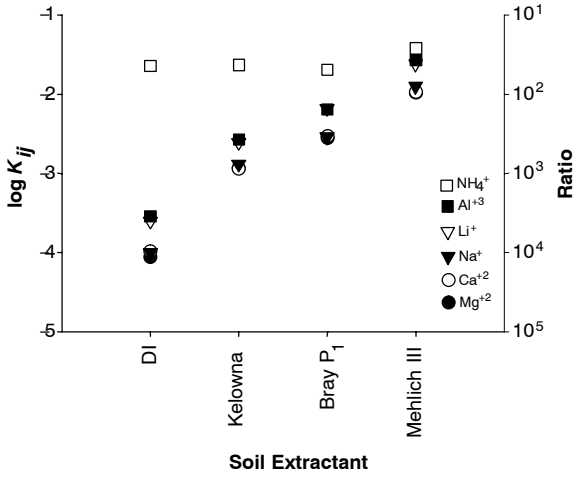

Figure 7. Effect of soil extractant on selectivity response of valinomycin-DOS potassium membranes.

enough to detect the usable range of soil nitrate and potassium concentrations (10 to 30 mg NO_3-N kg^{-1} soil and 50 to 150 mg K kg^{-1} soil at a dilution ratio (solution:soil) of 10:1, respectively), showing good selectivity for nitrate and potassium over interfering ions that may be present in soil extracts.

The TDDA-based nitrate membrane showed greater sensitivity and better selectivity for nitrate than did the MTDA-based membranes. The valinomycin-based membranes with DOS or DOA plasticizers proved to be good candidates for potassium sensing, exhibiting acceptable sensitivity and good selectivity.

All of the tested nitrate and potassium ion-selective membranes exhibited a linear response when nitrate and potassium concentrations were above 10^{-3} mole/L, irrespective of which soil extracting solution was used. However, at lower concentrations, i.e., below 10^{-4} mole/L, the sensitivity responses of all membranes were reduced when soil extractants were used as base solutions, as compared to that obtained in DI water. In particular, the use of the potassium membranes in the Mehlich III solution, which is one of the most commonly used universal soil extractants, was improper because the responses were almost insensitive to typical potassium concentrations (10^{-3} to 10^{-4} mole/L).

The selectivity of the nitrate and potassium membranes appeared to be satisfactory in measuring nitrates and potassium in the presence of chloride and ammonium ions because the nitrate and potassium membranes showed 47 to 603 and 26 to 56 times more sensitivity to NO_3^- and K^+ than to Cl^- and NH_4^+, respectively.

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References

Adamchuk, V. I. 2002. Feasibility of on-the-go mapping of soil nitrate and potassium using ion-selective electrodes. ASAE Paper No. 021183. St. Joseph, Mich.: ASAE.

Adamchuck, V. I., M. T. Morgan, and D. R. Ess. 1999. An automated sampling system for measuring soil pH. *Trans. ASAE* 42(4): 885-891.

Adsett, J. F., J. A. Thottan, and K. J. Sibley. 1999. Development of an automatic on-the-go soil nitrate monitoring system. *Applied Eng. in Agric.* 15(4): 351-356.

Ammann, D. 1986. *Ion-Selective Microelectrodes: Principles, Design, and Application.* Berlin, Germany: Springer-Verlag.

Artigas, J., A., C. J. Beltran, R. M. A. Baldi, C. Dominguez, and J. Alonso. 2001. Application of ion-selective field effect transistor based sensors to soil analysis. *Comp. and Elect. in Agric.* 31(3): 281-293.

Bae, Y. M., and S. I. Cho. 2002. Response of polymer membranes as sensing elements for an electronic tongue. *Trans. ASAE* 45(5): 1511-1518.

Bergveld, P. 1991. Future application of ISFETs. *Sensors and Actuators B* 4(1-2): 125-133.

Birrell, S. J., and J. W. Hummel. 2000. Membrane selection and ISFET configuration evaluation for soil nitrate sensing. *Trans. ASAE* 43(2): 197-206.

