ION-SELECTIVE ELECTRODES FOR SIMULTANEOUS REAL-TIME ANALYSIS OF SOIL MACRONUTRIENTS

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ABSTRACT

Automated sensing of soil macronutrients (i.e., N, P, and K) would allow more efficient mapping of soil nutrient variability for variable-rate nutrient management. Ion-selective electrodes (ISEs) are a promising approach because they have rapid response, directly measure the analyte with a wide range of sensitivity, and are small and portable. The capabilities of ion-selective electrodes for sensing macronutrients in soil extracts can be affected by the presence of other ions in the soil itself as well as by high concentrations of ions in soil extractants. Adoption of on-the-go sensing of soil nutrients would be enhanced if a single solution could be used for the concurrent extraction of soil macronutrients. This study reports on the development of a sensor array consisting of three different ion-selective electrodes for simultaneous determination of soil macronutrients. This sensor array could be used in a real-time soil analysis system based on automatic soil sampling and nutrient extraction. The sensitivity and selectivity of PVC membrane-based ion-selective electrodes with tetradodecylammonium nitrate (TDDA) and valinomycin for sensing nitrate and potassium, respectively, and of cobalt rod-based phosphate ion-selective electrodes were satisfactory for measuring N, P, and K ions over typical ranges of soil concentrations. The Kelowna multiple-ion extractant

(0.25M CH_3COOH + 0.015M NH_4F) was a viable candidate for concurrent extraction of soil macronutrients due to strong linear relationships between the amounts of NPK extracted with Kelowna and standard soil extractants from 37 Missouri and Illinois acidic soils. The nitrate and potassium ion-selective electrodes measured nitrate-N and K ions in Kelowna-based soil extracts with regression slopes near 1 ($r^2 > 0.92^{**}$) between the amounts determined by the ion-selective electrodes and by standard laboratory instruments. The nitrate ion-selective electrodes, when used in conjunction with the Kelowna extractant, provided soil NO_3-N values similar to those obtained with standard methods (i.e., automated ion analyzer and 1M KCl extractant). However, the soil K values obtained with the K electrodes and Kelowna extractant were about 50% lower than those obtained with an ICP (Inductively Coupled Plasma) spectrometer and Mehlich III extractant due to decreased K extraction by the Kelowna solution. The ISE-P values for soil were about 63% lower than ICP-P values (ICP and Mehlich III) due to both decreased P estimates in soil extracts and reduced P extraction by the Kelowna solution. Nevertheless, strong linear relationships ($r^2 > 0.78^{**}$) existing between the two methods would make it possible to use the K and P electrodes for soil K and P sensing.

CHAPTER 1
INTRODUCTION

The soil macronutrients, nitrogen (N), phosphorus (P), and potassium (K), are essential elements 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 (Havlin et al., 1999). The application of commercial NPK fertilizers has contributed to a tremendous increase in yields of agricultural crops that feed the world's population. Ideally, application rates should be adjusted based on estimates of the requirements for optimum production at each location because over-application results in increased production costs and may also cause environmental pollution due to runoff or leaching of chemicals into surface or ground water, whereas under-application can result in decreased yields due to deficiency of nutrients needed for crop growth (Sudduth and Hummel, 1991). It has been reported that the use of synthetic N fertilizer disturbs the N cycle, and is a major contributor to acid rain, nitrates and other compounds in waterways, and oxygen depletion in coastal waters (Kaiser, 2001). Also, high levels of soil P have been linked to degradation of water quality due to losses of P into surface water, resulting in excessive growth of algae in lakes and rivers (Mallarino, 1998; Vadas et al., 2004).

Precision agriculture, also called site-specific crop management (SSCM), is a soil and crop management system that assesses variability in soil properties (i.e., pH, organic matter, and soil nutrient levels), and field (i.e., slope and elevation) and crop parameters (i.e., yield and biomass), to optimize inputs such as fertilizers and herbicides based on information obtained at within-field locations (Sudduth et al., 1997). SSCM aims to improve profitability and to better protect soil and water resources as compared to past management practices (Kitchen et al., 2005).

Soil testing for monitoring nutrient levels in the field is a management tool that can help accurately determine the available nutrient status of soils and the efficient use of fertilizers. With the increasing awareness of fertilizer effects on environmental and soil quality, soil tests have been instrumental in determining where insufficient or excess nutrient levels occur (Hergert et al., 1997). Conventional soil testing methods typically include two main processes; soil sampling in the field, and soil processing and chemical analysis in the laboratory. Due to economic and time considerations, grid soil sampling with an area of approximately 1 ha has been commonly used by practitioners to characterize spatial variability of soil nutrient levels (Schepers and Schlemmer, 1998). The test value obtained at each grid is then assumed to represent the area of 100 m by 100 m and results in uniform application of fertilizer to the 1-ha-sized area of the field. Therefore, that the nutrient map cannot address any changes in soil properties occurring within distances of less than 100 m. In one study, higher resolution grid sampling provided a more realistic depiction of spatial resolution in soils whereas reducing soil sampling intensity increased the risk of developing an unrealistic map of P concentration (Schepers and Schlemmer, 1998).

With advances in analytical technology, current use of various automated instruments, such as ICP (inductively coupled plasma) spectrometers and automated ion analyzers, provides an improved ability to detect lower concentrations in soil extracts (Mallarino, 2003; Pittman et al., 2005). However, not only are these instruments quite expensive, but they also require complex sample pre-treatment, which increases the cost and time of sample analysis thereby limiting the number of samples tested in the field (Artigas et al., 2001). In particular, accurate monitoring of soil nitrate has been limited by the relatively long turn-around time of laboratory analysis because soil nitrate can be easily lost by leaching and denitrification between the time of testing and plant uptake (Magdoff et al., 1984; Blackmer et al., 1989). Therefore, quantifying soil test variability requires a fast on-site measurement at a high sampling intensity that will allow the variability to be mapped spatially and temporally with some degree of confidence (Sudduth et al., 1997; Wollenhaupt et al., 1997).

The success of SSCM depends on the ability to accurately characterize the variability in the soils in a field. The time and cost required for the intensive sampling needed in SSCM, when using conventional sampling and analysis techniques, may make implementation of a variable-rate nutrient fertilizer application system impractical (Birrell, 1995). In this situation, an on-the-go real-time sensor could be an alternative, allowing the collection of geographically referenced data on a much finer spatial resolution than is currently feasible with manual and/or laboratory methods while providing benefits from the increased density of measurements at a relatively low cost (Sudduth et al., 1997; Adamchuk et al., 2004). Such sensor-based data collection in the field may be the most desirable in SSCM, with the adoption of various engineering technologies, including the global positioning system (GPS), geographic information systems (GIS), and variable rate applicators (VRA).

A soil nutrient sensor that can rapidly and continuously measure chemical properties, such as pH, N, P, and K, while traveling across the field would be useful in the variable rate application of lime and fertilizers. In practice, control decisions for variable rate application could be made based on information obtained with such real-time sensors and the VRA equipment could effectively apply fertilizers as needed.

The goal of this research is to develop a real-time sensor that could be used as a sensing component for simultaneous determination of macronutrients (i.e., N, P, and K) in soil extracts. These sensors could then be employed in an on-the-go soil analysis system based on automatic soil sampling and nutrient extraction.

CHAPTER 2
REVIEW OF LITERATURE

This review describes sensor developments and related technologies that are applicable to the measurement of soil macronutrients in real-time for SSM. First, various analytical techniques commonly used in soil NPK analysis and the sensing principles of related laboratory instruments as applied with the use of various soil extractants are discussed. Second, various types of soil nutrient sensors, mainly based on optical and electrochemical methods, are reviewed to select the optimum sensing method suitable for the development of a sensor. Finally, to choose candidate sensing elements available for sensing N, P, and K ions, a specific discussion on the development of various ion-selective membranes is given, taken mainly from the area of analytical chemistry.

ANALYTICAL INSTRUMENTS AND SOIL EXTRACTANTS FOR SOIL ANALYSIS

In standard laboratory soil testing to measure macronutrients (N, P, and K), various automatic analyzers and extracting solutions have been used. According to soil test procedures widely used in the Midwest USA (Brown and Rodriguez, 1983; Brown, 1998), the automated ion analyzer has been commonly used for simultaneously measuring nitrate-N and ammonium-N. Phosphorus and K ions in soil extracts have been measured with a colorimetric spectrophotometer and an AAS (Atomic Absorption Spectrophotometer) analyzer, respectively. The use of an ICP (Inductively Coupled Plasma) spectrometer in soil testing laboratories has expanded rapidly since the early

1990s due to its ability to simultaneously measure multiple elements, including P and K, in one sample (Mallarino, 2003; Pittman et al., 2005).

In nitrate analysis with the automated ion analyzer in conjunction with FIA (Flow Injection Analysis), nitrate (NO_3^-) is first reduced to nitrite (NO_2^-) using a copperized cadmium column in an NH_4Cl matrix. The nitrite is then determined by addition of a diazotizing reagent and a coupling reagent to form reddish purple color in proportion to the concentration of nitrite. The sample absorbance is measured at a wavelength of 520 nm. A 1M or 2M KCl solution is the commonly used extractant for extracting soil inorganic N (Huffman and Barbarick, 1981; Dorich and Nelson, 1984; Wright and Stuczynski, 1996; Gelderman and Beegle, 1998).

The determination of P in solution with the colorimetric spectrophotometer, which measures the absorbance of a sample at a given wavelength, is achieved based on the reaction of P with a molybdate (Mo) ion to form a colored complex (ascorbic acid method). The resulting yellow color is intensified in the presence of vanadium (V). Alternately, the Mo can be reduced using ascorbic acid to form a characteristic blue color. The intensity of the yellow or blue color depends on the concentration of P in solution (Frank et al., 1998). According to an overall review about testing soils for phosphorus reported by Fixen and Grove (1990), soil extractants commonly used in soil test laboratories for extracting P are Bray P_1 (0.025M HCl + 0.03M NH_4F), Mehlich III (0.2M CH_3COOH + 0.015M NH_4F +0.25M NH_4NO_3+ 0.013M HNO_3 + 0.001M EDTA), and Olsen (0.5M $NaHCO_3$) (Bray and Kurtz, 1945; Olsen et al., 1954; Mehlich, 1984). They indicated that the Bray P_1 extractant is suitable for acid soils whereas the Olsen extractant is suitable for calcareous soils. The Mehlich III solution has been shown to provide good results for P over a wide soil pH range (Fixen and Grove, 1990; Haby et al., 1990; Mallarino, 2003). The Mehlich III solution has also been accepted as a universal extracting solution for extracting P and K, as well as other cations including Ca, Mg, Na, and Zn from soils (Mehlich, 1984; Haby et al., 1990). However, the Mehlich III solution is not useful for nitrate extraction because of the high concentration of nitrate in the extraction solution.

The determination of potassium in soil with the AAS analyzer is based on the passage of light at a wavelength specific for an element through an atomic vapor of the element produced by a flame from an air-acetylene mixture (Watson and Isaac, 1990). Extraction of total exchangeable K in soils including other cations, such as Ca, Mg, and Na has been typically accomplished with 1M NH_4OAc for many years, and the Mehlich III extractant has more recently been suggested (Haby et al., 1990; Warncke and Brown, 1998).

The measurement of both P and K with the ICP instruments is based on atomic emission spectroscopy that measures the intensity of light emitted at a specific wavelength when the excited electron returns to a lower energy state (Watson and Isaac, 1990). The ICP spectrometer that uses an argon gas plasma as an energy source is based on characteristic optical emission of atoms excited in a high-temperature (5000 – 8000K) argon plasma (Mallarino, 2003). Due to the high temperature of the plasma, chemical interferences are reduced, resulting in good linear responses to elements being tested. Soil analysis by ICP has recently become increasingly popular in soil-testing laboratories because as compared to other instruments (i.e., colorimetric and AAS spectrophotometers), the ICP spectrometer has many advantages: (1) minimum chemical interferences, (2) four to six orders of magnitude in linearity of intensity vs. concentration, (3) multi-element capabilities, (4) rapid analysis, and (5) better detection limits (Watson and Isaac, 1990).

For the simultaneous detection of NPK in automated on-the-go sensing, a universal extractant would be advantageous because its use would reduce the time and cost involved in the analysis, e.g., less soil preparation would be required for detecting different nutrients, and a reduced number of calibration solutions would be needed.

A search of the literature for universal extracting solutions to extract N, P, and K showed that the Kelowna solution (0.25M CH_3COOH + 0.015M NH_4F) used in soil testing laboratories of British Columbia could be a candidate soil extractant for simultaneous extraction of N, P, and K from soils. Van Lierop (1986) studied the applicability of the Kelowna extractant to soil nitrate determination by comparing the results obtained with nitrate ion-selective electrodes and the Kelowna extractant with those determined by steam distillation of 2M KCl extracts. He showed that nitrate ion-selective electrodes can determine nitrate in samples extracted using the Kelowna solution. However, since the electrode response was affected by chloride, the use of 0.05M Ag_2SO_4 solution was required to suppress the chloride interference.

Van Lierop (1988) evaluated the Kelowna extractant by changing its chemical composition, soil to extractant ratios, and extraction times for determining available P in acidic and calcareous soils. For comparison to standard methods, reference P values were obtained with the Bray P_1 solution for acidic soils and the Olsen solution for calcareous soils. Results indicated that, with the Kelowna solution, a 5-min extraction and a 1:10 soil-to-solution ratio with the Kelowna were optimal extraction parameters for obtaining the best relationships between extracted P values.

A study on the simultaneous determination of K and Na in acidic and calcareous soils with the Kelowna solution was carried out by Van Lierop and Gough (1989). The study showed high correlation coefficients ($r^2 > 0.97$) when relating concentrations of potassium and sodium extracted from soils by the Kelowna multiple extractant to those removed by 1M NH_4OAc. However, the Kelowna, on average, extracted 20% less K than did 1M NH_4OAc, though extracted Na levels were similar.

SENSORS FOR MEASURING SOIL MACRONUTRIENTS

Various types of sensors to measure mechanical, physical and chemical soil properties were reviewed by Sudduth et al. (1997) and Adamchuk et al. (2004). In this review, sensors for measuring macronutrients (N, P, and K) and pH levels in soils are considered.

Although there is a large variety of sensing techniques available, most of the soil nutrient sensors described in the literature involve one of two measurement methods:

- optical sensing that uses reflectance spectroscopy to detect the level of energy absorbed/reflected by soil particles and nutrient ions, or
- electrochemical sensing that uses ion-selective membranes which generate a voltage or current output in response to the activity of selected ions.

Reflectance Spectroscopy-Based Measurements

Optical methods for prediction of various soil properties, including soil organic matter (SOM) and soil nitrate, have been attempted by many researchers due to their attractive advantages over electrochemical technology, such as non-destructive measurement and no need to take a soil sample (Sudduth et al., 1997; Chang et al., 2001).

Sudduth et al. (1997) discussed a number of studies on optical measurement of soil organic matter (SOM), which is a source of mineralizable nitrogen and of plant nutrients. The optical estimation of SOM has been attempted with color data, and with wide-band and narrow-band spectral reflectance data, due to a historical observation that soils with a higher level of SOM appear darker. The best results with visible reflectance data have been obtained with red light (Vinogradov, 1981). However, color has been a good estimator of SOM only when limits were imposed on the variability of other soil parameters that affect soil reflectance (Sudduth et al., 1997).

Sudduth and Hummel (1991) applied a variety of calibration methods, including stepwise multiple linear regression, principal components analysis (PCA) and partial least squares regression (PLSR) calibration, to soil color and spectral reflectance data to predict SOM of a representative set of 30 Illinois soils. The results showed that NIR data analyzed by the PLSR approach was the most efficient in minimizing the effect of moisture by reducing the set of collinear independent variables (reflectance), thereby resulting in improved SOM prediction ($r^2 = 0.92$, standard error of prediction (SEP) = 0.34% SOM) as compared with single-wavelength sensing. Additional laboratory tests of this NIR sensor with soils obtained from across the continental United States showed that acceptable SOM predictive capability could be maintained with a single calibration equation for soils from the lower U.S. Corn Belt (Sudduth and Hummel, 1996).

Similarly to SOM measurements with optical methods, several researchers have attempted optical determination of soil macronutrients, especially N. Dalal and Henry (1986) used NIR (Near Infrared) reflectance spectroscopy to simultaneously predict water content, total organic carbon, and total N in air-dried soils by multiple linear regression. They reported the partial correlation coefficients (r) for each of three wavelengths selected for the three measurement parameters were highly significant (> 0.87). However, there was a significant difference in SEP between coarsely ground (< 2 mm) and finely ground soils (< 0.25 mm). Also, at lower concentrations of organic carbon and total nitrogen, the prediction by NIR techniques was relatively poor.

Upadhyaya et al. (1994) used NIR absorbance data in conjunction with FFT (Fast Fourier Transform) and PLSR analyses to determine soil NO_3-N over a concentration range of 0 to 300 mg/kg. The correlation between the NIR and standard methods was high ($r^2 > 0.9$). However, the SEP was fairly high (6 ~ 38 mg/kg NO_3-N). Additional research on optical measurement of soil nitrate was conducted through laboratory and field experiments (Ehsani et al., 1999). They were able to determine an optimal wavelength range (1800 ~ 2300 nm) for measuring soil nitrate, but a soil-specific calibration was needed to map nitrate variation over a large area due to the effect of soil type. More recently, Jahn et al. (2005) attempted to use wavelet spectral analysis for the determination of soil nitrate based on mid-infrared spectroscopy. The wavelet analysis was applied to soil Fourier transform infrared (FTIR) attenuated total reflectance (ATR) spectral data. They tested two types of soils (Yolo loam and Capay clay) treated with nitrate fertilizers by adding interfering compounds such as carbonate and humic acid. In the concentration range of 0 to 140 mg/L NO_3-N, the coefficient of determination (r^2) between the volume of obtained signal peak and nitrate concentration was 0.93. However, the results were not satisfactory when attempting to measure low concentrations of soil nitrate or to obtain consistent predictive capabilities across a range of soils due to relatively high standard errors of prediction (about 9.5 mg/L NO_3-N) and a significant effect of soil type. From a practical standpoint, they mentioned the sensor could not be applied to the determination of low nitrate concentrations around 15 mg/L NO_3-N detected in soils with residual nitrate tests. Instead, they recommended the technique be used in predicting nitrate concentrations during the growing season when nitrate amounts as large as 200 mg/L NO_3-N are typical.

As another example of simultaneous determination of soil properties using optical methods, Chang et al. (2001) applied principal component regression (PCR) to relate 33 soil chemical, physical, and biochemical properties to NIR absorbance data obtained from 802 soil samples. They demonstrated the possibility of measuring diverse soil properties such as total C, total N, moisture content, Cation Exchange Capacity (CEC), and extractable Ca with acceptable accuracy. Similarly, Yong et al. (2005) used NIR spectroscopy to estimate nitrogen and organic matter in soils of a province in China using a total of 125 soil samples. They reported that the coefficients of determination (r^2) between measured and predicted soil nitrogen and organic matter were 0.92 and 0.93, respectively, and slopes of 0.59 and 0.71 were obtained for N and SOM measurements.

Linker et al. (2004) used anion exchange membranes consisting of cross-linked polystyrene combined with mid-infrared reflectance (mid-IR) spectroscopy to determine nitrate concentration in three types of media (aqueous solution, soil extracts, and soil paste). When using a partial least squares (PLS) technique for calibration, the prediction model showed a standard error of about 5 mg NO_3^--N kg^{-1}. They mentioned that several technical improvements, such as how to shake the solution and dry the membrane, should be addressed in future research.

In summary, it was possible to obtain high correlation between the reflectance techniques and standard methods when using near-infrared reflectance (NIR) data in conjunction with various calibration and signal processing methods (i.e., partial least squares (PLS) regression, multivariate calibration, and FFT wavelet analysis). However, the results were not satisfactory when measuring low concentrations of soil nitrate and organic matter, and obtaining consistent predictive capabilities across a range of soils was not possible due to relatively high standard errors of prediction and significant effects of soil type and color.

Electrochemical Potentiometry-Based Sensing

Most of the electrochemical methods used to determine soil nutrient levels are based on the use of an ion-selective electrode (ISE, glass or polymer membrane) or an ion-selective field effect transistor (ISFET). The ISFET has the same theoretical basis as the ISE, i.e., both ISEs and ISFETs respond selectively to a particular ion in solution according to a logarithmic relationship between the ionic activity and electric potential (Birrell and Hummel, 2000).

Laboratory Soil Tests Using Commercial Ion-Selective Electrodes

Ion selective electrodes have been historically used in soil testing laboratories to conduct standard chemical soil tests, especially soil pH measurement. Many researchers in the 1970's and 1980's concentrated on the suitability of ISEs as an alternative to routine soil nitrate testing (Myers and Paul, 1968; Mahendrappa, 1969; Oien and Selmer-Olsen, 1969; Milham, 1970; Onken and Sunderman, 1970; Dahnke, 1971; Mack and Sanderson, 1971; Bound, 1977; Hansen et al., 1977; Black and Waring, 1978; Li and Smith, 1984).

Dahnke (1971) used a nitrate ISE for determination of nitrate in soil extracts while changing several factors, including interfering anions, extracting agents, soil-to-solution ratios, and reference electrodes. The results showed that the lowest detection limit of the NO_3 electrode was about 1~2 mg NO_3-N L^{-1} in solution. He reported this detection limit would be useful in measuring nitrate ions in routine soil testing.

Li and Smith (1984) investigated the suitability of a commercial nitrate electrode for the determination of NO_3-N at low concentrations (< 2 mg L^{-1}) in soil extracts obtained with saturated $CaSO_4$ solution by comparing the results to standard methods using 1M KCl solution and continuous flow analysis (CFA). The nitrate levels measured with the electrode were highly correlated with those obtained with the CFA analyzer ($r^2 = 0.94$), showing an almost 1:1 relationship (> 0.94) between the two methods. Also, they found that the $CaSO_4$ solution was effective for the extraction of nitrates from air-dried soils, removing 95% of the extractable amounts of nitrates after a 5-min shake period.

Similarly to the nitrate measurements with ISEs, several researchers used K-selective electrodes to estimate soil K concentration (Farrell, 1985; Farrell and Scott, 1987; Adamchuk, 2002; Brouder et al., 2003; Lemos et al., 2004).

Farrell and Scott (1987) evaluated the possibility of using valinomycin-based and cationic glass ion-selective electrodes for the determination of exchangeable soil K in $BaCl_2$ and NH_4OAc extracts. The Ba^{2+}-exchangeable K^+ values measured with the valinomycin-based electrode were highly correlated with and not significantly different from those obtained by AAS. However, direct measurement of the NH_4^+-exchangeable K^+ values using the electrode was not feasible due to a high concentration of NH_4^+ in the extracts. Instead, a comparison of the AAS values for the Ba^{2+} and NH_4^+-exchangeable K demonstrated the feasibility of using an alternative extractant for an evaluation of the ISE methods, where the K amounts extracted with the two different extracting solutions were highly correlated.

Adamchuk (2002) conducted a preliminary test of nitrate and potassium ion-selective electrodes to measure nitrate and K in soils as opposed to soil extracts. The laboratory test showed that it was feasible to determine soluble nitrate and K contents on moist soil samples as long as several limitations such as inconsistent contact between soil and electrode and potential drift due to continuous measurements were removed.

Brouder et al. (2003) performed a correlation study between plant-available K of 32 agricultural soils determined by two ISEs (glass and PVC-based) and by AAS analysis. Results showed that the ISE-K readings in soil slurries were highly correlated with AAS-K values in filtrates when using DI water for a 1:1 soil: solution ratio extraction (slope =

0.93, $r^2 = 0.76$). However, the PVC-based ISE was not usable for measurement in soil slurries due to durability problems. Also, the ISE-K values obtained using DI water for extracting K were not well correlated with those obtained with standard methods using 1M NH_4OAc solution and an AAS analyzer.

On-the-Go Vehicle-Based Soil Nutrient Sensing

Since the 1990s, several researchers (Adsett and Zoerb, 1991; Adamchuk et al., 1999; Adsett et al., 1999) have reported on real-time on-the-go soil nutrient sensing using particularly designed soil samplers and commercially available ion-selective electrodes for sensing nitrate and pH in soils.

Adsett et al. (1991; 1999) designed a prototype tractor-mounted field monitoring system to directly measure soil nitrate levels using ion-selective electrodes because they had found in their previous study (Thottan et al., 1994) that a nitrate ion-selective electrode showed reliable sensor readings and acceptable response times of less than 20 s. The system, consisting of a soil sampler, an extraction unit, a flow cell, and a controller, was tested in the laboratory and field. The soil sampler was designed with a chain saw blade and belt-conveying unit to gather and transport samples of known volume and density to the extraction and analysis unit. The results from laboratory testing indicated that the actual nitrate level could be predicted with 95% accuracy after 6 s of measurement. However, several mechanical and electrical problems were found during field testing, e.g., clogging of the extractor outlet with plant residue which resulted in unacceptable levels of noise in the electrode signal.

Adamchuk et al. (1999) developed an automated sampling system for measuring soil pH by using a flat-surface combination pH electrode. The system consisted of a lever situated below a soil tine, which collected a sample of soil and then rotated to press the soil slurry against the surface of the pH electrode. The test showed a high correlation between the electrode voltage output and soil pH in the laboratory and field ($r^2 = 0.92$ and 0.83, respectively). The system could measure pH while taking soil samples at a pre-selected depth between 0 and 20 cm every 8 s.

Based on the results reported by Adamchuck et al. (1999), a commercial soil pH mapping system (Veris Technologies, Salina, Kansas) has recently become available (Collings et al., 2003). A soil sampling system consisting of a cutting shoe and a sampling trough was built to collect soil samples. The pH measurements were carried out with a combination pH electrode, which were placed in contact with soil samples brought by the soil sampler. A microcontroller was used for controlling rinsing of the pH electrodes and communicating with a logging instrument. The accuracy of the system was evaluated by comparing collected pH data to laboratory analysis. The results showed a correlation coefficient of 0.79 between sensor readings and laboratory measurements. Afterwards, in a feasibility test of using the soil pH mapping system for the establishment of site-specific lime recommendations (Lund et al., 2004), they reported that on-the-go mapping of soil pH provided improved accuracy of lime prescription maps, showing a smaller lime estimation error of 1,340 kg/ha than that obtained using 1 ha grid sampling (2,109 kg/ha) when lime recommendations from validation samples were calculated based on buffer pH laboratory tests. As an extended study to develop an integrated system for on-the-go mapping of soil pH, K, and NO_3 (Sethuramasamyraja et al., 2005), a laboratory experiment was performed to investigate the effects of various measurement parameters, such as soil-water ratio and quality of water for electrode rinsing, on sensor performance. They reported that a 1:1 soil: water ratio and tap water for rinsing electrodes could be used in the simultaneous measurement of pH, K, and NO_3 with ion-selective electrodes.

Viscarra Rossel et al. (2004) built a soil analytical system comprising a batch-type mixing chamber with two inlets for 0.01M $CaCl_2$ solution and water. In the mixing chamber, there was a flat spinning disc ensuring efficient mixing of the solution and the soil. A pH ISFET was used to determine soil pH and estimate lime requirements. In the laboratory, using 91 Australian soils, the system was tested in soil solutions obtained by mixing 3 g of sieved soil and 15 ml of 0.01M $CaCl_2$. However, the coefficient of determination for the estimated pH was not high ($r^2 = 0.49$).

Another approach, using an ISFET chip combined with Flow Injection Analysis (FIA) for soil analysis has been reported (Birrell and Hummel, 2000; Artigas et al., 2001; Birrell and Hummel, 2001; Price et al., 2003). According to the literature, ISFET technology offers inherent features such as fast response, small dimensions, low output impedance, high signal-to-noise ratio, low sample volumes, and the ability to integrate several sensors on a single electronic chip -- all of which are desirable for a real-time sensor (Price et al., 2003).

Birrell and Hummel (2000; 2001) investigated the use of a multi-ISFET sensor chip to measure soil nitrate in a FIA system using low flow rates, short injection times, and rapid rinsing. The multi-ISFET/FIA system was successfully used to estimate soil nitrate-N content in manually prepared soil extracts ($r^2 > 0.90$). The rapid response of the system allowed samples to be analyzed within 1.25 s with sample flow rates less than 0.2 mL s^{-1}. However, their prototype automated soil extraction system did not consistently provide soil extracts that could be analyzed by the ISFET/FIA due to blockages in the filtration process. They suggested that considerable effort would be required for the development of an automated soil extraction system that enabled the soil sample to be well mixed with extracting solution and the nutrients to be effectively extracted from the soil solution.

Price et al. (2003) developed a rapid extraction system that might be used in the field for real-time prediction of soil nitrates using ISFETs developed by Birrell and Hummel (2001). Several design parameters affecting the nitrate extraction of the soil cores and output data of the ISFETs were studied. The results showed nitrate concentration could be determined 2 to 5 s after injection of the extracting solution when using data descriptors based on the peak and slope of the ISFET nitrate response curve.

ION-SELECTIVE MEMBRANES AND ELECTRODES

Polymer membrane-based ISEs and ISFETs require recognition elements, i.e., ion-selective membranes, which are integrated with a reference electrode and enable the chemical response (ion concentration) to be converted into a signal (electric potential) (Eggins, 2002). Due to an increased demand for the measurement of new ions, and tremendous advances in the electronic technology required for producing ISFET chips that allow for multiple sensing, numerous ion-selective membranes have been developed in many areas of applied analytical chemistry, e.g., in the analysis of clinical or environmental samples (Antonisse and Reinhoudt, 1999; Bakker, 2004).

It has been reported that there are ion-selective membranes available for sensing most of the important soil nutrients, including NO_3^-, K^+, Na^+ , Ca^{2+}, Mg^{2+}, and Cl^- (Moss et al., 1975; Nielson and Hansen, 1976; Tsukada et al., 1989; Morf et al., 1990; Knoll et al., 1994; Levitchev et al., 1998; Artigas et al., 2001; Gallardo et al., 2004).

Numerous reports on the development and application of nitrate ion-selective membranes have been described in various fields, such as food, plant, fertilizer, soil, and wastewater (Nielson and Hansen, 1976; Miller and Zhen, 1991; Sutton et al., 1999; Birrell and Hummel, 2000; Artigas et al., 2001; Le Goff et al., 2002; Gallardo et al., 2004).

Nielson and Hansen (1976) developed nitrate ion-selective electrodes using various quaternary ammonium compounds and plasticizers in non-porous PVC-based membranes. A combination of tetradodecylammonium nitrate (TDDA) and dibutylphthalate (DBP) as the ligand and plasticizer, respectively, was found to show the best response to nitrate. The optimal membrane composition was proposed to be 29% PVC, 67% DBP, and 4% TDDA.

Birrell and Hummel (2000) evaluated various PVC matrix membranes prepared based on different combinations of ligand and plasticizer materials using an automated testing device. The goal of this effort was to choose sensing materials for real-time soil nitrate analysis. They also developed multi-ISFET nitrate sensors using the nitrate membranes identified as potential candidates. The nitrate ISFETs were shown to effectively determine nitrate concentration over a range of nitrates in soil with acceptable selectivity levels that were at least 40 times greater for nitrate than for chloride and bicarbonate.

As an example of using different types of nitrate ion-selective membranes, Le Goff et al. (2002) developed a rubbery membrane based on N,N,N-trially leucine betaine using a free radical initiated co-polymerisation for use in measuring nitrate in agricultural drainage water over a 5 month period, because there was a need for more reliable measurements without any deterioration in sensor performance by leaching of chemicals from the membrane. In a concentration range of 0.47 to 16 mg NO_3-N L^{-1}, there was significant correlation ($r^2 = 0.99$) between the new membrane-based ISE and laboratory methods. The system did not require re-calibration during a four-month test.

To develop an automated electronic tongue system with four ion-selective membranes and a FIA system, Gallardo et al. (2004) applied an artificial neural network method to the determination of nitrate in complex samples containing variable amounts of chloride. The proposed approach improved the accuracy of the determination of nitrate concentration over a range from 0.1 to 100 mg/L NO_3 without the need to eliminate chloride. However, they mentioned as a drawback that a large number of known samples were needed for training the system.

Historically, a major interest for potassium (K^+) analysis came from clinical chemistry because changes in K^+ concentration in human serum bring about the risk of acute cardiac arrhythmia (Buhlmann et al., 1998). Therefore, the majority of the research on the use of potassium ion-selective membranes has been focused on continuous monitoring of the human body during periods of rapidly changing K^+ concentrations, such as during or after surgery (Buhlmann et al., 1998). From the results of numerous studies on ionophores for sensing potassium in analytical chemistry (Moss et al., 1975; Moody et al., 1988b; Moody et al., 1988a; Oh et al., 1998; Bakker, 2004), it is clear that valinomycin has been the most successful ionophore for sensing K^+ ion because of its strong K selectivity.

Many researchers have attempted to expand the application of the valinomycin-based K^+ membranes to monitoring of environmental samples, such as food, water and soil, by fabricating a sensor array with various ion-selective membranes for multiple ion sensing (Sibbald et al., 1984; Tsukada et al., 1989; Knoll et al., 1994; Artigas et al., 2001; Bae and Cho, 2002). In addition, most of these studies also included research on the adhesion of the PVC membrane to the gate region of ISFETs. The efforts were directed toward extending the consistent sensitivity period, and thus, the lifetime of the electrode (Kawakami et al., 1984; Moody et al., 1988a; Tsukada et al., 1989; Artigas et al., 2001). The results demonstrated that the valinomycin-based K membranes were useful in measuring K in environmental samples containing various interfering ions.

As an example of sensing multiple ions with ISFETs in soil analysis, Artigas et al. (2001) reported on the fabrication of pH, Ca^{2+}, NO_3^-, and K^+ ISFETs with photo-curable polymeric membranes and their evaluation in aqueous solutions to investigate the application of ISFET technology to soil analysis. The photo-curable polymeric membrane provided better adhesion to the surface of the ISFET and a longer lifetime than did PVC-based membranes. Sensor response characteristics were stable for two months. During that time no membrane damage occurred and no peel-off was observed in the laboratory.

Due to the importance of real-time monitoring of P in biological systems and living organisms, many researchers have tried to develop phosphate sensors in the form of ion-selective electrodes and biosensors. However, it has been reported that the design of an ionophore for selective recognition of phosphate is especially challenging for several reasons. Due to the very high hydration energy of phosphate, ion selective membranes have a very poor selectivity for phosphate (Liu et al., 1997; Buhlmann et al., 1998; Fibbioli et al., 2000). According to the characterization by the Hofmeister series (perchlorate > thiocyanate > iodide > nitrate > bromide > chloride > acetate > sulfate ~ phosphate), phosphate, being at the end of the series, shows the lowest selectivity response toward the anions (Ammann, 1986; Liu et al., 1997). 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.

According to an overall review of phosphate sensors (Buhlmann et al., 1998; Engblom, 1998), phosphate sensors can be mainly classified into three types, i.e., polymer membranes based on organotin, cyclic polyamine, or uranyl salophene derivative; protein-based biosensors; and cobalt-based electrodes.

The use of organotin compounds was initiated by Glazier and Arnold (1988; 1991). They prepared various dibenzyltin dichloride derivatives, such as bis(p-chlorobenzyl)tin dichloride, dibenzyltin dichloride, and bis(p-methylbenzyl)tin dichloride. The bis(p-chlorobenzyl)tin dichloride showed the best selectivity for dibasic orthophosphate (HPO_4^{2-}) against various anions, such as nitrate, bromide, chloride, and acetate. The sensitivity was satisfactory, yielding a detection limit of 3.2 x 10^{-5} M and a linear range of response from 2.2 x 10^{-4} to 1.2 x 10^{-2} M for dibasic phosphate activity when tested in standard solutions at pH 7. More recently, numerous studies on the development of new ionophores based on tin compounds have been reported to enhance the performance, in terms of selectivity and durability, of the phosphate sensor that Glazier and Arnold developed (Tsagatakis et al., 1994; Liu et al., 1997; Tsagkatakis et al., 2001; Sasaki et al., 2004).

Liu et al. (1997) reported that a binuclear compound bis(tribenzyltin) oxide incorporated in a PVC membrane with o-nitrophenyl octyl ether (NPOE) as the plasticizer yielded an improved linear response in the range of 5 (10^{-6}) to (10^{-1}) M HPO_4^{2-} and a lifetime of one month.

Recently, the direct use of a commercially available chemical as an ionophore for phosphate determination was reported by Sasaki et al. (2004). The electrode membrane containing tributyltin chloride as the ionophore and 25 mol% NaTFPB exhibited high selectivity for $H_2PO_4^-$ with a slope of -60 mV/decade.

Carey and Riggan (1994) tried four types of cyclic polyamines, N_3, N_4, N_5, and N_6-cyclic amines, as ionophores for sensing dibasic phosphate ions. The electrodes were tested in phosphate solutions at pH 7.2. The N_3-cyclic amine showed the greatest selectivity for HPO_4^{2-}, a linear calibration curve was achieved between 10^{-6} and 10^{-1}M, and the slope was -28.9 mV/decade. Surprisingly, the lifetime of the electrode was about nine months.

Wroblewski et al. (2000; 2001) developed a different type of PVC membrane based on uranyl salophene derivatives as ionophores for the determination of phosphate. The highest selectivity for $H_2PO_4^-$ over other ions tested in solutions of pH 4.5 was obtained when incorporating salophene III (with t-butyl substituents) and NPOE plasticizer in a PVC membrane containing 20 mol% of tetradecylammonium bromide (TDAB). This membrane had a sensitivity slope of -59 mV/decade and a maximum lifetime of two months.

As a biosensor for sensing phosphate, Kubo (2002) developed phosphate-bind protein(PBP) from *Escherichia coli*. The PBP was immobilized on a sheet of nitrocellulose membrane by cross-linking. It was shown that the response time was about 5 min in the concentration range of 10^{-4} ~1.5 (10^{-3}) M. He reported that there was no change in electric potential when other anions such as sulfate, nitrate, and bromide were added at a concentration of 5 (10^{-4}) M.

Xiao et al. (1995) introduced cobalt metal as a phosphate ion-selective electrode material. They reported that oxidized cobalt metal electrodes show potentiometric sensitivity to phosphate in the concentration range of 10^{-5} ~ 10^{-2} M in 0.025 M potassium hydrogen phthalate (KHP) solution at pH 4.0. The tested electrodes displayed good selectivity for $H_2PO_4^-$ over other anions, such as sulfate, chloride, nitrate, and acetate but responded to changes in the partial pressure of oxygen dissolved in solution. A host-guest mechanism involving formation of a nonstochiometric cobalt oxide species on the electrode surface was proposed to explain the response characteristic. Further study on the response mechanism was carried out by Meruva and Meyerhoff (1996). They suggested a mixed potential mechanism involving a slow oxidation of cobalt, a simultaneous reduction of oxygen and the formation of $CO_3(PO_4)_2$ at the electrode surface. The mechanism could better explain various characteristics previously found in the cobalt electrode, such as the effects of sample stirring rate and pH on electrode response.

Chen et al. (1997) investigated the applicability of cobalt wire as a phosphate electrode in FIA. The electrode showed a linear response with a slope of about -38 mV/decade change in phosphate when tested in a carrier of the FIA system containing 0.04 M KHP (pH 5). Also, additional research (Chen et al., 1998) was conducted to see if the system could be applied to the direct determination of phosphate in soil extract samples by spiking and diluting the soil samples with standard phosphate solutions. Spiked soil extracts showed good recoveries for phosphate in the concentration range of $10^{-4} \sim 10^{-3}$ M.

The use of the cobalt wire-based FIA system designed by the above authors was expanded to the determinations of phosphate in waste water and fertilizers, and in hydroponic nutrient solutions (De Marco et al., 1998; De Marco and Phan, 2003). In the waste water and fertilizer samples, the difference between data measured with the cobalt-based FIA system and with a standard spectrophotometer was generally $\pm$ 5% (relative) when correcting for a chloride interference. In the hydroponic nutrient solutions, the FIA system showed a relative error of ± 4.2 ~ 8.6 % in the phosphate concentration range of 58 ~ 120 mg/L as compared to standard methods.

Engblom (1999) studied the applicability of a cobalt wire electrode to the measurement of phosphate in soil extracts. Ammonium lactate-acetic acid (AL), commonly used in Sweden, was chosen as a soil extracting solution. He reported that the cobalt electrode was linearly sensitive to phosphate ranging from 10^{-4} to 10^{-3} M in the AL soil extractant with a sensitivity slope of -30 mV/decade. A five-soil study comparing cobalt wire electrode results with standard phosphate measurements including ICP and colorimetric analyses showed that the concentrations predicted by the cobalt electrode were the lowest among those obtained with the three different methods. He indicated that the effects of iron and organic matter in the soil extracts on electrode response resulted in a lower sensitivity than was expected.

Parra et al. (2005) developed a flow injection system using a tubular cobalt electrode for the determination of inositol phosphates in seeds and grains. Two different buffer solutions, 0.01M KHP (pH = 4) and 0.01M Tris-HCl (pH = 8), were used for inorganic and organic phosphates, respectively. A comparison of the results to standard methods (ICP and colorimetric analyzers) was conducted using some samples of seed and grain. They reported there were no significant differences among the results produced by the three different methods.

CHAPTER 3
OBJECTIVES

The literature review showed that electrochemical methods based on ion-selective membranes could be used to develop a real-time soil nutrient sensor for N, P, and K. However, the capabilities of ion-selective membranes, when tested in soil extracts, might be limited by the effects of interference from other inorganic and organic ions present in soil extractants and in the soil itself. Also, the identification of a multiple ion extractant that does not adversely affect the response of ion-selective membranes, and that can extract representative amounts of soil macronutrients is needed for simultaneous real-time analysis of soil macronutrients.

Therefore, the overall objectives of this research were 1) to investigate the applicability of various ion-selective electrodes and soil extractants to the simultaneous determination of soil macronutrients (N, P, and K), and 2) to identify combinations of sensing elements and extraction solutions which can be employed in a real-time soil analysis system based on automatic soil sampling and nutrient extraction.

Specific objectives were to:

- Characterize the capabilities of nitrate and potassium ion-selective membranes in soil extractants with respect to their sensitivity, lower detection limits, and selectivity against interferences of other ions, and identify the combination of ion-selective membranes and soil extractants suitable for measuring typical ranges of nitrate and potassium concentrations in soil.

- Conduct preliminary studies to find soil extractants usable for multiple-ion extraction of soil N, P, and K, and to investigate the potential of using the selected nitrate and potassium ion-selective membranes for the determination of nitrate-N and potassium concentrations of soil extracts.
- Evaluate two or more types of phosphate ion-selective sensors to test their sensitivity, selectivity, and compatibility with soil extractants, and select the optimum sensor for determination of phosphorus concentrations within typical soil ranges.
- Investigate the predictive capabilities of an array of the three selected ion-selective electrodes for simultaneous analysis of soil N, P, and K ions using a range of Missouri and Illinois soils by comparison to results obtained with standard soil testing methods.

CHAPTER 4

EVALUATION OF NITRATE AND POTASSIUM ION-SELECTIVE MEMBRANES

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 possible components of a soil fertility sensor. 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 study 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 solution to about 10^{-5} mole NO_3^-/L. 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 providing a consistent sensitivity when distilled 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.

INTRODUCTION

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.

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 (Adamchuk 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 the effects of 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 use in automated, on-the-go sensing systems.

OBJECTIVES

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 chapter 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., 1988a; 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 (0.25 ~ 0.35 mm in thickness), 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 prevent 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 (Appendix A) was designed for the simultaneous measurement of the electromotive forces (EMFs) of 16 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 program (Appendix B) 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, Calif.).

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. 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. Details of the test stand and control program are described in Appendices A and B.

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 600 Hz 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.

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:

$$\mathrm{EMF} = E_o + E_J + S \log a_i \tag{4.1}$$

where

EMF = electromotive force generated by the difference of membrane potentials

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:

$$a_i = \gamma_i c_i \tag{4.2}$$

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:

$$\log \gamma_i = \frac{-Az_i^2\sqrt{I}}{1 + B\mathbf{a}\sqrt{I}} \tag{4.3}$$

where A and B are constants with values of 0.5108 ($\text{mole}^{-1}\,\text{L}^{1/2}$) and 0.328 ($\text{mole}^{-1}\,\text{L}^{1/2}\,\text{Å}^{-1}$), 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:

$$I = \frac{1}{2}\sum_i c_i z_i^2 \tag{4.4}$$

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 Nikolskii-Eisenman equation (Equation 4.5) in terms of the electrode potential and a selectivity coefficient, as follows:

$$\text{EMF} = E_o + E_J + S \log\left[a_i + \sum K_{ij} (a_j)^{Z_i / Z_j} \right] \tag{4.5}$$

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:

$$K_{i,j} = 10^{(E_j - E_i)/S} \frac{a_i}{{a_j}^{Z_i/Z_j}} \tag{4.6}$$

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 4.6. 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 4.1 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 4.1a, 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 (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. 4.1b), 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.

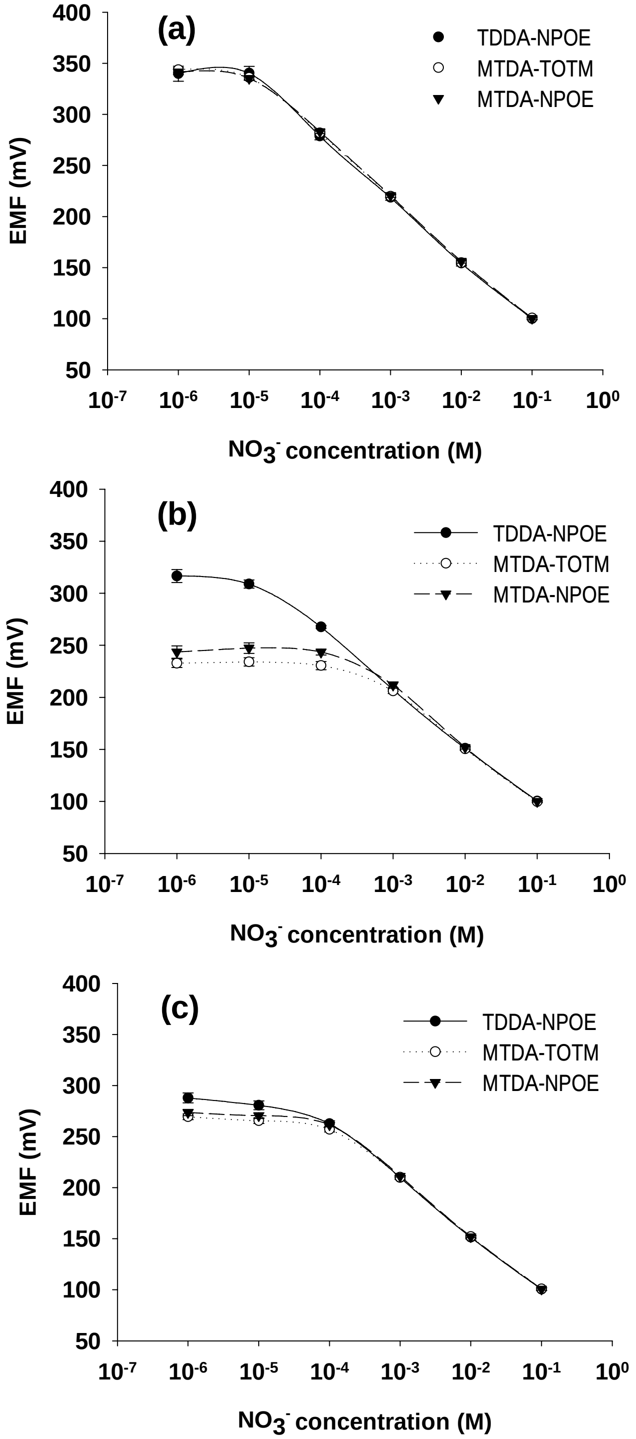


Figure 4.1. Electrode EMF vs. nitrate concentration for different nitrate membranes: (a) in DI water, (b) in 0.01M $CuSO_4$, and (c) in Kelowna extractants.

In the Kelowna solution (Fig. 4.1c), 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. 4.2) indicates that the sensitivity of nitrate membranes at low nitrate concentrations (<10^{-4} mole/L) is affected by the soil extracting solution. 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 in solution at a dilution ratio (solution: soil) of 10:1 for soil nitrate sensing.

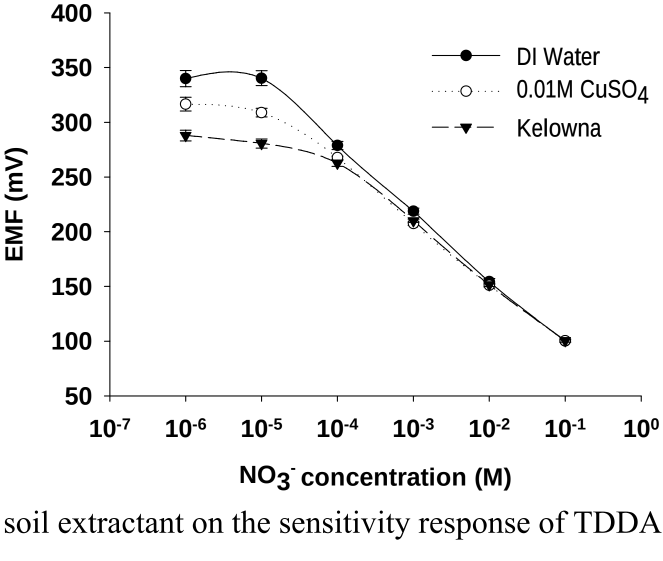


Figure 4.2. Effect of soil extractant on the sensitivity response of TDDA-NPOE nitrate membranes.