Birrell, S. J., and J. W. Hummel. 2001. Real-time multi-ISFET/FIA soil analysis system with automatic sample extraction. *Comp. and Elect. in Agric*. 32(1): 45-67.

Black, A. S., and S. A. Waring. 1978. Nitrate determination in an oxisol using K_2SO_4 extraction and the nitrate-specific electrode. *Plant and Soil* 49: 207-211.

Brown, J. R., ed. 1998. Recommended chemical soil test procedures for the north central region. Columbia, Mo.: Missouri Agricultural Experiment Station.

Carey, C. M., and W. B. Riggan. 1994. Cyclic polyamine ionophores for use in a dibasic-phosphate-selective electrode. *Anal. Chem.* 66(21): 3587-3591.

Collings, K., C. Christy, E. Lund, and P. Drummond. 2003. Developing an automated soil pH mapping system. ASAE Paper No. MC03205. St. Joseph, Mich.: ASAE.

Cuin, T. A., A. J. Miller, S. A. Laurie, and R. A. Leigh. 1999. Nitrate interference with potassium-selective microelectrodes. *J. Exp. Bot.* 50(340): 1709-1712.

Eggins, B. R. 2002. *Chemical Sensors and Biosensors.* West Sussex, U.K.: John Wiley and Sons.

Glazier, S. A., and M. A. Arnold. 1991. Selectivity of membrane electrodes based on derivatives of dibenzyltin dichloride. *Anal. Chem.* 63(8): 754-759.

IUPAC. 1994. IUPAC recommendation for nomenclature of ion-selective electrodes. *Pure and Applied Chem.* 66(12): 2527-2536.

Knoll, M., K. Cammann, C. Dumschat, M. Borchardt, and G. Hogg. 1994. Microfibre matrix-supported ion-selective PVC membranes. *Sensors and Actuators B* 20(1): 1-5.

Li, S., and K. A. Smith. 1984. The rapid determination of nitrate concentrations at low concentrations in soil extracts: Comparison of ion-selective electrodes with continuous-flow analysis. *Comm. Soil Sci. Plan.* 15(12): 1437-1451.

Mehlich, A. 1984. Mehlich III soil test extractant: A modification of Mehlich II extractant. *Comm. Soil Sci. Plan.* 15(12): 1409-1416.

Moody, G. J., J. D. R. Thomas, and J. M. Slater. 1988. Modified poly(vinyl chloride) matrix membranes for ion-selective field effect transistor sensors. *Analyst* 113(11): 1703-1707.

Nielson, H. J., and E. H. Hansen. 1976. New nitrate ion-selective electrodes based quaternary ammonium compounds in nonporous polymer membranes. *Anal. Chim. Acta* 85(1): 1-16.

Oh, K. C., E. C. Kang, Y. L. Cho, K. S. Jeong, and E. A. Yoo. 1998. Potassium-selective PVC membrane electrodes based on newly synthesized cis- and trans-bis(crown ether)s. *Anal. Sci.* 14: 1009-1012.

Oien, A., and A. R. Selmer-Olsen. 1969. Nitrate determination in soil extracts with the nitrate electrode. *Analyst* 94: 888-894.

Ruzicka, J., and E. H. Hansen. 1988. *Flow Injection Analysis.* 2nd ed. New York, N.Y.: John Wiley and Sons.

Tsukada, K., M. Sebata, Y. Miyahara, and H. Miyagi. 1989. Long-life multiple-ISFETs with polymeric gates. *Sensors and Actuators* 18(3-4): 329-336.

Van Lierop, W. 1986. Soil nitrate determination using the Kelowna multiple-element extract. *Comm. Soil Sci. Plan.* 17(12): 1311-1329.

Van Lierop, W. 1988. Determination of available phophorus in acid and calcareous soils with the Kelowna multiple-element extractant. *Soil Sci.* 146(4): 284-291.

Van Lierop, W., and N. A. Gough. 1989. Extraction of potassium and sodium from acid and calcareous soils with the Kelowna multiple-element extractant. *Canadian J. Soil Sci.* 69: 235-242.