The SAS TTEST procedure was used to investigate differences in sensitivity between membranes of the same composition (I and II) but prepared on different dates. The results (Table 4.1) 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 4.2) show that the sensitivity of the membranes varied considerably depending on soil extractant type. The low standard deviations of the means, ranging from 0.3 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.

Table 4.1. 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.	-43.7 ±0.7	-53.0 ±0.7	-55.0 ±0.9 a
	II	24 May	-43.3 ±0.6	-52.9 ±0.7	-56.0 ±0.5 b
MTDA-NPOE	I	27 Feb.	-45.3 ±0.3	-54.7 ±0.3	-55.78 ±0.3
	II	24 May	-44.9 ±0.8	-54.4 ±0.6	-55.9 ±0.5
TDDA-NPOE	I	20 Mar.	-47.1 ±1.5	-54.8 ±1.4	-56.0 ±2.2
	II	17 Apr.	-47.3 ±1.2	-55.0 ±1.0	-55.4 ±0.9

[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 4.2. 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	-61.3 ±0.3 b	-63.0 ±0.3 b	-62.5 ±0.5 b
MTDA-NPOE	-61.4 ±0.5 b	-63.7 ±0.8 a	-63.5 ±1.1 a
TDDA-NPOE	-62.2 ±1.6 a	-62.4 ±1.2 c	-62.7 ±1.3 b
Kelowna solution			
MTDA-TOTM	-43.6 ±0.7 c	-53.0 ±0.7 b	-55.2 ±0.9
MTDA-NPOE	-45.1 ±0.7 b	-54.5 ±0.5 a	-55.7 ±1.8
TDDA-NPOE	-47.2 ±1.4 a	-54.9 ±1.3 a	-55.8 ±0.4
0.01M $CuSO_4$ solution			
MTDA-TOTM	-35.2 ±1.1 c	-45.5 ±1.2 c	-54.6 ±1.2 b
MTDA-NPOE	-39.0 ±1.4 b	-49.8 ±0.8 b	-57.4 ±1.5 a
TDDA-NPOE	-54.0 ±0.8 a	-56.8 ±0.5 a	-55.0 ±0.8 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.

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 4.3. 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.

Table 4.3. 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.

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): -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

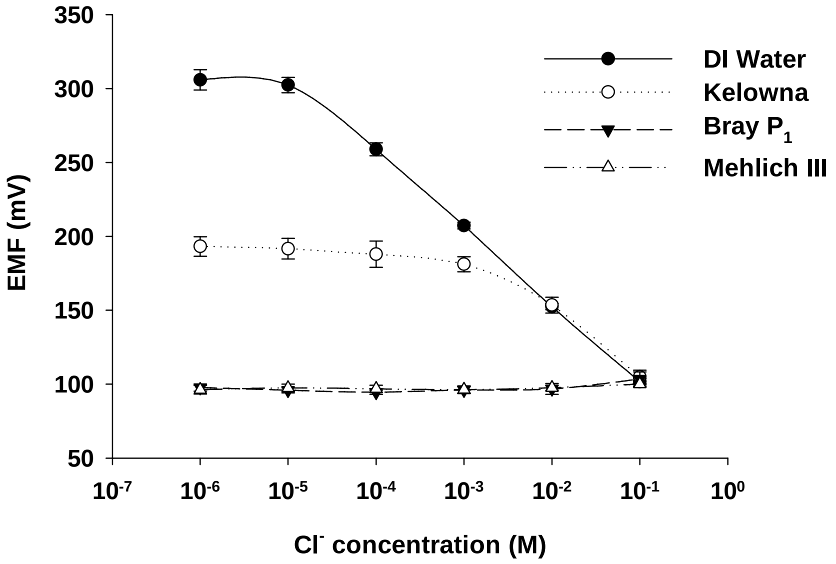


Figure 4.3. Effect of chloride on the sensitivity response of TDDA-NPOE nitrate membranes for various soil extractants.

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 4.3 shows the effect of the 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 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 4.3) more sensitive to 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. 4.4) when four different soil extractants (DI water, Kelowna, Bray P_1, and Mehlich III) were used as base solutions.

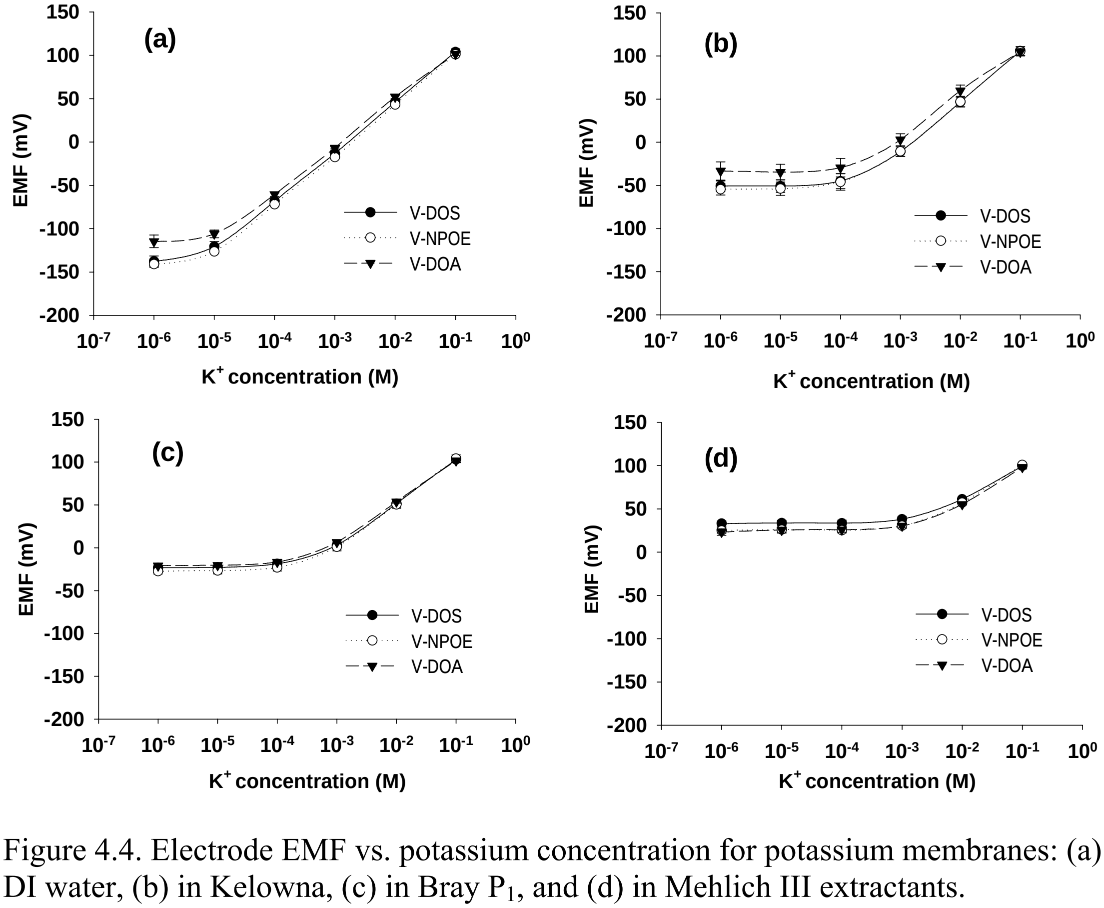


Figure 4.4. Electrode EMF vs. potassium concentration for potassium membranes: (a) in DI water, (b) in Kelowna, (c) in Bray P_1, and (d) in Mehlich III extractants.

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. 4.4a) 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. 4.4b and 4.4c, respectively), at low potassium concentrations ($<10^{-4}$ mole/L), the response slopes were considerably reduced as compared to those measured in DI water (Fig. 4.4a). 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. 4.4d) 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 various cations such as NH_4^+ and H^+ that interfere with potassium measurement.

Figure 4.5 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.

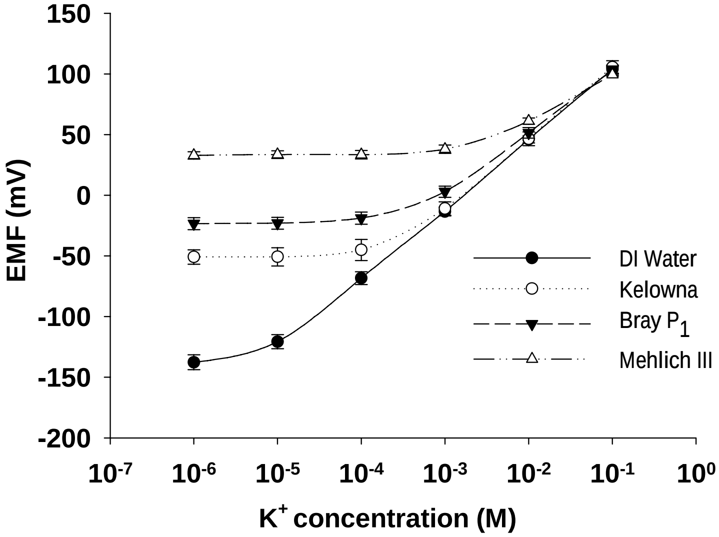


Figure 4.5. Effect of soil extractant on sensitivity response of valinomycin-DOS potassium membranes.

Table 4.4. 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	58.0 ±0.8 a	59.9 ±0.8 a	61.9 ±1.0 a
V-NPOE	58.6 ±0.3 a	60.2 ±0.5 a	62.7 ±0.7 a
V-DOA	54.2 ±1.3 b	56.6 ±1.2 b	57.1 ±0.9 b
Kelowna solution			
V-DOS	40.6 ±0.9 a	51.2 ±1.1 a	58.8 ±0.6 a
V-NPOE	41.3 ±0.9 a	51.5 ±1.4 a	58.6 ±0.8 a
V-DOA	36.9 ±1.6 b	46.2 ±2.3 b	51.5 ±2.0 b
Bray P_1 solution			
V-DOS	32.5 ±0.5 b	42.0 ±0.6 b	51.2 ±0.7 b
V-NPOE	33.8 ±0.6 a	43.7 ±0.6 a	52.9 ±1.0 a
V-DOA	31.7 ±0.5 c	40.8 ±0.5 c	48.7 ±0.1 c
Mehlich III solution			
V-DOS	16.0 ±0.6 b	22.2 ±0.8 b	30.9 ±1.2 b
V-NPOE	18.2 ±0.6 a	25.4 ±0.7 a	35.4 ±1.2 a
V-DOA	17.5 ±1.1 a	24.2 ±1.1 a	34.1 ±0.6 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.

Table 4.4 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).

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 4.5), 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 insensitivity of the NPOE-based membrane to potassium 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.

Table 4.5. 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 ±1.5	58.6 ±0.9	62.6 ±1.7	-4.3 ±1.7	53.4 ±3.0	57.5 ±1.1
Kelowna solution	59.8 ±1.7	54.7 ±1.7	59.7 ±1.4	-6.9 ±3.8	59.8 ±2.0	54.1 ±1.7
Bray P_1 solution	53.6 ±1.3	55.6 ±2.8	55.8 ±1.1	0.7 ±3.0	50.1 ±0.9	53.7 ±3.1
Mehlich III solution	38.7 ±1.7	47.5 ±1.5	44.2 ±2.0	3.9 ±3.4	43.1 ±1.1	45.5 ±2.0

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

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 4.6. Selectivity data for the NPOE-based potassium membrane are not presented since, as shown in Table 4.5, the response of the NPOE-based membrane was affected by high nitrate concentration of 0.1M contained in KNO_3 solutions, thereby resulting in unacceptable selectivity coefficients, which were determined by the separate solution method using equation 4.6.

The SAS multiple comparison analysis indicated that selectivity for potassium over other cations was enhanced when the DOA-based membrane was used (Table 4.6). The DOA- and DOS-based membranes showed the same order in selectivity magnitude for potassium: $NH_4^+ << Na^+ \sim Li^+ < Mg^{2+} \sim Ca^{2+} \sim Al^{3+}$.

Table 4.6. Comparison of selectivity coefficients (log *K*) of potassium membranes by extractant type.

Membrane	Interference Ion[b]					
Composition[a]	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 4.5).

[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.

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. 4.6), 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).

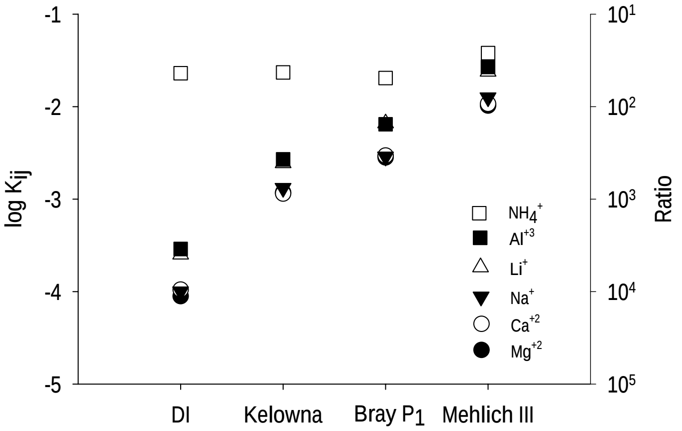


Figure 4.6. Effect of soil extractant on selectivity response of valinomycin-DOS potassium membranes.

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 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.

CHAPTER 5

SENSING NITRATE AND POTASSIUM IONS IN SOIL EXTRACTS USING ION SELECTIVE ELECTRODES

ABSTRACT

Automated sensing of soil macronutrients would allow more efficient mapping of soil nutrient variability for variable-rate nutrient management, and ion-selective electrodes or membranes are a promising approach. The capabilities of ion-selective electrodes for sensing macronutrients in soil extracts can be affected by the presence of other ions in the soil itself as well as by high concentrations of ions in soil extractants. Adoption of automated, on-the-go sensing of soil nutrients would be enhanced if a single extracting solution could be used for the concurrent extraction of soil macronutrients. This paper reports on the ability of the Kelowna extractant to extract macronutrients (N, P, and K) from US Corn Belt soils and whether previously developed PVC-based nitrate and potassium ion-selective electrodes could determine the nitrate and potassium contents of soil extracts obtained using the Kelowna extractant. The extraction efficiencies of nitrate-N and phosphorus obtained with the Kelowna solution for seven US Corn Belt soils were comparable to those obtained with 1M KCl and Mehlich III solutions when measured with automated ion and ICP analyzers, respectively. However, the potassium levels extracted with the Kelowna extractant were, on average, 42% less than those obtained with the Mehlich III solution. Nevertheless, it was expected that Kelowna could extract proportional amounts of potassium ion due to a strong linear relationship ($r^2 = 0.96$). The use of the PVC-based nitrate and potassium ion-selective electrodes proved to

be feasible in measuring nitrate-N and potassium ions in Kelowna - soil extracts with almost 1:1 relationships and high coefficients of determination ($r^2 > 0.9$) between the levels of nitrate-N and potassium obtained with the ion-selective electrodes and standard analytical instruments. However, to obtain consistently good results with the nitrate ion-selective electrodes, an automated measurement system that could maintain good quality control during continuous measurements was needed due to potential drifts of the nitrate ion-selective electrodes observed over a period of time.

INTRODUCTION

The soil macronutrients, nitrogen (N), phosphorus (P), and potassium (K), are essential elements 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 (Havlin et al., 1999).

Standard soil testing methods, consisting of soil sampling in the field and chemical analysis in the laboratory, have been routinely used to determine available nutrient status of soils for efficient use of fertilizers as well as for reduction of environmental impact. However, the methods are costly and time consuming because they require complex processes for pre-treatment and expensive instruments for samples to be quantitatively analyzed, thereby limiting the practical sampling density. In particular, monitoring of soil NO_3-N levels through conventional methods has been limited by relatively high temporal and spatial variability of NO_3-N across the field, which requires fast on-site measurements with a high sampling intensity (Sudduth et al., 1997). An on-the-go real-time soil nutrient sensor that can simultaneously measure levels of macronutrients while traveling across the field could be an alternative, providing benefits from increased density of measurements at a relatively low cost and an optimum timing (Adamchuk et al., 2004).

The need for such fast on-site monitoring for field use has led to the application of ion-selective electrode (ISE) technology to measurement of soil macronutrients, because of advantages over analytical methods (spectroscopic techniques), such as simple methodology, direct measurement of analyte, sensitivity over a wide concentration range, low cost, and portability. 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).

Historically, ISEs have been used for the measurement of soil pH in soil testing laboratories. Many researchers in the 1970's and 1980's concentrated on the suitability of ISEs as complementary methods to routine soil nitrate testing (Myers and Paul, 1968; Mahendrappa, 1969; Oien and Selmer-Olsen, 1969; Milham, 1970; Onken and Sunderman, 1970; Dahnke, 1971; Mack and Sanderson, 1971; Bound, 1977; Hansen et al., 1977; Black and Waring, 1978; Li and Smith, 1984). Similarly, several researchers have used K-selective electrodes to estimate soil potassium concentration (Farrell, 1985; Farrell and Scott, 1987; Adamchuk, 2002; Brouder et al., 2003; Lemos et al., 2004).

In standard soil testing for the determination of soil macronutrient content, various soil extracting solutions (soil extractants) are used for extracting nutrients from soil in a shaking and filtering process. For example, distilled water, 2M KCl, and 0.01M $CuSO_4$ solutions are used for nitrate extraction (Oien and Selmer-Olsen, 1969; Van Lierop, 1986) and in the US 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; Mehlich, 1984) is currently being used in some commercial laboratories for the extraction of phosphorus, potassium, and other cations in soil. However, the Mehlich III solution is not useful for nitrate extraction because of the high concentration of nitrate in the extracting solution. Meanwhile, 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.

It has been reported that there are ion-selective membranes available for sensing most of the important soil nutrients, including NO_3^-, K^+, Na^+, Ca^{2+}, Mg^{2+}, and Cl^- (Moss et al., 1975; Nielson and Hansen, 1976; Tsukada et al., 1989; Morf et al., 1990; Knoll et al., 1994; Levitchev et al., 1998; Artigas et al., 2001; Gallardo et al., 2004). Furthermore, 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, 1988; 1991; Carey and Riggan, 1994).

However, the application of electrodes based on ion-selective membranes to soil nutrient sensing might be limited by the presence of other ions in the soil itself, and high concentrations of ions in soil extractants. In addition, a universal extracting solution that does not adversely affect the response of ion-selective electrodes and that can extract representative amounts of soil macronutrients is needed in fast real-time sensing for simultaneous measurement of soil macronutrients.

OBJECTIVES

The overall objective of this study was to investigate the potential of using ion-selective electrodes for the determination of nitrate-N and potassium concentrations in soil extracts.

Specific objectives included:

- Evaluate the Kelowna soil extracting solution for multiple element extraction of N, P, and K ions from US Corn Belt soils, comparing extraction efficiencies with those of various soil extractants used in standard soil testing procedures.
- Investigate the applicability of previously selected nitrate and potassium ion-selective electrodes to the simultaneous determination of NO_3-N and K concentrations in Kelowna-based soil extracts.

MATERIALS AND METHODS

Evaluation of Soil Macronutrient Extraction Using the Kelowna Solution

Soil extraction tests were conducted to investigate whether the Kelowna extracting solution could be used as a universal soil extractant for extracting NPK ions from seven central US Corn Belt soils (Table 5.1). The Kelowna solution, which was proposed as a multiple element extractant in British Columbia, Canada (Van Lierop, 1986; 1988; Haby et al., 1990; Van Lierop and Tran, 1990), was evaluated by comparing the quantity of soil N, P, and K extracted with the Kelowna and standard soil extractants by means of simple linear regression analysis.

Reference NO_3-N values were obtained with two different extracting agents (deionized (DI) water and 1M KCl) and P and K were extracted using three different standard soil extractants (1M NH_4OAc, Bray P1, and Mehlich III). These extracting agents were prepared according to methods described previously (Mehlich, 1984; Van Lierop, 1988).

Three sub-samples of each of the seven air-dried soils from sites in Missouri and Illinois (Table 5.1), which had been ground and screened using a 2-mm sieve and stored at room temperature, were extracted with each soil extractant. Soil textural properties were determined by the sieve-pipette method.

Table 5.1. Characteristics of the 4 Missouri and 4 Illinois soils used in the study.

Sample	Soil	Textural		Textural properties (%)			
Origin	Name	Class	ID	Sand	Silt	Clay	pH
MO	Mexico	Silt loam	ARS-A	19.1	67.9	13.0	6.5
	Mexico	Silt loam	ARS-C	8.1	67.2	24.7	6.0
	MU Check[a]	Silt loam	Check	24.8	62.3	13.0	--[b]
	Leonard[c]	Silt loam	ARS-LoPK	15.2	68.3	16.3	6.1
IL	Drummer	Silt loam	26	19.4	64.6	16.0	5.5
	Drummer	Silt loam	29	14.0	65.0	21.0	5.7
	Proctor	Silty clay loam	8	16.0	61.0	23.1	5.4
	Ade	Sandy loam	1	93.3	4.0	2.7	6.6

[a] Composite of soil samples obtained from throughout Missouri.
[b] Not determined.
[c] The Leonard soil was not used in extraction tests.

Soil NO_3 and K were extracted by shaking 2 g of the air-dried soils with 20 mL of soil extractant for 5 min and filtering the soil solution through Whatman No. 42 paper (Van Lierop and Gough, 1989; Brown, 1998). The manually extracted solutions were then analyzed by a commercial soil testing laboratory (A&L Great Lakes Laboratories, Fort Wayne, Indiana) using the Lachat Flow Injection Analyzer (Lachat Instruments, Milwaukee, Wisc.) for NO_3-N analysis and the ARL Accuris ICP (Inductively Coupled Argon Plasma) spectrophotometer (Fixons ARL Accuris, Ecublens, Switzerland) for P and K analysis. These instruments were separately calibrated with each tested soil extractant to reduce any differences in absorbance between the background solution and the sample matrix. The regression results for extraction efficiencies obtained with Kelowna and the other soil extractants were compared using mean N, P, and K values of three replicates of each soil determined by the analytical instruments.

Sensing NO_3-N and K in Soil Extracts Using Ion-Selective Electrodes

Potentiometric determinations of nitrate-N and K were made with two nitrate ion-selective electrodes and two potassium ion-selective electrodes, respectively. The nitrate ion-selective electrodes were prepared using quaternary ammonium compounds as reported in previous studies (Birrell and Hummel, 2000). Two ligands – tetradodecyl ammonium nitrate (TDDA) and methyltridodecyl ammonium chloride (MTDA); and a plasticizer - nitrophenyl octyl ether (NPOE) were used for producing the two different PVC-based nitrate membranes: i.e., TDDA-NPOE and MTDA-NPOE. For potassium sensing, two membranes were prepared according to previously reported methods (Knoll et al., 1994), using valinomycin (V, potassium ionophore I) as an ionophore, bis(2-

ethylhexyl) sebacate (DOS) and bis(2-ethylhexyl) adipate (DOA) as plasticizers, and potassium tetrakis (4-chlorophenyl) borate (KTpClPB) as a lipophilic additive: i.e., V-DOS and V-DOA.

The Kelowna solution was used to prepare calibration solutions and to obtain soil extract samples for N and K analysis. The soils utilized in this test included the seven soils used in the soil extraction tests and a Leonard silt loam soil from Missouri (Table 5.1). Similar to methods used in the soil extraction tests, three replicates of soil extracts for NO_3 and K analyses of each soil were obtained by shaking 2 g of the air-dried soil with 20 mL of Kelowna extractant for 5 min using a reciprocating shaker, and then filtering through Whatman No. 42 filter paper. The filtrates were split for laboratory and ISE measurements.

The potential outputs (EMF, electromotive force) of the electrodes were collected at a sampling rate of 10 Hz using a computer equipped with a Daqbook 200 A/D board and a custom-designed 16-channel buffering circuit module (Appendix A). All electric potentials of the ISEs were measured relative to a double-junction Ag/AgCl reference electrode (model PHE 3211, Omega Engineering, Stamford, Conn.), while the test solution was being stirred by a small magnetic stir bar. At the beginning of each replication, calibration measurements were carried out in sequence from dilute to more concentrated solutions. The electrodes were rinsed with the Kelowna solution between measurements.

The concentration ranges of nitrate-N and potassium calibration solutions needed to cover a full range of soil test values were determined according to criteria used for classifying soil test results into low, medium, and high ratings (Buchholz et al., 1983). However, since Missouri has no rating criteria for interpreting soil nitrate-N levels, previously reported research correlating soil nitrate concentrations in late spring and corn yields in Iowa (Blackmer et al., 1989) was used to determine critical nitrate-N levels.

Figure 5.1 shows the response curves of the TDDA-NPOE-based nitrate (a) and valinomycin-DOS-based potassium (b) ISEs obtained from previous standard sensitivity tests (chapter 4) compared to the typical ranges of soil NO_3-N and K concentrations when using a 10:1 solution to soil ratio. It is apparent that the ranges of interest (i.e., low to high) would be measurable with the electrodes if the non-linear portion of the response curve could be well-described in calibration. Thus, separate N and K calibration solutions were prepared, each with seven different concentration levels (i.e., 0.8, 2, 4, 6, 10, 16, and 20 mg NO_3-N L^{-1} and 4, 8, 16, 20, 24, 32, and 40 mg K L^{-1}, respectively). Calibration curves relating EMF (mV) to concentration (mg/L) for each type of electrode were constructed based on non-linear logarithmic regression.

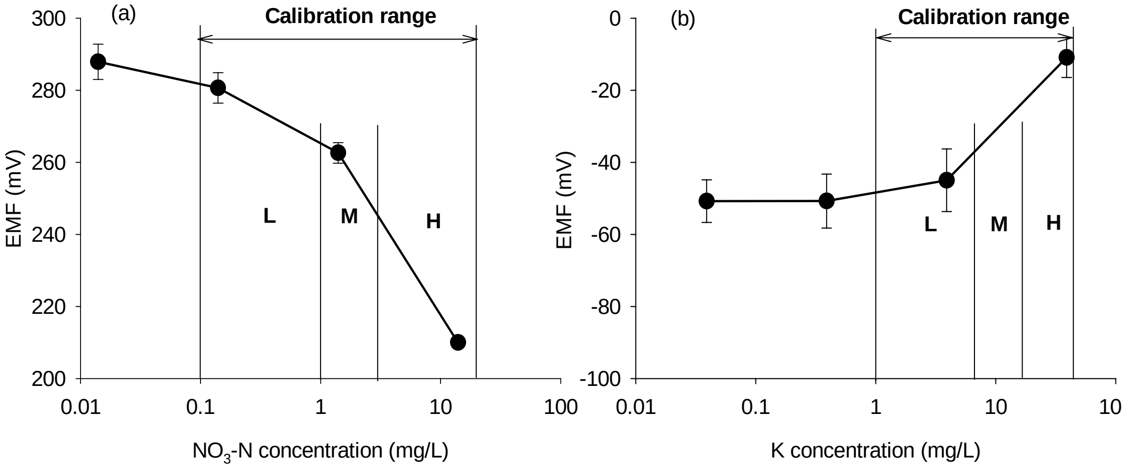


Figure 5.1. Response curves of (a) TDDA-based nitrate and (b) valinomycin-DOS-based potassium electrodes and typical soil test N and K concentrations to determine required concentration ranges for calibration: L, M, and H designate low, medium, and high levels, respectively.

Immediately after each complete calibration sequence, the electrodes were immersed in 40-ml soil extract samples in randomized order (Fig. 5.2a). The length of the insertion period was 60 s. Between insertions into the different soil extract samples, the electrodes received three 15-s rinses by sequential dipping of the electrodes into three 250-ml beakers of the rinse solution, i.e., Kelowna extractant containing no N and K ions (Fig. 5.2b).

The EMF value at the end of the third rinse was used as the baseline EMF for the subsequent soil extract test. For each sample, values of the baseline and sample EMFs were obtained from EMF data collected at 10 Hz at approximately 10 s and 45 s after the electrodes were inserted in the rinse and sample solutions. A corrected EMF value for each sample was obtained by subtraction of the baseline EMF from the sample EMF to minimize drift and hysteresis. Three iterations of each sequence were conducted using the three replicate samples obtained from each soil.

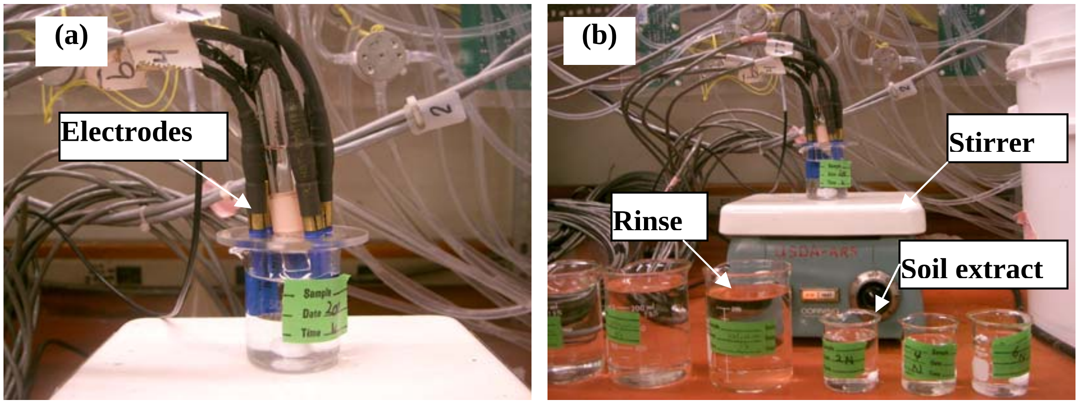


Figure 5.2. Electrodes inserted in (a) soil extract sample and (b) rinse solutions and stirrer.

The levels of nitrate-N and potassium for each soil determined by each ISE were compared with those obtained with the automated ion analyzer and ICP spectrometer for NO_3-N and K analysis, respectively, by means of simple linear regression analysis.

Because nitrate levels of soils in the first extract test did not sufficiently represent the full range of concentrations present in agricultural soils, a second soil extract test was performed. Seven of the original eight soils (Table 5.1) were coupled with varying levels of NO_3-N addition or extract dilution, similar to methods reported previously (Oien and Selmer-Olsen, 1969; Black and Waring, 1978). Eleven soil extract samples based on a 10:1 solution-soil ratio were prepared by adding a small amount of 0.001M $NaNO_3$ (14 mg of NO_3-N L^{-1}) to mixtures of the tested soils and Kelowna extractant prior to shaking. Two extracts were prepared by diluting the sample with additional Kelowna solution, while the remaining three were neither spiked nor diluted (Table 5.2). In the test

Table 5.2. Soil extract samples prepared for second extract test.

No.	Soil name	Soil ID	Amount of solution used (mL) Kelowna	 0.001M $NaNO_3$
1	Mexico	ARS-A	17	3
2	MU Check	Check	20	0
3	MU Check	Check	19	1
4	Proctor	8	15	5
5	Proctor	8	10	10
6	Drummer	26	18	2
7	Drummer	26	11	9
8	Drummer	29	20	0
9	Drummer	29	18	2
10	Drummer	29	16	4
11	Drummer	29	12	8
12	Drummer	29	10	10
13	Ade	1	15	5
14	Leonard	ARS-LoPK	20	0
15	Leonard	ARS-LoPK	25	0
16	Leonard	ARS-LoPK	30	0

sequence, immediately after the electrodes were calibrated with seven different nitrate solutions ranging from 0.014 to 50 mg NO_3-N L^{-1}, three iterations of each sequence were conducted using the three replicates of the sixteen soil extract samples.

Two known nitrate solution samples (1.4 and 14 mg/L) were included in the extract sample sequence to allow compensation of the data for changes in EMF values of the electrodes occurring between replications. This method assumed that calibration slopes for each membrane are constant during the test and EMF offsets should be compensated using EMF readings obtained with the two known samples. For example, in each replicate measurement, if the two standard samples gave an average reading 2 mV below the value obtained from calibration, 2 mV was added to all of the soil extract EMF data.

To improve acquisition of baseline EMF data in the rinse solution, the electrodes were rinsed in three 300-ml beakers of 10^{-6}M $NaNO_3$ Kelowna solution, corresponding to 0.014 mg/L nitrate-N, because it was expected that a solution containing a small amount of nitrate would provide a more stable and repeatable baseline EMF than the blank Kelowna solution used previously.

RESULTS AND DISCUSSION

Extraction of Soil Macronutrients Using Kelowna Solution

The results of nitrate extraction from the seven US Corn Belt soils with Kelowna, DI water, and 1M KCl solutions, with subsequent analysis using the automated ion analyzer, are shown in Figure 5.3. When comparing extraction efficiencies of the Kelowna and DI water with those of 1M KCl solution, almost all the points lie near the 1:1 line and the y-intercepts were close to zero, indicating there was little difference in the amount of nitrate extracted with the two solutions for most of the tested soils.

An exception occurred with the Ade loamy sand, where the NO_3-N amounts extracted with DI water were much lower than those obtained with the 1M KCl and Kelowna solutions (mean values for three replicates, 4.9, 17.5, and 16.9 mg L^{-1} soil with DI, 1M KCl, and Kelowna, respectively). Such decreased extraction of nitrate for the Ade soil with DI water indicates that DI water might be ineffective for extracting nitrate from some soil types. For example, a search of the literature revealed that DI water cannot be used as an extractant in weathered soils high in kaolinite and sesquioxides which have a significant capacity to adsorb nitrate (Black and Waring, 1978). Perhaps a similar problem occurred with this sample. Exclusion of the data for the DI water extraction of the Ade loamy sand resulted in improved regression results (i.e., increase in

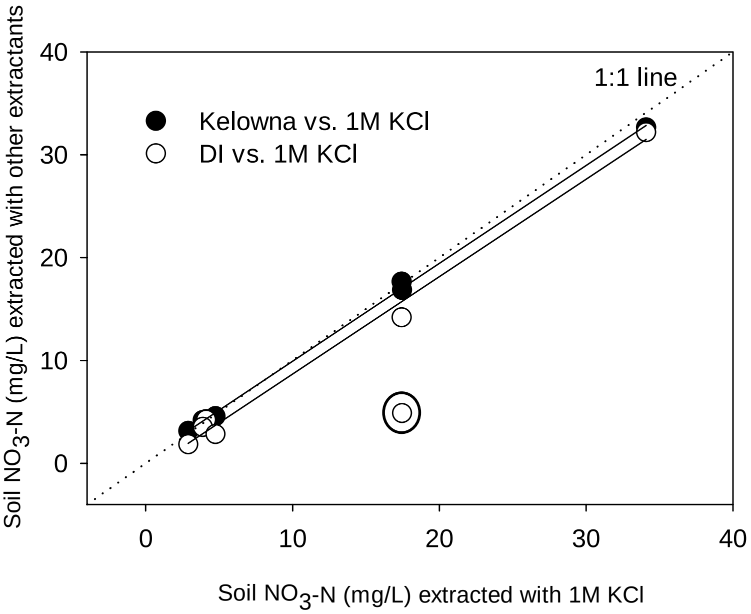


Figure 5.3. Comparison of nitrate-N amounts extracted with different solutions (encircled point was excluded from regression).

regression slope from 0.88 to 0.95 and increase in r^2 from 0.89 to 0.99 when relating nitrate concentrations obtained with DI water as the dependent variable (Y) to those obtained with the 1M KCl solution as the independent variable (X) (Table 5.3). These results are comparable to those reported by Van Lierop (1986).

A highly significant relationship ($r^2 = 0.99$, $p < 0.01$) was found between phosphorus amounts extracted from the tested soils with the Kelowna extractant and Mehlich III solution (Fig 5.4 and Table 5.3). The regression slope of 0.95 was close to 1 ($p < 0.01$) and there was only a small y-intercept of -5.90 in the range of 11.9 to 149.9 mg P L^{-1} soil. The Bray P_1 extractant, on average, extracted about 29 % less P than did the Mehlich III solution from these soils. These results are different from those obtained in previous research (Van Lierop, 1988), which showed that similar amounts of P were extracted from the British Columbia soils by the Kelowna and Bray P_1 solutions, using a dilution ratio of 10:1 and 5-min stirring period. A different pH adjustment of the Bray P_1 solution

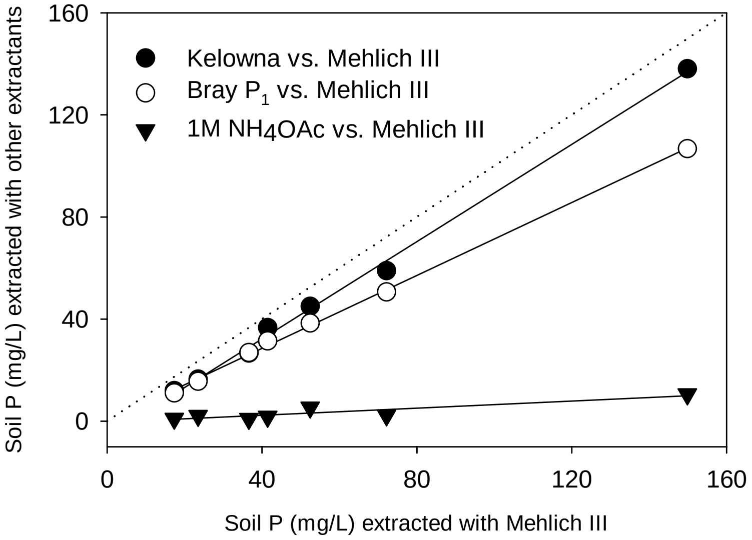


Figure 5.4. Comparison of phosphorus amounts extracted with different solutions.

in our tests (pH 4.2), as compared to the reported tests (pH 2.6) (Van Lierop, 1988) may have produced these differences. As expected, the 1M NH_4OAc, which is a neutral extractant commonly used for extracting cations, such as potassium and magnesium, was not effective in extracting phosphorus from these soils.

The potassium levels extracted from the seven soils with the Kelowna and Bray P_1 extractants were much lower as compared to those obtained with the Mehlich III solution, whereas the 1M NH_4OAc and Mehlich III solutions extracted similar quantities of K (Fig. 5.5). On average, potassium concentrations obtained with the Kelowna and Bray P1 solutions were 42 to 43% less than those extracted with Mehlich III (Table 5.3). These extraction levels were lower than the results reported by Van Lierop and Gough (1989) where the Kelowna solution extracted about 20% less K than did the 1M NH_4OAc when using 60 soils having pH values of 4.1 to 6.9 from various regions of British Columbia, Canada. These differences in the amounts of K extracted with the Kelowna and Mehlich III

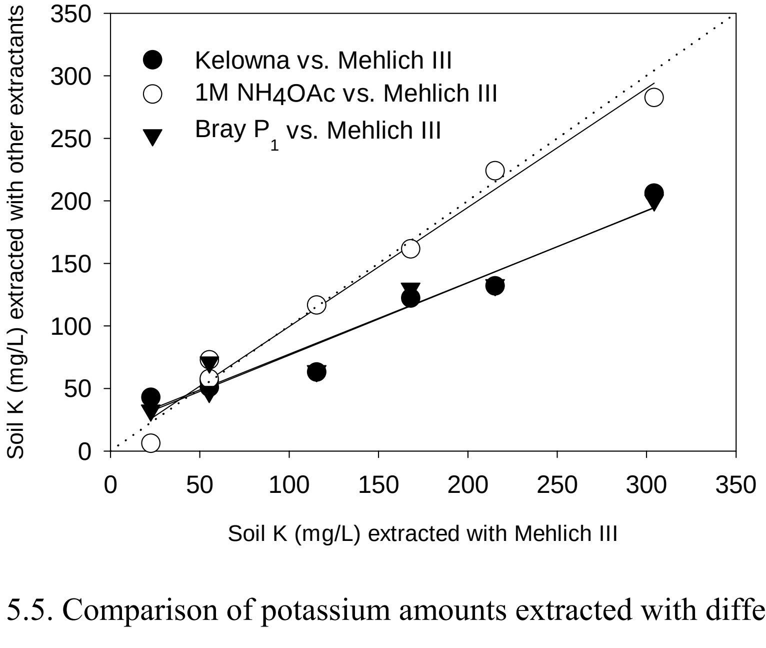


Figure 5.5. Comparison of potassium amounts extracted with different solutions.

or 1M NH_4OAc might be attributed to differences in the soils in the two studies. Nevertheless, it was expected that the Kelowna extractant would be able to extract proportional amounts of K from the tested soils, as illustrated by a strong linear relationship between the results with two solutions ($r^2 = 0.96$, $p < 0.01$).

Table 5.3. Regression results between NPK concentrations extracted with Kelowna and standard soil extractants for seven US Corn Belt soils.

Reference Extractant (X)	Y	Nutrient Extracted	Regression equation	Coefficient of Determination (r^2)
1M KCl	Kelowna	NO_3-N	Y = 0.95X + 0.40	0.99**
	DI	NO_3-N	Y = 0.95X - 0.80[a]	0.99**
Mehlich III	Kelowna	P	Y = 0.95X - 5.90	0.99**
		K	Y = 0.58X + 18.8	0.96**
	Bray P1	P	Y = 0.71X - 0.08	0.99**
		K	Y = 0.57X + 20.3	0.94**
	1M NH_4OAc	P	Y = 0.07X - 0.45	0.82**
		K	Y = 0.95X + 4.34	0.98**

** Significant at $p < 0.01$.

[a] The Ade soil was excluded from the regression.

Analysis of NO_3-N and K in Soil Extracts Using Ion-Selective Electrodes

The EMF responses of the nitrate and potassium ion-selective electrodes measured in a series of N and K calibration solutions are shown in Figure 5.6. Since the nitrate ion-selective electrodes showed unstable EMF readings in the first replication, those data were excluded from the regression and graph.

Non-linear logarithmic regression analysis based on the Nikolskii-Eisenman equation (Ammann, 1986) was utilized to develop the calibration equations relating membrane response and nutrient concentration. All of the calibration equations obtained using SIGMA Plot 9.0 (Systat Software Inc., Richmond, Calif.) provided coefficients of determination (r^2) > 0.98 and standard errors of calibration (SEC) of < 2.05 mV.

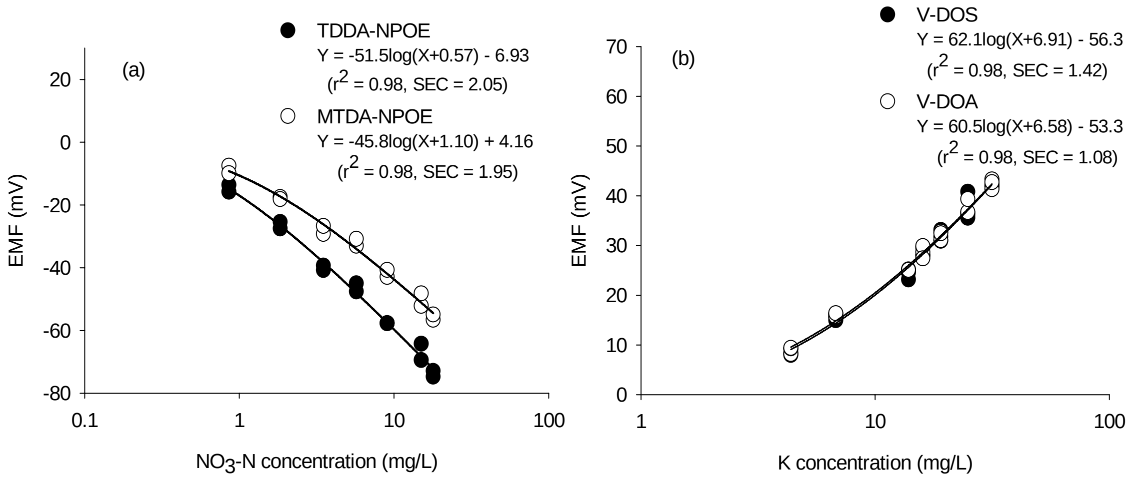


Figure 5.6. Calibration curves for nitrate (a) and potassium (b) ISEs relating nitrate-N concentration (X) and electric potential (Y).

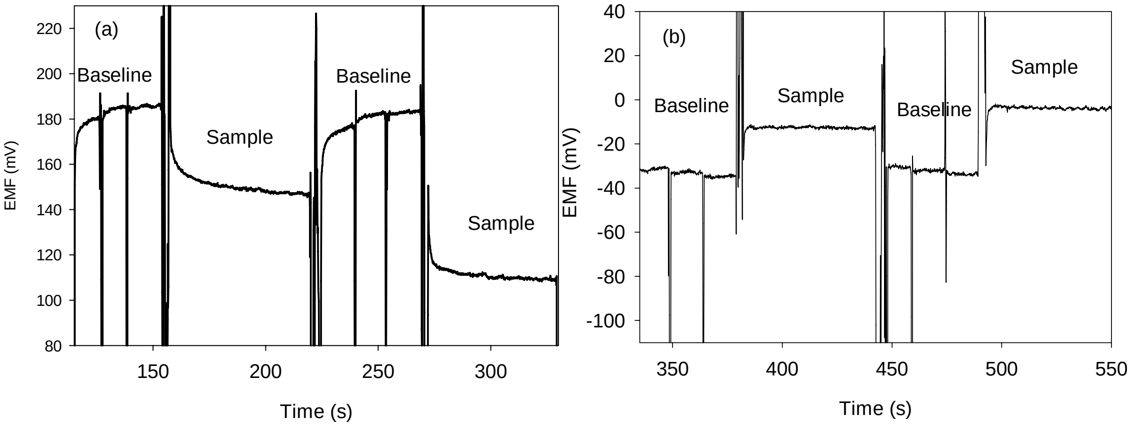


Figure 5.7. Response behavior of (a) TDDA-NPOE nitrate ISE and (b) V-DOS potassium ISE (b) in rinse solution and soil extract samples.

Figures 5.7 shows the response profiles of (a) the TDDA-NPOE nitrate electrode, and (b) the valinomycin-DOS potassium electrode. For each measurement, the electrodes were sequentially inserted into three rinse solutions contained in three 250 mL beakers followed by placement in a soil extract. A difference in dynamic response was observed between the nitrate and potassium electrodes. Immediately after the electrodes were immersed in the soil extracts, the nitrate electrode displayed a rather slow, somewhat exponential response (Fig. 5.7a), whereas the changes in potential of the potassium membranes occurred rapidly and approached an equilibrium level within 1 to 2 s (Fig. 5.7b). Such a difference in response shape is due to different time constants of the nitrate and potassium electrodes. Previous research (Lindner et al., 1978) reported that the transient function of an ion-selective electrode following an activity step can be characterized by the mathematical function describing the potential-time behavior using fitted parameters, such as time constants. In the dip-type measurement using three 15-s rinses, as illustrated in Figure 5.7, it appeared that both response and recovery times of the nitrate electrode were longer than those of the potassium electrode. Thus, the potassium electrodes appear to be better suited than the nitrate electrodes for real-time applications requiring rapid measurement of low ion concentrations.

Figure 5.8 shows the regression results between Kelowna extractable N and K values determined by ion-selective electrodes (Y) and standard instruments (X), i.e., the automated ion and ICP analyzers for N and K measurements, respectively. Solution NO_3-N concentrations determined by the two nitrate ion-selective electrodes and the automated ion analyzer ranged from 1.32 to 27.9 mg L^{-1} solution and 1.96 to 19.1 mg L^{-1} solution, respectively. Highly significant relationships ($r^2 > 0.90$, $p < 0.01$) were observed between the two methods, yielding slopes of 1.05 and 1.24 for TDDA and MTDA nitrate electrodes, respectively. However, as shown in figure 5.8 and a histogram (Fig. 5.9a) showing sample distribution in terms of nitrate-N concentrations, the measured nitrate samples were not normally distributed, with three of the twenty-four samples having concentrations higher than 15 mg L^{-1} solution whereas the remainder had concentrations lower than 5 mg L^{-1} solution.

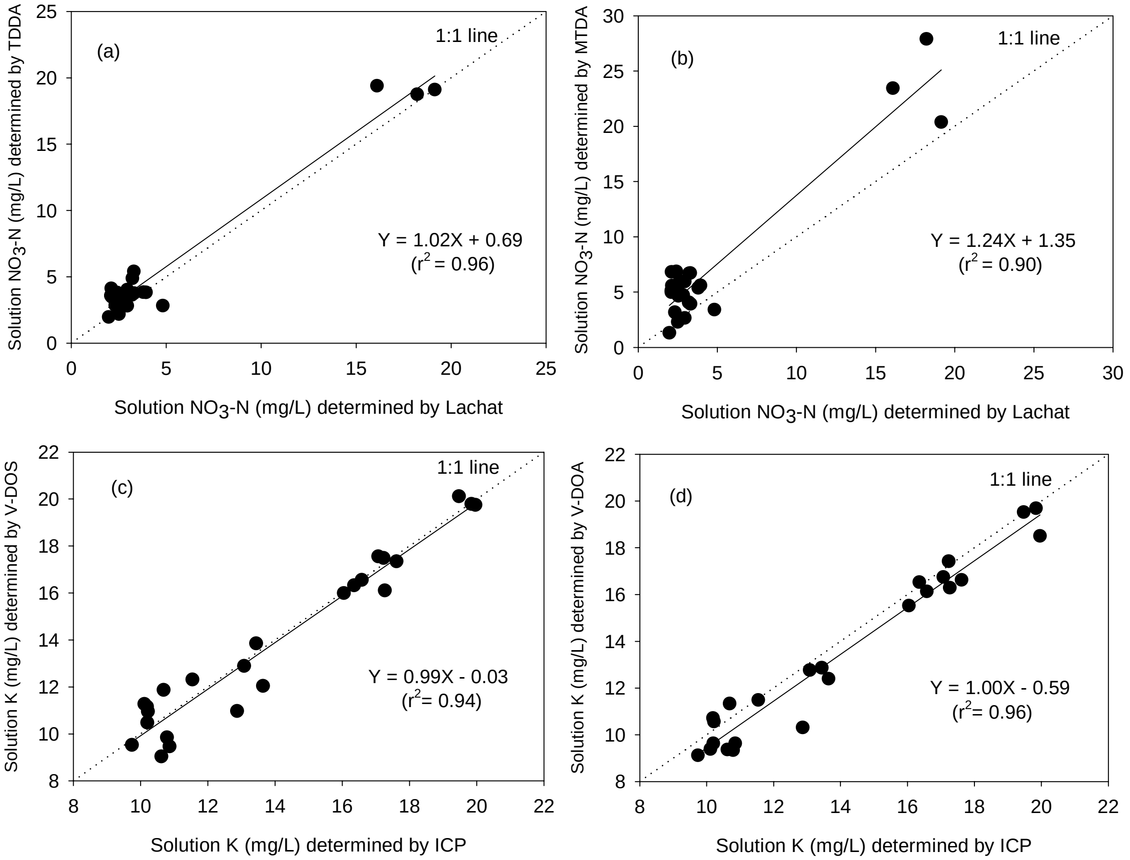


Figure 5.8. Relationships between soil extract nitrate-N and potassium determined by ion-selective electrodes and standard instruments: (a) TDDA-based N ISE vs. Lachat , (b) MTDA-based N ISE vs. Lachat, (c) V-DOS based K ISE vs. ICP, and (d) V-DOA based K ISE vs. ICP.

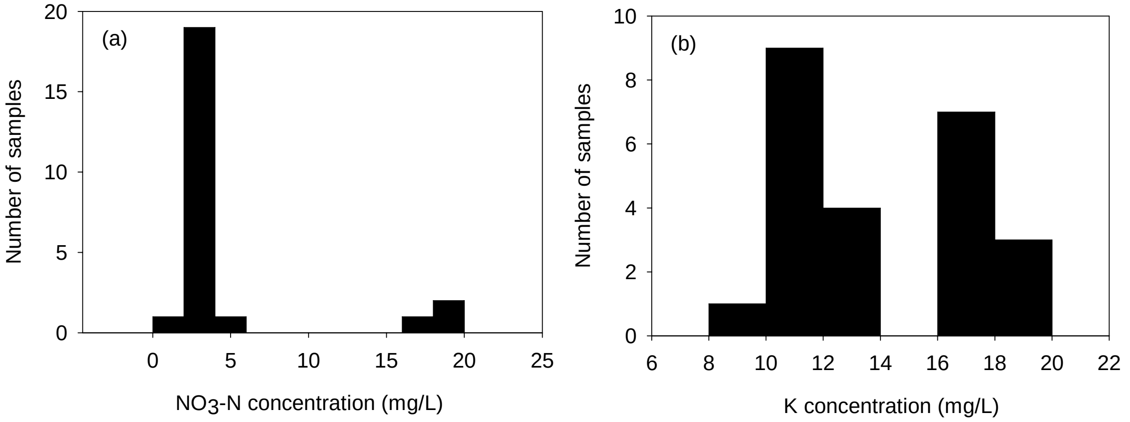


Figure 5.9. Histograms of sample distributions for (a) NO_3-N and (b) K concentrations.

This distribution biased the regression results, with the three samples with the higher concentrations being overly influential. Without these three points, a low coefficient of determination ($r^2 = 0.21$, $p < 0.05$) was found between the two methods. Therefore, additional samples with nitrate-N concentration between 5 and 15 mg/L were needed to more completely cover the range of nitrate concentrations and better define the relationship between nitrate ISE results and standard methods.

In the comparison of potassium values determined by potassium ISEs and the ICP analyzer (Figure 5.8), the potassium levels in solution measured with the valinomycin-DOS-based and valinomycin-DOA-based potassium ISEs were significantly related with those obtained the ICP analyzer ($r^2 > 0.94$, $p < 0.01$), showing almost 1:1 relationships and no significant y-intercept over the concentration range of 9.74 to 20.0 mg K L^{-1} solution (Fig. 5.9b). The DOS and DOA-based potassium ISEs predicted similar levels of potassium in the tested soil extract samples.

Before the 2nd nitrate-N measurement of soil extracts with spiked samples was performed, the TDDA-based and MTDA-based nitrate electrodes were calibrated with seven calibration solutions containing 0.014, 0.14, 0.5, 1.4, 5, 14, and 50 mg NO_3-N L^{-1}. Calibration curves for the nitrate ion-selective electrodes (Fig. 5.10) show that non-linear logarithmic regression in the form of the Nikolskii-Eisenman equation fit the data well with high coefficients of determination ($r^2 = 0.99$). As observed in previous sensitivity tests of the two nitrate membranes in Kelowna solution (Chapter 4), the TDDA-based ISE showed higher sensitivity to nitrate than did the MTDA-based ISE.

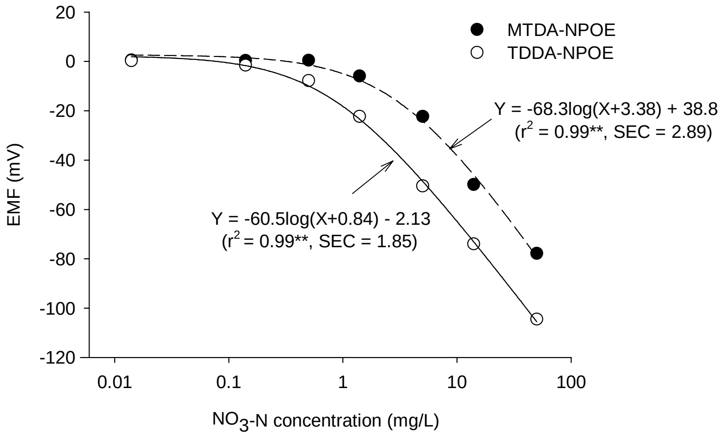


Figure 5.10. Calibration curves for TDDA and MTDA-based ISEs relating nitrate-N concentration (X) and electric potential (Y).

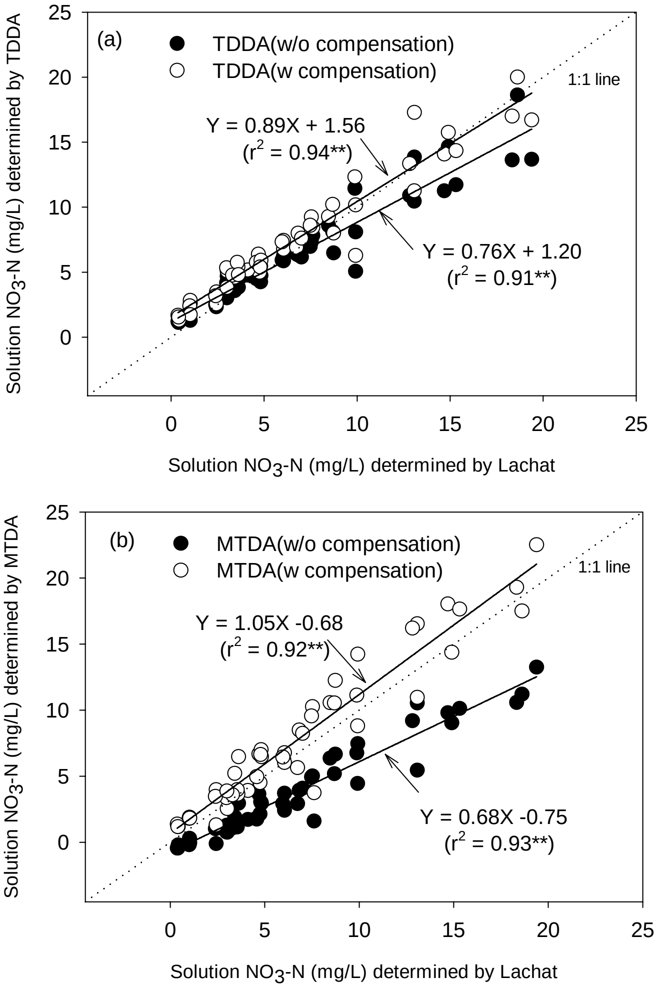


Figure 5.11. Relationships between soil extract NO_3-N determined by membranes ((a) TDDA and (b) MTDDA) and Lachat analyzer with and without compensation.

The regression results relating nitrate-N determined by the ISEs (Y) and Lachat analyzer (X) for the sixteen soil extract samples showed that the nitrate-N values obtained with the TDDA membrane (Fig 5.11a) and the MTDA membrane (Fig 5.11b) were highly related to those determined by the Lachat analyzer ($r^2 > 0.91$, $p < 0.01$). The regression slopes were increased when using the EMF compensation method: i.e., from 0.76 to 0.89 for the TDDA-based ISE and from 0.68 to 1.05 for the MTDA-based ISE. Therefore, the TDDA and MTDA-based ISEs provide compensated NO_3-N values within 12% of those for the Lachat analyzer.

As described in the regression results above, the use of the EMF compensation method, which inserted two known samples in the test sequence, improved agreement between the ISE and Lachat methods. These results indicate that the responses of the nitrate electrodes might not be repeatable during the test due to potential drifts and hysteresis. The problem might be related to a graphical observation (fig. 5.7) that the times of response and recovery of the nitrate electrodes are relatively slow. The response and recovery times might be strongly affected by several experimental factors, including the incomplete removal of previous samples, variations in solution stirring speed, and inconsistent collection of EMF data due to manually operated testing conditions. Therefore, it was concluded that an automatic measurement system, which can maintain good quality control, would be needed for improved results without the use of EMF compensation.

CONCLUSIONS

This chapter reports on the ability of the Kelowna extractant to extract macronutrients (N, P, and K) from US Corn Belt soils and whether previously developed PVC-based nitrate and potassium ion-selective electrodes could be applied to the determination of nitrate and potassium contents of Kelowna soil extracts.

The extraction efficiencies of nitrate-N and phosphorus using the Kelowna solution with seven US Corn Belt soils were comparable to efficiencies obtained with 1M KCl and Mehlich III solutions, respectively. However, the potassium amounts extracted with the Kelowna extractant were, on average, 42 % less than those obtained with the Mehlich III solution. Nevertheless, it was expected that the Kelowna solution could extract proportional amounts of potassium ion due to a strong linear relationship ($r^2 = 0.96^{**}$).

The use of PVC-based nitrate and potassium ion-selective electrodes was feasible for measuring nitrate-N and potassium ions in Kelowna-based soil extracts due to almost 1:1 relationships and high coefficients of determination between the levels of nitrate-N and potassium obtained with the ion-selective electrodes and standard instruments. However, since the nitrate ion-selective electrodes showed potential drifts that resulted in relatively poor reproducibility over a period of time, the use of an EMF compensation method, which inserts two known samples in the test sequence, was required to obtain acceptable results. This problem might be related to the fact that the times of response and recovery of the nitrate electrodes were slower than those of the potassium electrodes. Therefore, the nitrate electrodes might be strongly influenced by several experimental factors caused by manual operation of the tests, including incomplete removal of previous samples and a variable solution stirring speed. From the experiments, it was concluded that an automated measurement system was needed to obtain more accurate measurements of nitrate-N.

CHAPTER 6

EVALUATION OF PHOSPHATE ION-SELECTIVE MEMBRANES AND COBALT-BASED ELECTRODES

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. Ion-selective electrodes are a promising approach because they have rapid response, directly measure the analyte, and are small and portable. Our goal was to investigate whether two types of phosphate ion-selective electrodes using organotin compound-based PVC membranes, and one using cobalt rods could be used in conjunction with Kelowna soil extractant to determine phosphorus over the typical range of soil concentrations. Organotin compound-based PVC membranes containing bis(p-chlorobenzyl)tin dichloride as an ionophore exhibited sensitive responses to HPO_4^{2-} over a range of 10^{-4} to 10^{-1} mol/L in Tris buffer at pH 7. The membranes were nearly insensitive to phosphate when using Kelowna soil extractant as the base solution, perhaps because of the presence of a high concentration of fluoride (0.015 mol/L) in the Kelowna solution. In addition, the life of the membranes was less than 14 days. Another tin-compound-based PVC membrane containing tributyltin chloride as an ionophore also provided unsatisfactory results, showing much less sensitivity to $H_2PO_4^-$ than previously reported. The cobalt rod-based electrodes exhibited sensitive responses to $H_2PO_4^-$ over a range of 10^{-5} to 10^{-1} mol/L total phosphate concentration with a detection limit of 10^{-5} mol/L in the Kelowna solution. This detection range would encompass the typical range

of soil phosphorus concentrations measured in agricultural fields. The selectivity of the cobalt electrodes was satisfactory in measuring phosphates in the presence of each of six interfering ions, i.e., HCO_3^-, Cl^-, Br^-, NO_3^-, Ac^-, and F^-, being 47 to 1072 times more selective to phosphate than to the tested ions. Although the cobalt electrodes with different purities (99.95% and 99.99%) showed similar sensitivity and selectivity performances, the lower-purity cobalt rod is a better choice because sensors of that material provided more reproducible responses than did electrodes fabricated using the higher-purity cobalt rod.

INTRODUCTION

Phosphates have been extensively used in agricultural fertilizers and detergents. The measurement of phosphorus concentration levels is important in many areas of science and technology, such as environmental monitoring, clinical chemistry, and biomedical research (Glazier and Arnold, 1988).

The plant-available phosphorus in soil, forming as monobasic ($H_2PO_4^-$) or dibasic (HPO_4^{2-}) phosphate, is one of the major essential nutrients for crop growth. However, excessive use of commercial NPK fertilizers has been cited as a source of contamination of surface and groundwater (Staver and Brinsfield, 1990). Furthermore, high levels of phosphorus in the soil have been reported to leach into water ecosystems and create an imbalance that results in excessive growth of algae in lakes and rivers (Mallarino, 1998; Vadas et al., 2004).

There is high spatial variability of soil phosphorus within individual agricultural fields (Page et al., 2005). Monitoring of phosphorus in soil, using real-time on-site methods, can allow accurate estimation of required rates for fertilizer application within the field, thereby increasing the efficiency of variable-rate application of fertilizers and reducing the potential for environmental pollution in water and soil.

Various analytical methods have been routinely used for phosphorus quantification in soil testing laboratories. These techniques, based mostly on colorimetric or atomic emission spectroscopy, provide fairly accurate results due to their good linear sensitivity and relatively low interference from other ions (Watson and Isaac, 1990; Brown, 1998). However, such analytical methods cannot be adapted for field use, because not only are these instruments quite expensive, but they also require complex sample pre-treatment, which increases the time and cost of sample analysis and thereby limits the number of samples analyzed in the field (Artigas et al., 2001).

The need for fast, on-site monitoring methods allowing the analysis of a large number of samples has led to the application of ion-selective electrode (ISE) technology to phosphate measurement. This technology offers several advantages over current analytical methods (spectroscopic methods), e.g., simple methodology, direct measurement of analyte, sensitivity over a wide concentration range, low cost, and portability (Carey and Riggan, 1994). However, for several reasons, the design of a sensing material (i.e., ionophore) for selective recognition of phosphate is especially challenging. Due to the very high hydration energy of phosphate, ion selective membranes have a very poor selectivity for phosphate (Liu et al., 1997; Buhlmann et al., 1998; Fibbioli et al., 2000). According to the characterization by the Hofmeister series ($ClO_4^- > SCN^- > I^- > NO_3^- > Br^- > Cl^- > HCO_3^- > SO_4^{2-} > HPO_4^{2-}$), phosphate, being at the end of the series, shows the lowest selectivity response toward the anions (Ammann, 1986; Liu et al., 1997). 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.

In the late 1980s and early 1990s, 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). Their ionophores, such as tin compounds and cyclic polyamine, provided good selectivity and favorable sensitivity with a detection limit of 10^{-5} mol/L dibasic phosphate in a solution at pH 7.2. More recently, new ionophores have been reported to enhance selectivity and durability (Tsagatakis et al., 1994; Liu et al., 1997; Fibbioli et al., 2000; Tsagkatakis et al., 2001; Wroblewski et al., 2001). These ionophores were synthesized in research laboratories, whereas Sasaki et al. (2004) used a commercially available chemical as an ionophore. Their electrode membrane containing tributyltin chloride as the ionophore and 25 mol% NaTFPB exhibited high selectivity for $H_2PO_4^-$ with a slope of -60 mV/decade.

Xiao et al. (1995) introduced cobalt metal as a phosphate ion-selective electrode material. They reported that oxidized cobalt metal electrodes showed potentiometric sensitivity to phosphate in the concentration range of 10^{-5} to 10^{-2} M in 0.025 M potassium hydrogen phthalate (KHP) solution at pH 4.0. The detailed response mechanism of the cobalt electrodes toward phosphate was examined by Meruva and Meyerhoff (1996). Cobalt electrodes have been applied to the determination of phosphate levels in waste water, fertilizers, hydroponic nutrient solution, and soil extract samples (Chen et al., 1997; Chen et al., 1998; De Marco et al., 1998; Engblom, 1999; De Marco and Phan, 2003). In particular, Engblom (1999) studied the applicability of a cobalt rod-based electrode to the measurement of phosphate in soil extracts of ammonium lactate-acetic acid (AL) solution commonly used in Sweden.

OBJECTIVES

The overall objective of this study was to investigate the applicability of tin-compound-based PVC membranes and cobalt rod electrodes as phosphate ion-selective electrodes for the determination of phosphorus content in soil extracts, and to evaluate the sensitivity of previously developed nitrate and potassium ion-selective electrodes (chapter 4) to phosphate. This chapter reports on the response characteristics of three different phosphate sensors, two tin-compound-based PVC membranes (Glazier and Arnold, 1988; 1991; Sasaki et al., 2004) and a cobalt-based metal electrode (Xiao et al., 1995), to monobasic or dibasic phosphates.

Specific objectives were to:

- Characterize the capabilities of tin-compound-based PVC membranes and cobalt-based metal electrodes for measurement of soil phosphorus in terms of sensitivity and selectivity.
- Investigate the effects of base solution, membrane age, and sensing material purity on sensitivity and selectivity responses of phosphate ion-selective electrodes.
- Select an optimum sensor for phosphorus determination over the typical range of soil phosphorus concentrations.

MATERIALS AND METHODS

Reagents and Solutions

Based on previous studies (Glazier and Arnold, 1988; 1991; Sasaki et al., 2004), two different phosphate ion-selective membranes were prepared using two tin compounds, bis(p-chlorobenzyl)tin dichloride and tributyltin chloride as ionophores. The bis(p-chlorobenzyl)tin dichloride was synthesized at the University of Missouri Chemistry Department according to the procedures outlined in Glazier (1988), whereas the tributyltin chloride was commercially available from Sigma-Aldrich Corp. (St. Louis, Mo.).

Based on results obtained from previous tests (chapter 4), nitrate and potassium ion-selective membranes were prepared using tetradodecylammonium nitrate (TDDA, Sigma-Aldrich Corp., St. Louis, Mo.) and valinomycin (potassium ionophore I, Sigma-Aldrich Corp., St. Louis, Mo.) as ionophores for N and K sensing, respectively.

Dibutyl sebacate, nitrophenyl octyl ether (NPOE), and bis(2-ethylhexyl) sebacate (DOS) as plasticizers, N, N-dimethylformamide as a solvent for organic compounds, and sodium tetrakis [3,5-bis(trifluoromethyl)-phenyl]borate (NaTFPB) and potassium tetrakis (4-chlorophenyl) borate (KTpClPB) used as anionic and cationic additives, respectively, were purchased from Sigma-Aldrich Corp. Two 5-mm diameter cobalt rods (99.95 % and 99.99 % purities) were also obtained from Sigma-Aldrich Corp.

All base solutions 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). Tris buffer solution (pH 7) 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 KHP buffer solution (pH 4) was prepared using 0.025 mol/L potassium acid phthalate (KHP, Sigma-Aldrich). The Kelowna extractant solution contained 0.25 mol/L CH_3COOH (acetic acid, Sigma-Aldrich) and 0.015 mol/L NH_4F (ammonium fluoride, Sigma-Aldrich). All other chemicals used 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

A phosphate membrane-casting solution containing bis(p-chlorobenzyl)tin dichloride was prepared with a mixture of 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, as reported in previous studies (Glazier and Arnold, 1991). The phosphate membranes were formed by dipping the free ends of Hitachi ISE electrode bodies in the casting solution three times. Membranes were allowed to dry overnight after the first two dips. Following the final dip, membranes were again allowed to dry and then were stored in a blank buffer solution. 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 (1 mm in diameter) into the top.

According to the methods described in a previous study (Sasaki et al., 2004), the tributyltin-based PVC membranes were prepared from the mixture of 1.5 mg (1% wt) of tributyltin chloride, 99 mg (66% wt) of NPOE, 49.5 mg (33% wt) of PVC, and 1.0 mg

(25% mol) of NaTFPB in 1.5 mL of THF. The cocktail was poured into a 23-mm glass ring resting on a hot polished glass set at 40 °C, and allowed to evaporate. Three disks with a diameter of 2.5 mm were cut from each membrane. The membrane disks were attached to the ends of the ISE electrode bodies using THF solvent. The tributyltin-based electrode was filled with 0.1M NaCl.

The cobalt-based metal electrodes with 99.95% and 99.99% purities (5 mm in diameter) were prepared according to the following procedures. The cobalt rods were cut into 6-mm-long segments and soldered to copper wires with a diameter of 1 mm. A rubber O-ring (6 mm outer diameter, 1 mm thickness) was inserted into a hole (6 mm diameter and 7 mm depth) drilled in a Hitachi ISE body. The cobalt rod was then pressed into the hole of the electrode. To make sure that there was no electric contact between the brass shield of the ISE body and the rod and to provide a liquid-tight seal, the gap between the electrode body and the rod was filled with silicone and allowed to dry overnight.

Nitrate and potassium ion-selective membranes based on TDDA and valinomycin ionophores, respectively, were prepared as reported in previous studies (chapter 4). 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 of the reference electrode.

Electrode Conditioning and Pretreatment

As described in previous studies (Glazier and Arnold, 1991), the two PVC-based phosphate ISEs (bis(p-chlorobenzyl)tin dichloride and tributyltin chloride) were conditioned overnight in blank buffer solutions (Tris at pH 7 and KHP at pH 4, respectively). Prior to testing, the electrodes were immersed in the 0.01M phosphate solutions three times for about 10 minutes each so that steady electrical potentials could be obtained in the presence of phosphate.

In accordance with the methods prescribed by Xiao et al. (1995), the pretreatment of each cobalt electrode was done using the following steps. Prior to testing, the surface of the cobalt electrode was polished using first 400 and then 1,500 grit emery sheets. The cobalt electrode was then immersed in DI water for about 20 min. After a steady-state potential was obtained, the electrode was immersed in a blank base solution containing no phosphate (potassium hydrogen phthalate (KHP) or Kelowna) for about 20 min. After a new steady state potential was established as an indication of completion of the pretreatment process, the electrode was ready for use.

Equipment

Potentials (EMFs) of 15 channels were measured relative to a double-junction reference electrode using an automated test stand (Appendix A). EMF values for the electrodes were measured and recorded at 15 s and 60 s after each of test solutions was automatically introduced into the pan. At each of the two data collection times, three measurements, each consisting of the mean of a 0.1-s burst of 600 Hz data, were obtained on a 3-s interval and averaged. Each solution was stirred by rotation of the sample holder at 37 rpm during data collection. Three rinses were used at each solution exchange to completely remove any residues of the previous solution. Test and rinse solutions were expelled by increasing the rotational speed of the sample holder to 290 rpm. Details of the test stand and control program are described in Appendices A and B.

Test Classification

Since the phosphate species in solution is a function of pH (Lindsay, 1979), the pH levels of tested samples during each test were kept constant so that the pH effects on sensing performance could be removed (Fig. 6.1). According to information reported in previous studies (Glazier and Arnold, 1991; Xiao et al., 1995; Sasaki et al., 2004), the PVC-based membranes containing bis(p-chlorobenzyl)tin dichloride respond to dibasic phosphate (HPO_4^{2-}) whereas the tributyltin-based PVC membranes and cobalt-based electrodes are sensitive to monobasic phosphate ($H_2PO_4^-$). Thus, two separate tests (i.e., dibasic and monobasic tests) were conducted using two different sets of the phosphate ISEs and a set of nitrate and potassium ISEs.

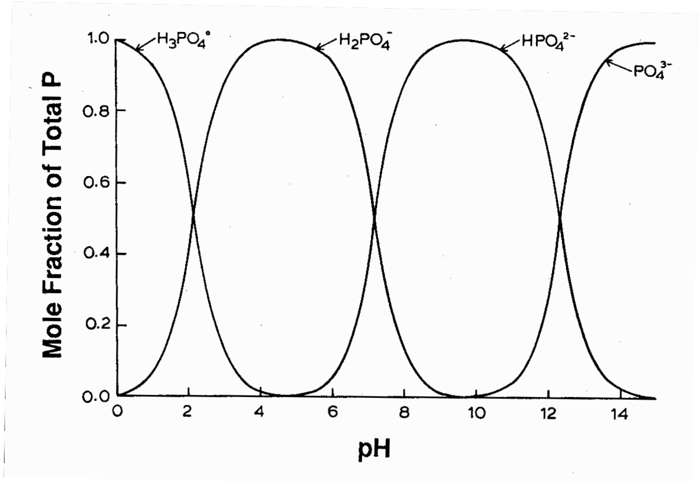


Figure 6.1. Distribution of orthophosphate ions depending on pH level (Lindsay, 1979).

Dibasic Phosphate Sensitivity Tests

For dibasic phosphate sensing, a set of phosphate ISEs based on bis(p-chlorobenzyl)tin dichloride was tested. Membrane ages prepared on four different dates were included in the test - six electrodes of age 4 days, and one each of 14, 20, and 33 days - in order to investigate 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. Nine phosphate ISEs, two potassium ISEs, and two nitrate ISEs were included in the test set.

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 Kelowna solution). To remove any pH effect, the pH levels of the tested solutions were adjusted to be constant across a range of tested phosphate concentrations: i.e., Tris buffer pH = 7.0 and Kelowna solution pH = 8.5. The pH adjustment was monitored with a combination pH electrode (Model 81-72, Orion, Cambridge, Mass.) and a pH meter (Model SA-720, Orion, Cambridge, Mass.) while adding either 0.05M H_2SO_4 or 0.1M NH_4OH.

Duplicating the pH level ($pH = 7.00 \pm 0.01$) for the Tris buffer solutions 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 (Fig. 6.1). When using the Kelowna extractant as the base solution, the pH of the standard solutions (originally, pH =3.2) was readjusted to 8.5 ± 0.01, where the predominant form is dibasic phosphate (Fig. 6.1). 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. 6.2).

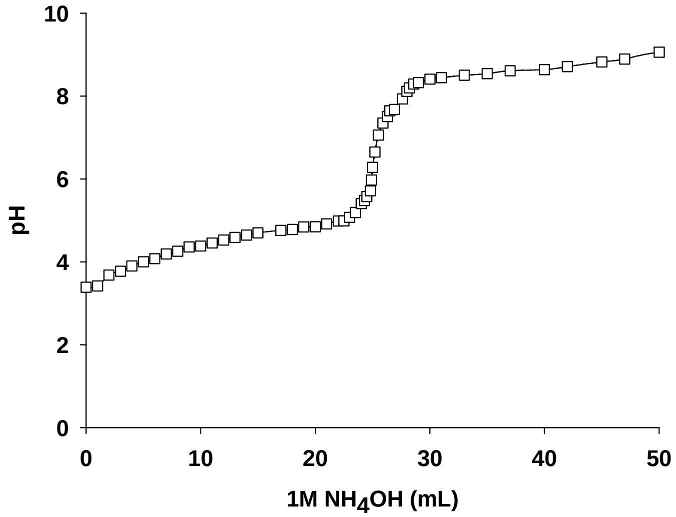


Figure 6.2. Titration curve for 90 mL of Kelowna solution.

Monobasic Phosphate Sensitivity and Selectivity Tests

Two different types of phosphate ISEs (i.e., three tributyltin-based PVC membranes and six cobalt-based electrodes) were tested along with TDDA-based nitrate and valinomycin-based potassium ISEs using the KHP buffer and Kelowna solutions. Two sets of three cobalt-based electrodes with purities of 99.99% and 99.95%, respectively, were tested to investigate how cobalt purity affects sensing performance in terms of sensitivity and selectivity. Three high purity cobalt ISEs (99.99%), three lower purity cobalt ISEs (99.95%), three tributyltin-based phosphorus ISEs, three nitrate ISEs and three potassium ISEs were included in the test set.

The sensitivity responses of the electrodes were characterized by measuring the EMFs of each ISE in seven standard solutions of monobasic potassium phosphate (KH_2PO_4) containing from 10^{-7} 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 the two different base solutions (KHP buffer and Kelowna solutions).

As in previous studies on cobalt phosphate electrodes by Xiao et al. (1995), 0.025M potassium hydrogen phthalate (KHP) solution at pH 4 was used as a base solution to determine if the responses of the cobalt electrodes to phosphate would be comparable to results previously reported. The seven standard solutions prepared using the Kelowna extractant were titrated with 1M NH_4OH to pH 4.00 ± 0.01, where the predominant form is monobasic phosphate (Fig. 6.1).

Using each of the two different base solutions, the selectivity of each phosphate electrode for phosphate over six interference ions was investigated in the following order: bicarbonate ($KHCO_3$), chloride (KCl), bromide (KBr), nitrate (KNO_3), acetate (CH_3COOK), and fluoride (KF).

The selectivity coefficient (K_{ij}) of the phosphate electrode for an interfering ion (j) relative to phosphate (i) was calculated based on the separate solution method (SSM) (IUPAC, 1994) by using EMF values obtained with pure single electrolyte solutions of the primary ion (0.01M) and interference ion (0.1 M) in the following way:

$$K_{i,j} = 10^{(E_j - E_i)/S} \frac{a_i}{a_j^{Z_i/Z_j}} \tag{6.1}$$

where:

E_i = the electrode potential measured with a solution of 0.01M phosphate ion

E_j = the electrode potential measured with a solution of 0.1M interfering ion

a_i = activity of 0.01M phosphate ion

a_j = activity of 0.1M interfering ion

S = Nernstian slope obtained with 0.01M and 0.1M phosphate solutions.

As in a previous study (Birrell and Hummel, 2000), the EMFs in 0.1M and 0.01M phosphate solutions were measured to determine Nernstian slopes (S) for each phosphate electrode. The effect of each interfering ion (i.e., E_j - E_i) was measured based on the EMF difference between the responses of the 0.01M phosphate ion and the 0.1M interfering ion. Thus, in the test sequence, initially the electrode response in the 0.01M KH_2PO_4 solution was recorded, followed by the response in the 0.1M KH_2PO_4 to calculate the Nerstian slope of each electrode. Then, the response in the 0.01M KH_2PO_4 was re-measured to calculate E_i, followed by the response in the 0.1M interfering ion being tested to calculate E_j. The latter two steps were repeated until the responses of the electrodes to all six interference solutions were recorded. The initial two steps were then repeated to check for any significant change in the phosphate response of the electrodes during each replication.

Calculation of Phosphate Species Activities

To calculate sensitivity slopes for monobasic or dibasic phosphate-selective electrodes in the tested concentration ranges, the 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 equilibrium with the hydrogen ion activity (Lindsay, 1979; Carey and Riggan, 1994).

The total orthophosphate concentration can be calculated as:

$$[PO_4]_{total} = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] \tag{6.2}$$

where:

$[PO_4]_{\text{total}}$ = total orthophosphate concentration

$[H_3PO_4]$ = concentration of phosphoric acid

$[H_2PO_4^-]$ = concentration of monobasic (dihydrogen) phosphate

$[HPO_4^{2-}]$ = concentration of dibasic (hydrogen) phosphate

$[PO_4^{3-}]$ = concentration of phosphate.

The equilibrium constant between monobasic and dibasic phosphates in the pH range of 5 to 10 can be represented as:

$$\log\frac{[H_2PO_4^-]}{[HPO_4^{2-}]} = 7.20 - pH \tag{6.3}$$

The equilibrium constants in the pH range of 0 to 5 and 10 to 14, respectively, can be described as:

$$\log\frac{[H_3PO_4]}{[H_2PO_4^-]} = 2.15 - pH \tag{6.4}$$

$$\log\frac{[HPO_4^{2-}]}{[PO_4^{3-}]} = 12.35 - pH \tag{6.5}$$

The ionic strength was calculated using the concentrations estimated by the equations for equilibrium constants described above, and activity coefficients for dibasic or monobasic phosphate species were then determined using the Debye-Hückel formula (Lindsay, 1979; Eggins, 2002).

RESULTS AND DISCUSSION

Dibasic Phosphate Sensitivity Tests

Response Characteristics to Dibasic Phosphate

The response (EMF) curves of the six newest dibasic-selective phosphate ISEs based on bis(p-chlorobenzyl)tin dichloride (membrane age - 4 days at the time of testing), and the 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 solution (pH = 8.5) are shown in Figure 6.3.

In each of the three replicates of the test sequence, successively more concentrated test solutions were presented to the ISEs. The bis(p-chlorobenzyl)tin dichloride-based phosphate membranes in the Tris buffer solution (Fig. 6.3a) were sensitive to different phosphate concentrations and the responses were repeatable during three replicate measurements. Similarly, the potassium ISEs responded to the potassium in the K_2HPO_4 with consistent sensitivity (Fig. 6.3b). The nitrate ISEs had a slight sensitivity to the potassium phosphate (Fig. 6.3b) with a decrease in EMF (<15 mV) at 10^{-1}mol/L concentration.

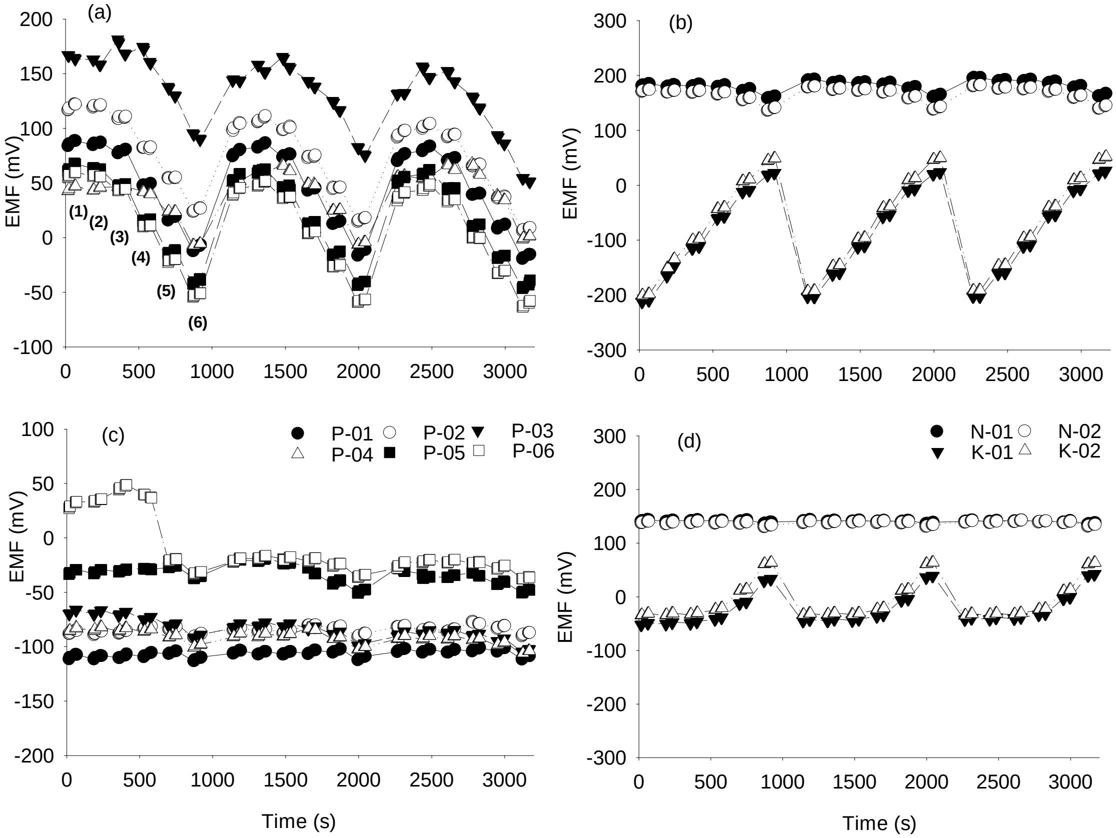


Figure 6.3. Response test profiles for different K_2HPO_4 concentrations: (a) the response of phosphate membrane with bis(p-chlorobenzyl)tin dichloride in Tris buffer, (b) the responses of TDDA-NPOE-based nitrate and V-DOS-based potassium ion-selective membranes in Tris buffer, (c) the phosphate membrane response in Kelowna extractant, and (d) nitrate and potassium membrane response in Kelowna extractant. 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.

Apparently, the use of Kelowna solution influenced the responses of all ISEs. In particular, as shown in Figure 6.3c, 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 total phosphate concentration. Similarly, at low potassium concentrations below 10^{-3} mol/L, there was little change in response for the potassium membranes (Fig. 6.3d). However, the potassium ISEs exhibited a linear response over a range of 10^{-3} to 10^{-1} mol/L potassium concentrations.

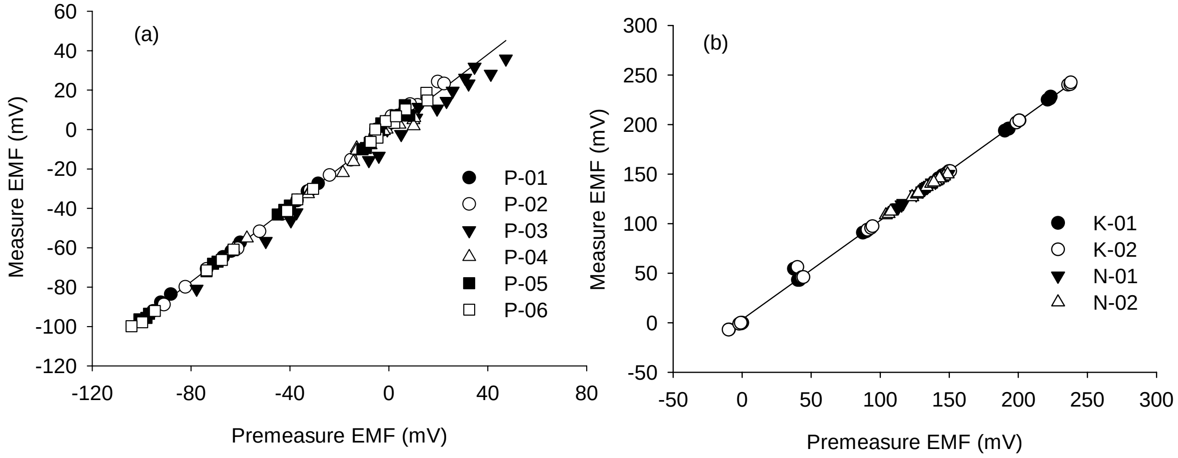


Figure 6.4. Relationship between EMF values measured 15s and 60s after the injection of test solutions for (a) dibasic phosphate and (b) nitrate and potassium membranes.

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 Figure 6.4, the measure EMF (Y) values were highly correlated with the premeasure EMFs (X), with an almost 1:1 relationship between the two values: Y= 0.96X - 0.41 (r^2=0.99**) for dibasic phosphate (Fig. 6.4a) and Y= 0.99X + 3.39 (r^2=0.99**) for nitrate and potassium ISEs (Fig. 6.4b). Therefore, it was evident that the ISEs could reach an equilibrium response within 15 s after immersion in a test solution.

Variability of response between membranes

The variability of response among the six tested dibasic phosphate ISEs was examined by comparing the standard deviation in EMF measured with each ISE for the three replicate measurements and the average sensitivity of each ISE (Fig. 6.5). One electrode, P-03, showed relatively poor repeatability (Fig. 6.5a) with a standard deviation in EMF of >10 mV. When comparing sensitivity slopes in the concentration ranges of 10^{-5} to 10^{-1}, and 10^{-4} to 10^{-1} mol/L total phosphate (Fig. 6.5b), one electrode, P-04, showed less sensitivity than did the other electrodes. Obviously, two electrodes (P-03 and P-04) were producing questionable data, which were considered to be outliers. Based on data obtained with the other four electrodes (P-01, P-02, P-05, and P-06), the bis(p-chlorobenzyl)tin dichloride-based phosphate ISEs, on the average, responded to total phosphate over a concentration range of 10^{-5} to 10^{-1} mol/L with an average slope of -28.2 mV per activity decade of dibasic phosphate(HPO_4^{2-}), yielding a standard deviation in EMFs of 5.3 ± 3.0 mV for three replicate measurements.

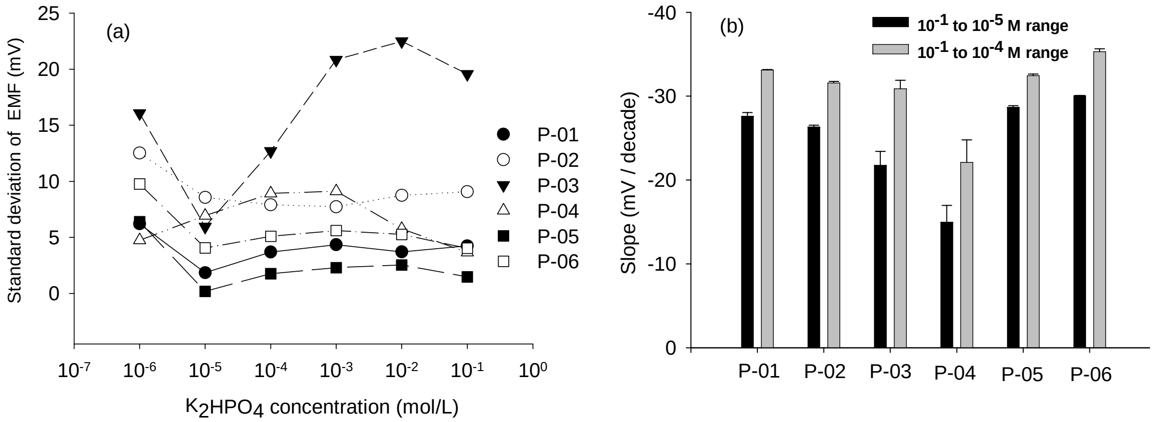


Figure 6.5. Comparison of dibasic phosphate ISEs containing bis(p-chlorobenzyl)tin dichloride in terms of (a) standard deviation of EMF values and (b) sensitivity slope.

Sensitivity of Membranes in Tris Buffer and Kelowna Solutions

Since standard potentials among electrodes vary normally due to differences 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^{-1}M total phosphate concentration in the first replication to 0 mV. This procedure removed variability between electrodes in terms of standard potential, while allowing differences between replications to be evaluated.

The sensitivity curves of each membrane type to varying phosphate and potassium concentrations were obtained when using the Tris buffer (Fig. 6.6a and 6.6b) and the Kelowna solution (Fig. 6.6c and 6.6d) as base solutions. In the Tris buffer solution (pH = 7.00 ± 0.01), the EMF values obtained with the phosphate membranes (Fig. 6.7a) were nearly linearly proportional to the logarithm of total phosphate concentration in the range of 10^{-4} to 10^{-1} mol/L with a mean sensitivity slope of -33.1 ± 1.5 mV per activity decade of HPO_4^{2-}, 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. 6.7c), regardless of the level of phosphate in the tested solutions (except 0.1M total phosphate concentration).

The potassium membranes in the Tris buffer solution (Fig. 6.6b) showed a slope of 50.3 ±1.3 mV per activity decade of K^+ in the full range of tested potassium concentrations. In the Kelowna solution (Fig. 6.6d), at low potassium concentrations below 10^{-3} mol/L, the sensitivity of potassium membranes was considerably decreased, thereby resulting in a detection limit of about 10^{-3} mol/L, which is higher than that (10^{-4} mol/L) obtained in previous studies (chapter 4). This decrease in sensitivity for the potassium membranes, as compared to that seen 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 NH_4OH was added to adjust the pH of the Kelowna solution to 8.5.

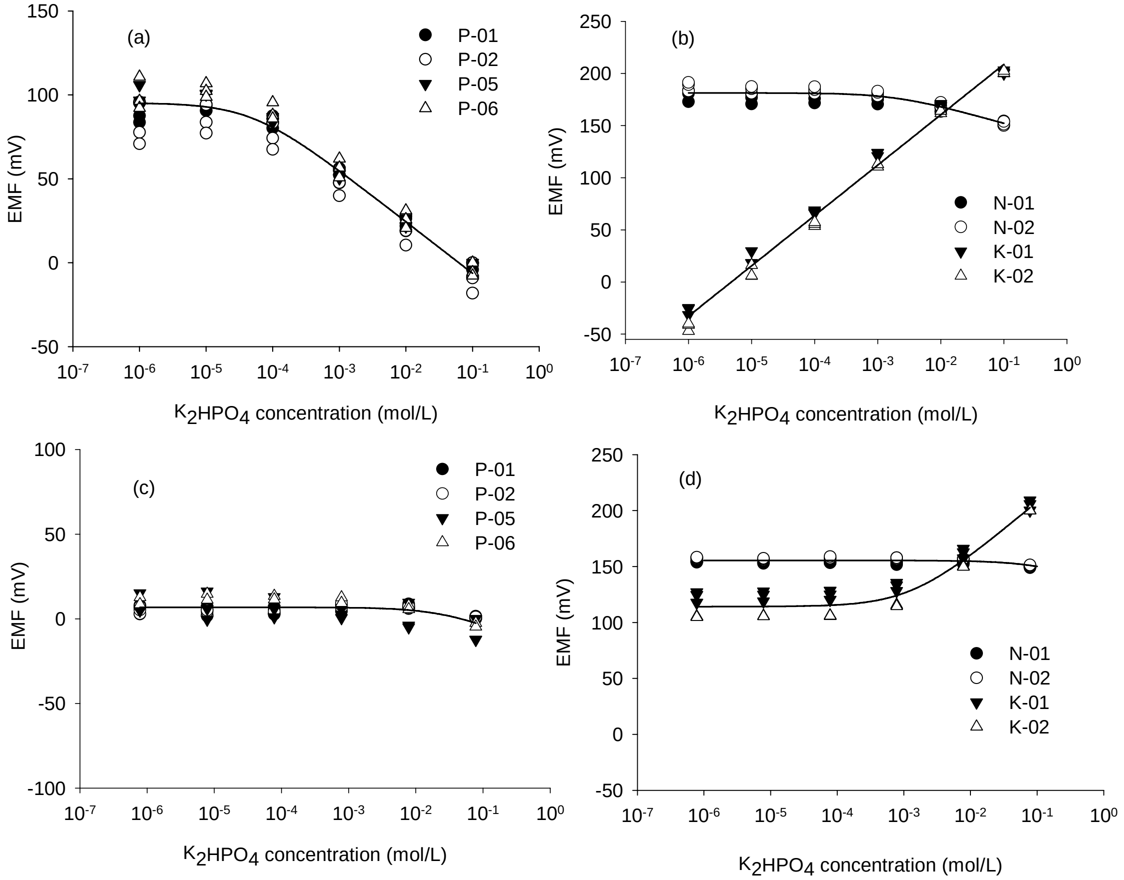


Figure 6.6. Response of each membrane to different K_2HPO_4 concentrations: (a) phosphate membrane response in Tris buffer, (b) nitrate and potassium membrane response in Tris buffer, (c) phosphate membrane response in Kelowna extracting solution, and (d) nitrate and potassium membrane response in Kelowna extracting solution.

Effects of Base Solution Type and Membrane Age on Sensitivity

As observed from a plot (Fig. 6.7a) comparing responses of the phosphate membranes in different base solutions, the average EMF values 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 obtained over the same concentration range 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) showed that the selectivity coefficient of the membrane for fluoride is 0.279, which means that the tin-compound-based 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.

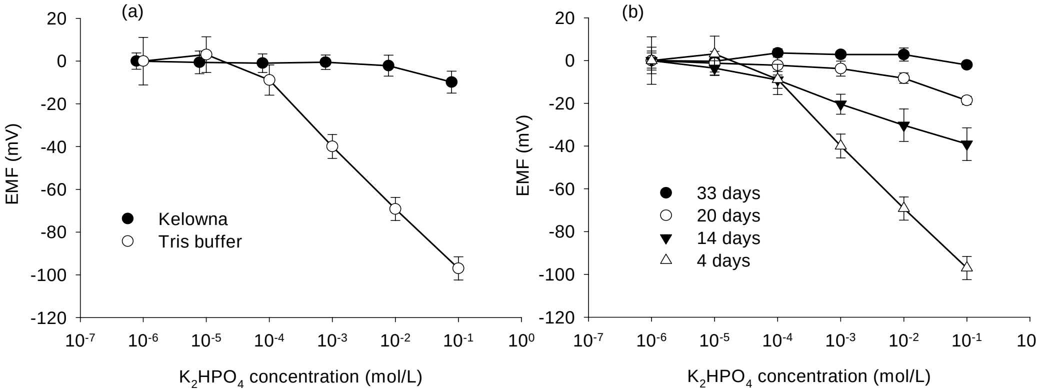


Figure 6.7. Effects of (a) base solution and (b) membrane age on change in electrode response.

The change in response to phosphate due to membrane age is shown in Figure 6.7b. Electrodes of different ages were stored in the pH 7 Tris buffer at room temperature (22.5 to 23.5 °C) between measurements, and then tested simultaneously. As shown in the Figure, 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 might be rapid leaching of the tin compound ionophore from the membrane or a rapid breakdown of the tin compound structure.

Monobasic Phosphate Sensitivity and Selectivity Tests

Response Characteristics to Monobasic Phosphate

Figure 6.8 shows the EMF responses for the six cobalt electrodes with two different purities of cobalt (three of each 99.95 % and 99.99 %), three tributyltin-based phosphate ISEs, and three nitrate and three potassium ISEs to seven varying potassium phosphate (KH_2PO_4) concentrations ranging from 10^{-7} M to 10^{-1} M in the KHP buffer (Figs. 6.8a and 6.8b) and Kelowna solutions (Fig. 6.8c and 6.8d) at pH 4.

The cobalt electrodes responded to phosphate over a wide range of 10^{-5} to 10^{-1}mol/L total phosphate concentrations, yielding negative sensitivity slopes and repeatable responses during three replicate measurements. Meanwhile, the responses of two of the three tributyltin-based phosphate ISEs (Tributyltin-01 and Tributyltin-03) were in the opposite direction, which is unreasonable because typical anion-selective electrodes, including nitrate and phosphate ISEs, exhibit negative sensitive slopes to increases in the test solution concentrations. Moreover, the sensitivity of the tributyltin-based PVC membranes was much lower than that reported in previous studies. Since the KHP buffer solution contained a high concentration of potassium (> 0.025M), there appeared to be little change in EMF for the potassium ISEs in the KHP buffer (Fig 6.8b). However, the potassium membranes in the Kelowna solution (Fig. 6.8d) were sensitive to different potassium concentrations ranging from 10^{-4} to 10^{-1} mol/L with good repeatability during the three replicate measurements. The nitrate membranes in the two tested solutions were nearly insensitive to different KH_2PO_4 concentrations.

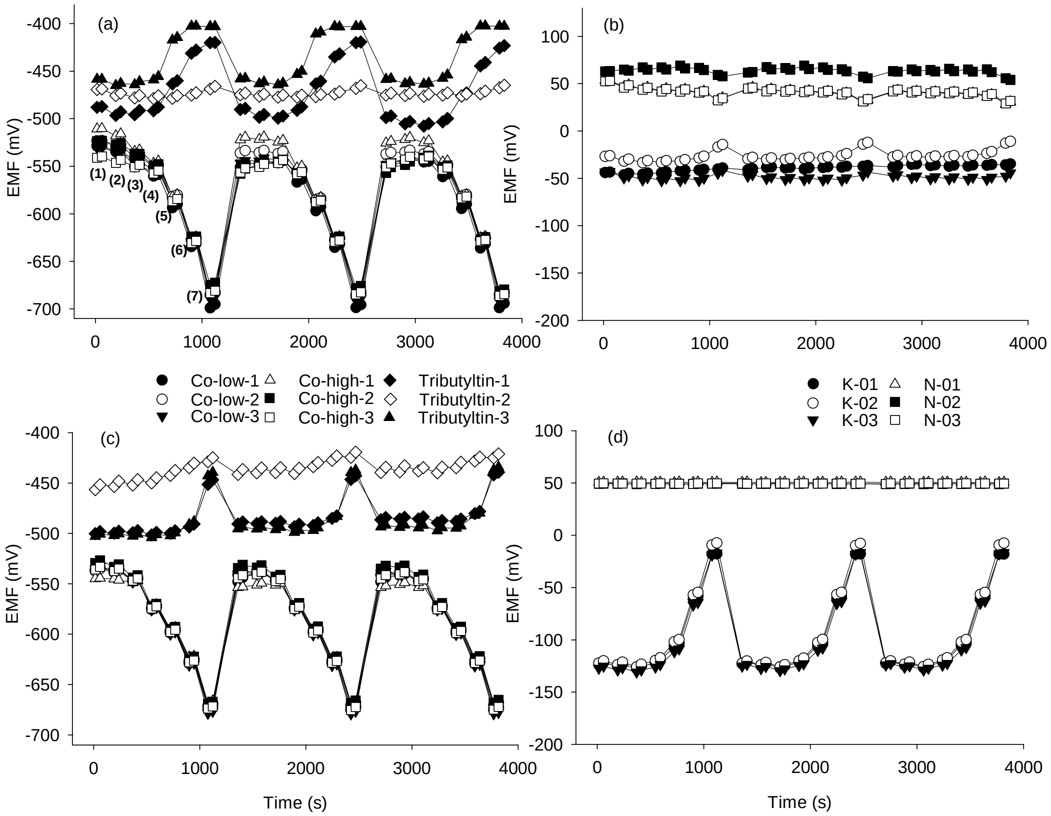


Figure 6.8. Response test profiles for different KH_2PO_4 concentrations: (a) the responses of cobalt rod electrode and PVC membrane containing tributyltin chloride in KHP buffer of pH 4, (b) the responses of TDDA-NPOE-based nitrate and V-DOS-based potassium ion-selective membranes in KHP buffer, (c) phosphate electrode response in Kelowna extractant of pH 4, and (d) nitrate and potassium electrode response in Kelowna extractant. The numbers in (a) identify the different KH_2PO_4 concentrations: (1) 10^{-7}; (2) 10^{-6}; (3) 10^{-5}; (4) 10^{-4}; (5) 10^{-3}; (6) 10^{-2}; and (7) 10^{-1} mol/L.

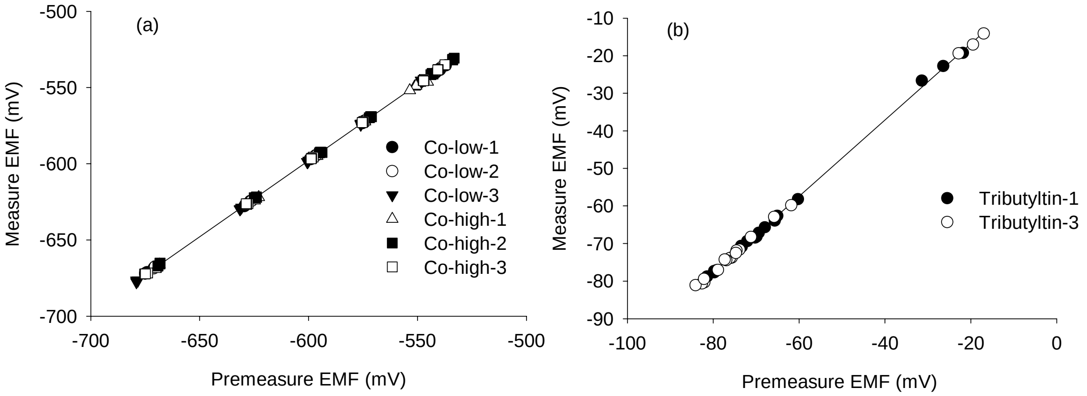


Figure 6.9. Correlation between EMF values measured 15 s (premeasure) and 60 s (measure) after the injection of test solutions for (a) cobalt electrodes and (b) tributyltin PVC membranes.

As observed with the polymer-based membranes (Fig. 6.4), the two tested monobasic phosphate-selective electrodes also reached steady state responses (Fig. 6.9) within 15 s after being immersed in the test solutions, and high correlation was found ($r^2 = 0.99^{**}$, slope = 0.99) between EMFs measured at the premeasure time (15 s) and measure time (60 s).

Comparison of Electrode Sensitivity in KHP Buffer and Kelowna Solutions

The sensitivity curves of each electrode type to varying concentrations of potassium monobasic phosphate (KH_2PO_4) are shown in Figures 6.10 and 6.11 for the KHP buffer and the Kelowna solutions as base solutions, respectively.

In each of the two different solutions titrated to pH 4, the cobalt electrodes showed sensitive responses to phosphate over a range of 10^{-5} to 10^{-1} mol/L total phosphate concentration, with a linear range of 10^{-4} to 10^{-1} mol/L and a detection limit of about 10^{-5} mol/L total phosphate concentration.

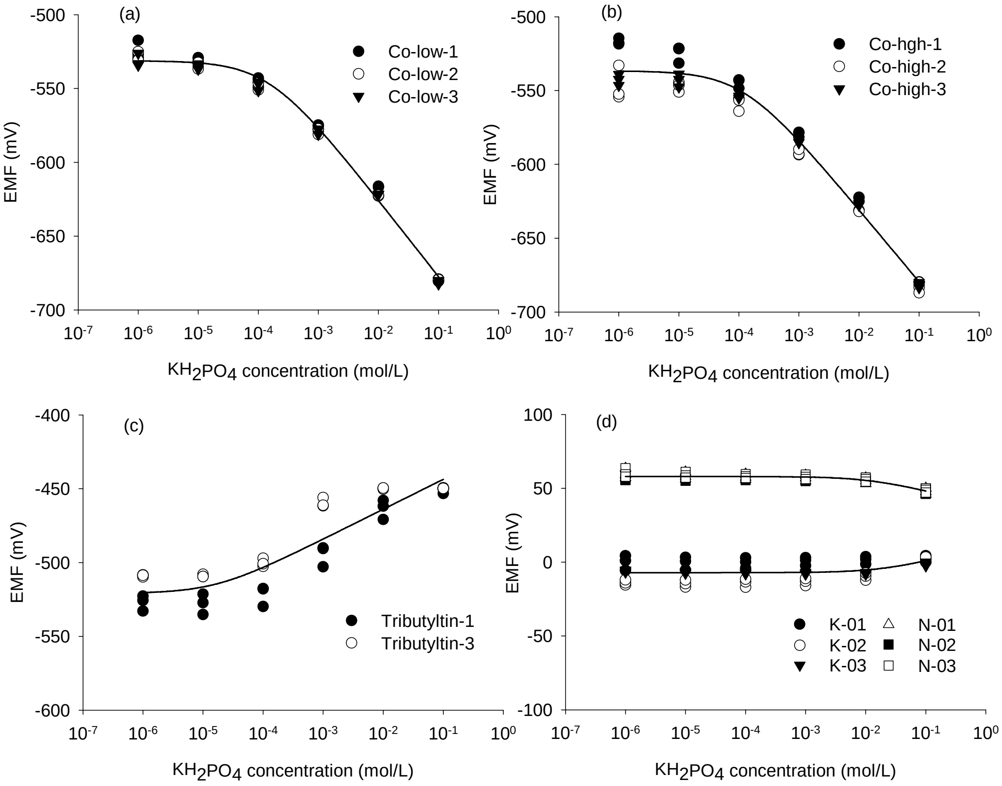


Figure 6.10. Response of each electrode to different KH_2PO_4 concentrations in KHP buffer (pH=4): (a) cobalt electrode (99.95% purity) response in KHP buffer, (b) cobalt electrode (99.99%) response, (c) tributyltin-based phosphate electrode response, (d) nitrate and potassium electrode response.

As shown in Table 6.1, the sensitivity of the cobalt electrodes over different total phosphate concentration ranges was significantly affected by the base solution. In general, the sensitivity slopes in the Kelowna solution were decreased by 6 ~ 14 mV per activity decade of $H_2PO_4^-$ as compared to those obtained in the KHP buffer. However, when tested in the Kelowna solution, the usable portion of the phosphate concentration:EMF curve appears to be from 10^{-5} to 10^{-1} mol/L total phosphates (Fig. 6. 11a, 6.11b). This encompasses a range of interest from 3.2 x 10^{-5} to 9.7 x 10^{-5} mole/L, corresponding to a 10 to 30 mg/L soil P range at a dilution ratio (solution: soil) of 10:1 (Buchholz et al., 1983).

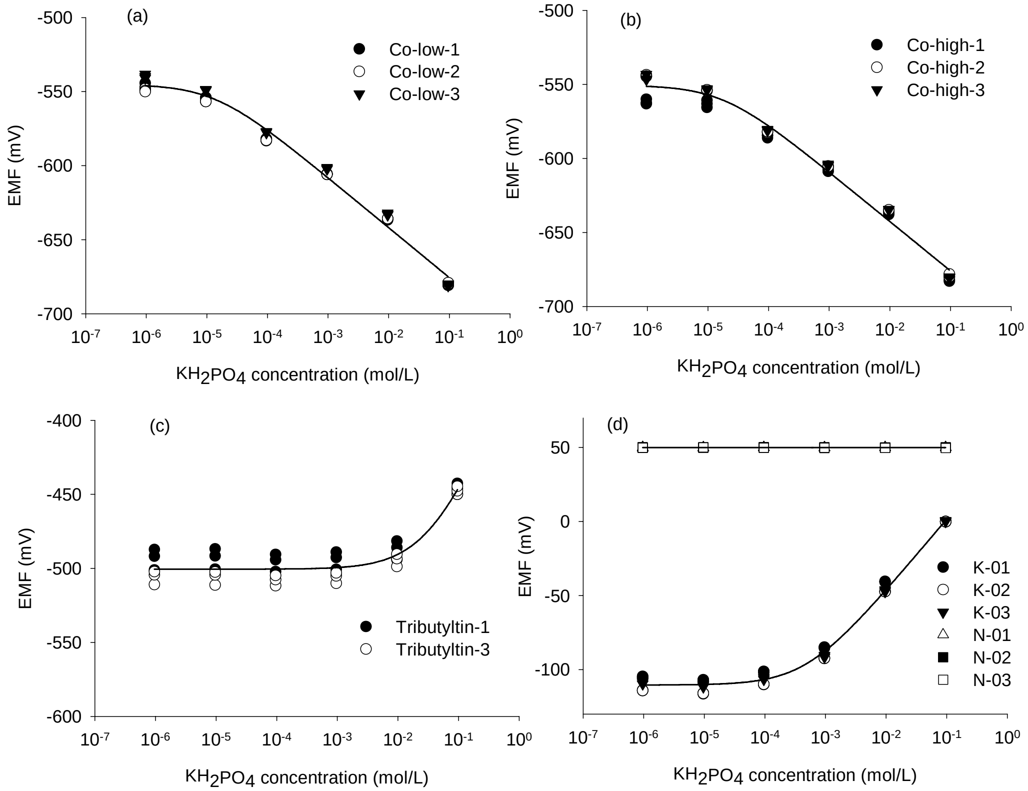


Figure 6.11. Response of each electrode to different KH_2PO_4 concentrations in Kelowna solution (pH=4): (a) cobalt electrode (99.95% purity) response in KHP buffer, (b) cobalt electrode (99.99%) response, (c) tributyltin-based phosphate electrode response, (d) nitrate and potassium electrode response.

Table 6.1. Means and standard deviations of sensitivity slopes (mV/decade) of cobalt ISEs with different purities.

Base Solution	Total Phosphate Concentration Range		
Electrode	10^{-1}M to 10^{-5}M	10^{-1}M to 10^{-4}M	10^{-1}M to 10^{-3}M
<u>KHP Buffer</u>			
Cobalt-low	-37.2 ±0.4 a[a]	-45.0 ±0.9 a	-52.7 ±1.0 a
Cobalt-high	-36.5 ±2.3 a	-43.8 ±2.0 a	-49.7 ±2.8 b
<u>Kelowna Solution</u>			
Cobalt-low	-30.9 ±0.9 a	-32.9 ±0.9 a	-38.0 ±1.1 a
Cobalt-high	-30.9 ±2.5 a	-32.6 ±1.8 a	-36.2 ±2.6 a

[a] Mean membrane sensitivities within a phosphate concentration and extractant combination with the same letter are not significantly different at the 5% level, based on the SAS TTEST.

SAS TTEST results show that there was generally no significant difference in sensitivity between electrodes of different purities of cobalt (99.95% and 99.99%) in the phosphate concentration range. However, the standard deviations of the sensitivity of the low-purity cobalt electrodes were lower than those measured with the high-purity cobalt phosphate electrodes. The superior repeatability of the lower-purity cobalt rod electrodes makes them a better choice as compared to the higher-purity cobalt rod electrodes for phosphate sensing.

As previously noted (Fig. 6.8), one of the three tributyltin-based phosphate electrodes (Tributyltin-02) showed unacceptable responses, and thus, results for only two electrodes were plotted in Figures 6.10 and 6.11. Their responses to phosphate were different from those obtained with the cobalt electrodes, showing positive sensitivity slopes and relatively poor repeatability (Figs. 6.10c and 6.11c). In addition, these test results show a much lower sensitivity, 60 mV over the tested total phosphate range, as compared to a maximum EMF difference of about 160 mV reported in a previous study (Sasaki et al., 2004). Therefore, it was concluded that the tributyltin-based PVC membranes would not be usable for sensing phosphate. The details of the mechanism responsible for the decreased sensitivity of the membrane and opposite slope are difficult to explain. However, a possible cause might be the use of different base solutions. The 0.025 mol/L KHP solution at pH 4.0 was used in this test, whereas in previous work, the sensitivity of the membrane to $H_2PO_4^-$was investigated using 0.1M Tris buffer solution at pH 7.0.

Tested TDDA-based nitrate membranes were insensitive to phosphate, regardless of the level of phosphate in the tested solutions, except for a slight decrease in EMF (< 5 mV) at 0.1M phosphate concentration in the KHP buffer. The sensitivity for the valinomycin-based potassium membranes in the Kelowna solution was comparable to that reported in previous tests (chapter 4), yielding a measurable range of 10^{-4} to 10^{-1} M potassium concentrations.

Selectivity of Cobalt Electrode

The sequence of responses for the electrodes in the two different base solutions when tested with three pure solutions (0.1M and 0.01M KH_2PO_4, and 0.01M interfering ion) for each interfering ion are shown in Figure 6.12. The sequence of 0.01M KH_2PO4 → 0.1M KH_2PO4→ 0.01M KH_2PO4 → 0.1M interfering ion was repeated for all six tested ions. As observed in the previous sensitivity tests, the absolute EMF values of the two different cobalt electrodes were increased when more concentrated phosphate solutions (i.e., from 0.01M to 0.1M) were presented. However, the EMF responses to the pure solutions of the six anions (0.1M) were reduced as compared to the EMF responses of the pure solutions at 0.01M phosphate concentration. Such an observation indicates the cobalt phosphate electrodes are at least 10 times more sensitive to phosphate than to the other anions. When tested in the Kelowna solution, the selectivity of the cobalt electrodes was improved as compared to selectivity in the KHP solution. In the KHP buffer (Fig. 6.12a), the potassium and nitrate membranes were nearly insensitive to anions, regardless of the ion tested. However, in the Kelowna solution (Fig. 6.12b), the nitrate and potassium membranes showed sensitivity responses to nitrate and potassium.

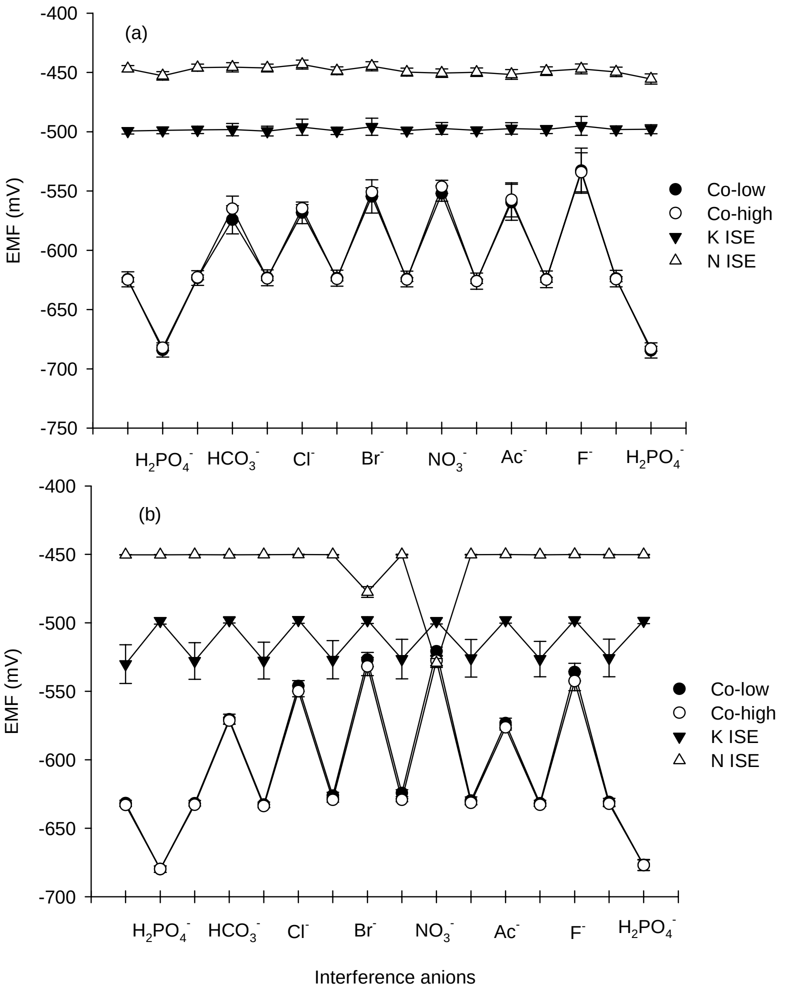


Figure 6.12. Responses of the NPK electrodes to various interference anions of 0.1M concentration in (a) the KHP buffer and (b) the Kelowna solutions.

A comparison of potentiometric selectivity coefficients (log K) with respect to the interference anions, bicarbonate (HCO_3^-), chloride (Cl^-), bromide (Br^-), nitrate (NO_3^-), acetate (Ac^-), and fluoride (F^-), in different base solutions obtained using the separate solution method, is summarized in Fig. 6.13 and Table 6.2. As shown in Figure 6.13, the selectivity for monobasic phosphate over the tested anions was enhanced when the cobalt electrodes were tested in the Kelowna solution.

The selectivity patterns for these electrodes tested in different base solutions can be described in the following order, as shown in Figure 6.13,

$H_2PO_4^- >> HCO_3^- > Cl^- > Ac^- > Br^- > NO_3^- > F^-$ in KHP buffer

$H_2PO_4^- >> Ac^- > HCO_3^- > Cl^- > F^- > Br^- > NO_3^-$ in Kelowna solution.

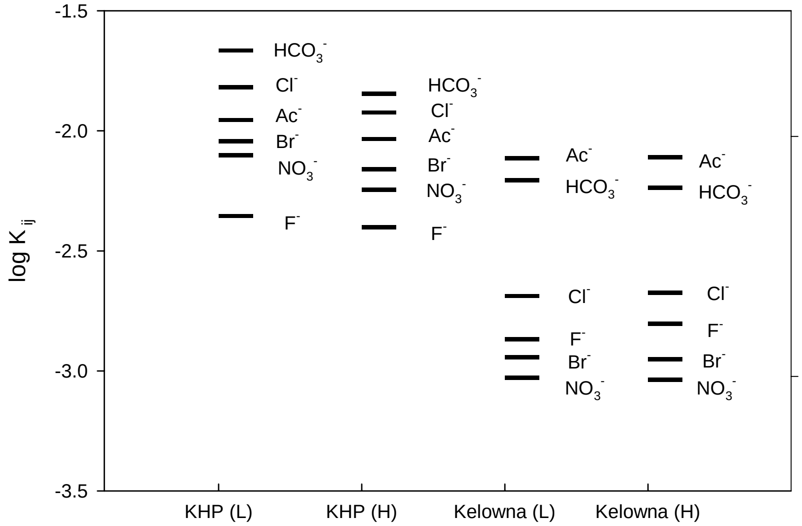


Figure 6.13. Selectivity coefficients of cobalt electrodes with purities of 99.95% (L) and 99.99% (H) measured in KHP and Kelowna solutions.

Table 6. 2. Comparison of selectivity coefficients (log K_{ij}) of cobalt ISEs by extractant type.

	Interference Ion					
Electrode	HCO_3^-	Cl^-	Br^-	NO_3^-	Ac^-	F^-
<u>KHP Buffer</u>						
Cobalt-Low	-1.67 a[a]	-1.82 a	-2.04 a	-2.10 a	-1.96 a	-2.36 a
Cobalt-High	-1.85 b	-1.92 b	-2.16 b	-2.24 b	-2.04 a	-2.40 a
<u>Kelowna Solution</u>						
Cobalt-Low	-2.21 a	-2.69 a	-2.94 a	-3.03 a	-2.11 a	-2.87 a
Cobalt-High	-2.24 a	-2.68 a	-2.95 a	-3.04 a	-2.11 a	-2.80 a

[a] Membrane selectivity coefficients within an ion species and extractant combination with the same letter are not significantly different at the 5% level, based on the SAS TTEST.

SAS TTEST (Table 6.2) results show that in the KHP buffer, the cobalt ISEs with high purity (99.99%) exhibited higher selectivity for monobasic phosphate over four anions (i.e., bicarbonate, chloride, bromide, and nitrate) than did the 99.95%-purity cobalt electrodes. However, in the Kelowna solution, there were no significant differences in selectivity coefficients between the different purities of cobalt electrodes.

CONCLUSIONS

Two types of phosphate sensors, tin compound-based PVC membranes and cobalt rods with different purities, along with TDDA-NPOE-based nitrate and V-DOS-based potassium sensors were evaluated for sensitivity and selectivity in standard buffer solutions (pH 7 Tris and pH 4 KHP) and Kelowna soil extractant.

The PVC-based phosphate membranes containing an organotin compound, bis(p-chlorobenzyl)tin dichloride, exhibited sensitive responses over a range of 10^{-4} to 10^{-1} mol/L total phosphate concentrations in the Tris buffer of pH 7 with an average slope of -33.1 $\pm$1.5 mV per activity decade of HPO_4^{2-}, which is comparable to results obtained in previous studies (Glazier and Arnold, 1988; 1991). However, the membrane was not usable for determination of phosphates when using the Kelowna solution because the high concentration of fluoride (0.015 mole/L) in the Kelowna extractant reduced sensor performance considerably, resulting in insensitivity to phosphate over the 10^{-6} to 10^{-2} mol/L concentration range. Also, the short functional lifetime of this membrane (less than 14 days) was less than expected. Moreover, the results of another tin-compound-based PVC membrane containing tributyltin chloride as the ionophore were not satisfactory, showing much less sensitivity with a different direction of sensitivity slope than reported in previous studies (Sasaki et al., 2004).

The cobalt rod-based electrodes with purities of 99.95% and 99.99% exhibited sensitive responses over a range of 10^{-5} to 10^{-1} mol/L total phosphate concentration with a detection limit of 10^{-5} mol/L when tested in the Kelowna solution. This range encompasses the range of phosphorus concentrations typically found in agricultural soil, assuming a 10:1 dilution ratio. The selectivity of the cobalt electrodes was satisfactory for measuring phosphates in the presence of each of six possible interfering ions, i.e., HCO_3^-, Cl^-, Br^-, NO_3^-, Ac^-, and F^-. The electrodes were 47 to 1,072 times more selective to phosphate than to the tested ions. Although the cobalt electrodes with different purities (99.95% and 99.99%) showed similar sensitivity and selectivity performance, the lower-purity cobalt rod is a better choice when using the Kelowna extractant because sensors of that material showed more reproducible responses than did electrodes fabricated using the higher-purity cobalt rod.

CHAPTER 7

SIMULTANEOUS ANALYSIS OF SOIL MACRONUTRIENTS USING ION-SELECTIVE ELECTRODES

ABSTRACT

The need for fast in-field monitoring of soil nutrients has led to the use of ion-selective electrodes, because of their advantages over spectrophotometric methods, including simple methodology, direct measurement of analyte, sensitivity over a wide concentration range, and low cost. This study evaluates the predictive capabilities of a sensor array of three different ion-selective electrodes, based on TDDA-NPOE and valinomycin-DOS membranes, and cobalt rod, for the simultaneous determination of nitrate-N, phosphate, and potassium ions in soil extracts. Thirty seven Illinois and Missouri soils, with a pH range of 4.3 to 6.9, were extracted using the Kelowna soil extractant. The responses of each type of electrode in both separate and mixed solutions were effectively modeled based on the Nikolskii-Eisenman equation with high coefficients of determination (r^2) > 0.97** when using baseline correction and 2-point normalization. The tested nitrate and potassium electrodes were feasible for measuring NO_3-N and K ions in Kelowna-based soil extracts, showing almost 1:1 relationships (r^2 > 0.92**) between the amounts obtained with the ion-selective electrodes and with standard instruments, the Lachat and ICP analyzers for NO_3-N and K analysis, respectively. However, the cobalt rod-based phosphate electrodes predicted about 53 % less P than did the ICP spectrophotometer (r^2 = 0.80**). In a study comparing the ion-selective electrode methods to standard soil laboratory tests, a highly significant relationship (r^2 =

0.89**) existed between the amounts of soil NO_3-N obtained with the Kelowna extractant and nitrate electrodes and with the 1M KCl extractant and a Lachat automated ion analyzer, with a regression slope of 1.00 and a y-intercept of 22.1 mg/L NO_3-N. The P extracted with the Kelowna extractant and measured with the cobalt electrode was 63 % less than P extracted with the Mehlich III extractant and analyzed with the ICP (r^2 = 0.78**). Likely causes for the lower P estimates are the lower estimate of soil extract P determined by the cobalt electrode (53 % less as compared to ICP) and reduced P extraction with the Kelowna extractant (26 % less as compared to Mehlich III). A significant relationship (r^2 = 0.85**) existed between soil potassium levels determined by the potassium ISE and the Kelowna extractant, and those determined by the ICP and the Mehlich III extractant. However, the potassium ISE estimated soil potassium levels 47 % lower than the Lachat and Mehlich III test, because the levels of soil K extracted with the Kelowna were about 50 % less than those obtained with the Mehlich III extractant.

INTRODUCTION

The soil macronutrients, nitrogen (N), phosphorus (P), and potassium (K), are essential elements 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 (Havlin et al., 1999). Chemical fertilizers have been extensively applied to soils as sources of macronutrients for increasing crop yields. However, the excessive use of these substances can lead to runoff of nutrients into surface or ground water, causing undesirable environmental pollution (Mallarino, 1998; Artigas et al., 2001).

Monitoring nutrient levels in soils can provide useful information for the efficient use of fertilizers and for minimizing the environmental impact of these practices. However, conventional soil testing methods, including soil sampling in the field and chemical analysis in the laboratory, are costly and time consuming, thereby limiting the number of samples analyzed in the field and making it difficult to characterize the variability in soil nutrient levels at a fine spatial resolution (Schepers and Schlemmer, 1998).

From the standpoint of site-specific crop management (SSCM), a higher resolution than the current commercially practiced 1-ha grid sampling is needed to more accurately characterize within-field variability (Schepers and Schlemmer, 1998). For example, accurate monitoring of soil NO_3-N levels has been limited by relatively high temporal and spatial variability of NO_3-N in the field, leading to the need for real-time measurements with a high sampling intensity (Sudduth et al., 1997).

The need for fast in-field monitoring has led to the application of ion-selective electrode (ISE) technology for the determination of soil chemical properties, because of advantages over current analytical methods (e.g., spectroscopic techniques), such as simple methodology, direct measurement of analyte, sensitivity over a wide concentration range, low cost, and portability (Carey and Riggan, 1994).

An important component of an ISE is the ion-selective membrane that selectively responds to one analyte in the presence of other ions in a solution. Due to an increased demand for measurement of new ions, and advances in MEMS (Micro-Electro-Mechanical Systems) technology, 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^+, Na^+, and Ca^{2+} (Nielson and Hansen, 1976; Tsukada et al., 1989; Knoll et al., 1994; Levitchev et al., 1998). Furthermore, due to the importance of monitoring phosphorus in biological systems and living organisms, many researchers have tried to develop phosphate sensors in the form of ion-selective electrodes (Glazier and Arnold, 1991; Carey and Riggan, 1994; Xiao et al., 1995; Chen et al., 1997; Wroblewski et al., 2000).

A universal extracting solution for extracting multiple ions from soils would be advantageous for simultaneous analysis of soil macronutrients because its use could reduce the time and cost involved in the analysis. 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 a multiple element solution for extracting phosphorus, potassium, and other cations in soil (Mehlich, 1984; Fixen and Grove, 1990). Recently, the use of the Mehlich III solution has been expanded with increased adoption of the inductively coupled argon plasma (ICP) analyzer that simultaneously measures P, K and other cations. However, the Mehlich III solution is not useful for nitrate extraction because of the high concentration of nitrate in this extracting solution. The Kelowna extractant (0.25M CH_3COOH + 0.015M NH_4F), which is used as a multiple ion extractant in British Columbia, Canada, can simultaneously extract phosphorus and potassium as well as nitrate from soils (Van Lierop, 1986; 1988; Van Lierop and Gough, 1989). The identification of a multiple ion extractant that does not adversely affect the response of ion-selective membranes, and that can extract representative amounts of soil macronutrients is needed for simultaneous real-time analysis of soil macronutrients.

Since ion-selective electrodes are not truly specific but respond more or less to a variety of interfering ions (Ammann, 1986), the applicability of ion-selective electrodes to perform simultaneous analysis on mixtures of NPK ions in soil extracts can be limited by the effect of interference from other ions present in soil extracting solutions and in soil itself. To overcome these limitations, various data processing methods using computer programs and mathematical models have been used in the area of analytical chemistry. For example, multivariate calibration models have been proposed which allow cross responses arising from primary and interfering ions to be decoupled, thus allowing accurate determination of individual ion concentrations within mixtures (Forster et al., 1991). Also, to determine calibration parameters for each electrode and the form of the nonlinear model, multiple linear regression based on the Nikolskii-Eisenman equation and projection pursuit regression, a nonparametric method, were developed by Otto and Thomas (1985) and Beebe and Kowalski (1988), respectively. In recent years, an artificial neural network (ANN) with an array of multiple electrodes was used for the simultaneous determination of NH_4^+, K^+, and Na^+ ions in waste water and fertilizer samples (Gallardo et al., 2005). The ANN was able to predict the concentrations of the tested ions accurately in waste water without the need to remove interfering effects, but showed biased results for Na^+ and K^+ ions in fertilizer samples.

Stability and repeatability of response might be a concern in the use of an array of multiple ion-selective electrodes to measure individual ion concentrations in a series of samples because accuracy of the measurement might be limited by electrode potential drifts that occurring during replicate measurements (Dybko, 2001). The use of a computer-based automatic measurement system would improve accuracy and precision in the determination of macronutrients in soil extracts.

OBJECTIVES

The overall objective of this research was to evaluate a sensor array of three selected ion-selective electrodes for simultaneous determination of soil macronutrients (N, P, and K). Specific objectives included:

- Develop calibration models for N, P, and K sensors by relating sensor responses to analyte concentrations using single-ion solutions and mixtures of N, P, and K ions.
- Validate the applicability of the developed calibration models to the simultaneous determination of N, P, and K ions in solution, across ranges of N, P, and K concentrations commonly found in soil extracts.
- Evaluate the ability of an array of selected ion-selective electrodes to estimate N, P, and K concentrations in a range of Illinois and Missouri soils.

MATERIALS AND METHODS

Preparation of NPK Ion-Selective Electrodes

Following the detailed procedures reported in previous chapters, a PVC-based nitrate ion-selective membrane was prepared with a mixture of 30 mg (15% wt) of ligand (TDDA, tetradodecylammonium nitrate), 80 mg (40% wt) of plasticizer (NPOE, nitrophenyl octyl ether) and 90 mg (45% wt) of high-molecular-weight polyvinyl chloride (PVC) dissolved in 2 mL of THF (tetrahydrofuran). The composition of the potassium ion-selective membrane was 4 mg (2% wt) of ionophore (valinomycin), 1 mg (0.5% wt) of lipophilic additive (KTpClPB), 129.4 mg (64.70% wt) of plasticizer (DOS, bis(2-ethylhexyl sebacate), and 65.6 mg (32.80% wt) of PVC in 2 mL of THF. The membrane disks were attached to the ends of Hitachi ISE electrode bodies using the THF solvent. 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.

For sensing phosphorus, cobalt electrodes with a purity of 99.95% were prepared according to procedures reported in chapter 6. A double junction Ag/AgCl electrode (Model PHE 3211, Omega Engineering, Stamford, CT) was used as the reference electrode. The test array consisted of sixteen sensors: five sensors each for nitrate, potassium, and phosphate, and one reference electrode.

Test Equipment and Procedures

The tests of the fifteen N, P, and K sensors were conducted with an automated test stand that allowed simultaneous sampling of EMF data from the 15 ISE electrodes measured relative to the reference electrode. A 16-channel circuit board was constructed using LF 356N operational amplifiers in follower configuration for buffering the impedance of each sensor. A Daqbook 200 A/D convert data acquisition system was used to collect ISE voltage outputs. Details of the test stand components are described in Appendix A.

The electrodes were triple-rinsed with a solution of 10^{-6}M KNO_3 prior to each sample measurement. Under computer software control, sample holder rotational speed was increased during each rinse to expel the rinse solution, and then slowed while fresh rinsing solution was being introduced. After the rinse sequence, the sample holder was rotated at 37 rpm while 110 ml of sample solution was manually loaded. A computer hotkey was used to accurately reference the data collection time to introduction of the new test solution. Thus, each individual test began when the desired volume of test solution had been delivered to the solution holder. Details of the control and data collection program are given in Appendix B.

For each test of a different solution concentration, EMF data were collected for the rinse solution and the test solution at two times; i.e., 15 s and 60 s, after injection of each 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. The sample holder was rotated at a constant speed of 37 rpm from sample injection through data collection.

Baseline Correction and Two-Point Normalization

Baseline EMF data obtained during the third rinse cycle prior to each test solution were used to minimize potential drift and bias that might occur during continuous measurement. Baseline-corrected EMF measurements were calculated by subtraction of the baseline EMF from each sensor reading.

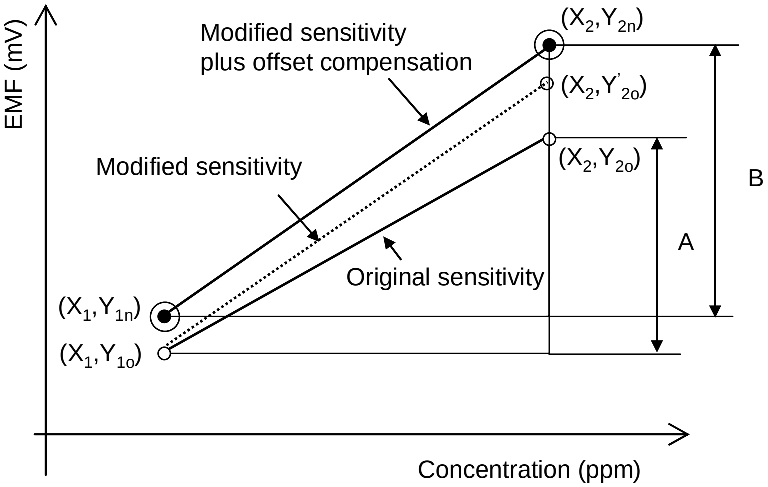


Figure 7.1. Schematic diagram for 2-point normalization.

Since standard potentials (i.e., initial EMF values) and sensitivity slopes vary normally among electrodes due to difference in internal resistance or physical conditions of the electrodes, a procedure for standardizing responses of multiple electrodes for each ion was developed. These standardized responses allowed the application of a single calibration equation across all electrodes of given type.

As shown in Figure 7.1, two reference points (circled) were first determined by averaging EMF readings of the five electrodes and three replications of each sensor type measured at the lowest and highest concentrations of the primary ion corresponding to that sensor. Individual sensitivity slopes of each of the five electrodes were normalized by multiplying baseline-corrected EMF data by the ratio of B/A (Equation 7.1), and the calibration data modified by sensitivity compensation were then re-calibrated by subtracting the difference between the highest reference point and the modified highest concentration point (Equation 7.1) from all the other points. The normalization was applied to all data points obtained within each replication.

$$
\begin{aligned}
ratio &= \frac{B}{A} = \frac{Y_{2n} - Y_{1n}}{Y_{2o} - Y_{1o}} \\
offset &= Y_{2n} - Y_{2o}^{'}
\end{aligned}
\tag{7.1}
$$

where:

Y_{2n} = EMF value of reference point for the highest concentration

Y_{1n} = EMF value of reference point for the lowest concentration

Y_{2o} = initial EMF value measured at the highest concentration

Y_{1o} = initial EMF value measured at the lowest concentration

$Y_{2o}^{'}$ = EMF value at the highest concentration after sensitivity (ratio) compensation.

Development of Calibration Equations Using Single Ion Solutions

A series of EMF measurements were taken by using three sets of single ion calibration solutions each with seven different concentration levels. The concentrations of primary ions were chosen to encompass the typical concentration ranges of soil samples based on a dilution ratio of 10:1 (solution: soil) (Buchholz et al., 1983; Brown, 1998), i.e., a set of seven nitrate and a set of seven phosphorus solutions, each containing 0.1, 0.5, 1, 2, 5, 10, and 20 mg/L NO_3-N and P, respectively, and a set of seven potassium solutions with 1, 2, 3, 5, 10, 20, and 50 mg/L K, respectively. The three sets of standard calibration solutions were prepared by adding highly concentrated individual N, P, and K solutions containing 400 mg/L NO_3-N, 400 mg/L P, and 1,000 mg/L K, respectively, to a base solution. All calibration solutions were prepared with the Kelowna extractant containing 0.25M CH_3COOH and 0.015M NH_4F as the base solution, and were titrated to pH 4.0 using 1M NaOH to remove the effect of pH on the equilibrium between phosphorus ionic forms (Lindsay, 1979).

In each replication, samples were tested in sequence, first from lowest to highest concentration of the test ion, and then from highest to lowest concentration. This procedure minimized the hysteresis effect on the sensor output due to concentration level of the solution in which the electrode was previously immersed. Three iterations of each sequence were conducted.

As discussed in the previous section, the EMF outputs measured with five electrodes for each ion were normalized using baseline correction and 2-point normalization methods so that general calibration equations for each sensor type could be developed. The calibration equations for each sensor were obtained by relating EMF reading as the response variable to ionic concentration as the independent variable, based on the Nikolskii-Eisenman equation (Equation. 7.2):

$$\mathrm{EMF} = E_o + E_J + S\log\left[a_i + \sum K_{ij}(a_j)^{Z_i/Z_j}\right] \tag{7.2}$$

where:

EMF = potential measured with each electrode

E_o and E_J = standard and liquid-junction potentials

S = the slope of the electrode

a_i and a_j = activities of primary and interference ions

Z_i and Z_j = charges of primary and interference ions

K_{ij} = the selectivity coefficient of the electrode.

Development of Calibration Equations Using Mixtures of NPK Ions

Mixed solutions containing nitrate, phosphorus, and potassium ions, each at four different levels (very low, low, medium, and high), were tested with the electrodes to investigate how those three ions, as primary or interfering ions, contributed to signals of each sensor, and to develop optimum calibration equations that allowed accurate determination of individual ions in mixtures.

The concentration ranges for each ion were determined by referring to typical ranges of NPK concentrations measured in soil testing laboratories over a range of soils, i.e., 0.1, 1, 5, and 20 mg/L of NO_3-N and P and 1, 3, 10, and 50 mg/L of K represented very low, low, medium, and high concentration levels, respectively.

Using a three-factor, four-level, randomized complete block design, each replication consisting of sixty-four mixtures of NPK ions was tested on a separate day. The mixed calibration solutions were prepared by adding three highly concentrated N, P, and K solutions to the Kelowna solution and then adjusting the pH to 4.0. To verify whether all of the solutions were correctly prepared as planned, they were also analyzed in a commercial soil testing laboratory (A&L Great Lakes Laboratories, Fort Wayne, Ind.).

The EMF data measured with all five sensors for each ion were normalized using the baseline correction and 2-point normalization within each replication. As reference points for normalization, a solution containing a mixture of NPK ions at concentration levels of 0.1-0.1-1 mg/L, respectively, was chosen as the low-concentration normalization point for all NPK sensors and three other solutions containing a mixture of NPK ions at concentration levels of 20-0.1-1, 0.1-20-1, and 0.1-0.1-50 mg/L were prepared to provide high concentration levels for the N, P, and K sensors, respectively.

The SAS GLM procedure was used to test if the primary ions, i.e., N, P, and K, had significant effects on the responses of each sensor.

The method employed to build calibration equations from the mixed solution tests was based on the transformation of the Nikolskii-Eisenman equation (Equation 7.2). When there were significant effects of additional ions, the original Nikolskii-Eisenman equation was modified by adding variables to the equation, i.e., each of the slope and primary activity terms. SAS nonlinear regression (NLIN) was used to develop optimum calibration models where the slopes, S, as well as the sums of standard and liquid junction potentials, E_S and E_J, and the selectivity terms, $\sum K_{ij}(a_j)^{Z_i/Z_j}$ were determined iteratively.

Validation of Calibration Models

To investigate the effectiveness of the two different calibration equations built using data obtained from the single ion solution and mixed NPK solution tests, respectively, the separate calibration equations were applied to the determination of NPK ions in the mixed solutions. The validation of mixed calibration equations was conducted by splitting three replications of data into two sets, i.e., a calibration dataset including the data of two of the three replications, and a validation dataset with one replication of data.

Soil Extract Tests

Soil selection

A total of 37 soils, 17 from Illinois and 20 from Missouri (Table 7.1), were selected to represent important agricultural areas of Illinois and Missouri, and to provide a range

Table 7.1. Chemical and physical characteristics of the 17 Illinois and 20 Missouri soils used in the study.

State	Soil name	MLRA[a]	County	Textural class	ID No.	pHs[b]	OM (%)	CEC (meq/100g)
IL	Ade	114	Clark	sandy loam	1	6.6	0.3	3.4
	Carmi	114	Clark	sandy loam	2	5.4	1.6	10.7
	Ambraw	114	Clark	loam	3	6.8	1.9	12.9
	Plainfield	98	Iroquois	loamy sand	4	5.4	1.5	7.3
	Sparta	98	Iroquois	loamy sand	5	5.1	0.4	4.6
	Maumee	98	Iroquois	loamy sand	6	6.9	1.6	9.1
	Proctor	110	Champaign	clay loam	7	5.4	3.1	20.6
	Saybrook	110	Champaign	silt loam	8	5.4	4.1	24.5
	Catlin	110	Champaign	silt loam	9	4.8	2.8	18.4
	Saybrook	110	Champaign	silt loam	10	5.7	2.8	17.5
	Drummer	108	Champaign	silty clay loam	11	5.5	2.2	14.8
	Flanagan	108	Champaign	silty clay loam	12	5.0	3.7	27.5
	Drummer	108	Champaign	silty clay loam	13	5.7	2.6	13.4
	Flanagan	108	Champaign	silty clay loam	14	6.4	2.6	13.9
	Birkbeck	108	Champaign	silt loam	15	6.8	1.6	11.0
	Flanagan	108	Champaign	silty clay loam	16	6.1	3.6	18.4
	Drummer	108	Champaign	silty clay loam	17	6.2	2.9	15.4
MO	Barden	112	Vernon	silt loam	18	5.2	3.7	9.6
	Hartwell	112	Bates	silt loam	19	6.8	4.4	9.5
	Creldon	112	Lawrence	silt loam	20	5.3	2.4	10.6
	Lilbourn	131	Stoddard	fine sandy loam	21	5.4	2.6	5.7
	Gideon	131	Stoddard	loam	22	4.4	1.5	7.1
	Crowley	131	Dunklin	silt loam	23	4.3	0.6	11.4
	Lilbourn	131	Stoddard	-- [c]	24	6.3	1.5	7.0
	Commerce	131	Mississippi	silty clay loam	25	5.8	1.3	9.6
	Higginsville	107	Saline	silt loam	26	6.2	3.2	16.0
	Sibley	107	Clay	silt loam	27	5.5	3.7	17.5
	Lagonda	107	Ray	silty clay loam	28	5.5	2.2	12.2
	Lagonda	107	Linn	silty clay loam	29	6.0	3.4	17.1
	Higginsville	107	Saline	silt loam	30	6.6	2.5	11.9
	Mexico	113	Audrain	silt loam	31	7.1	3.3	11.4
	Putnam	113	Audrain	silt loam	32	6.6	3.9	9.0
	Putnam	113	Audrain	silt loam	33	6.4	2.1	10.5
	Mexico	113	Boone	silt loam	34	6.5	2.1	9.5
	Mexico	113	Boone	silt loam	35	6.0	2.6	20.7
	Leonard	113	Boone	silt loam	36	6.1	2.9	18.4
	Putnam	113	Boone	silt loam	37	6.1	2.9	19.9

[a] Major Land Resource Areas as defined by USDA (1981)
- MLRA 114, Southern Illinois and Indiana Thin Loess and Till Plain
- MLRA 98, Southern Michigan and Northern Indiana Drift Plain
- MLRA 110, Northern Illinois and Indiana Heavy Till Plain
- MLRA 108, Illinois and Iowa Deep Loess and Drift
- MLRA 112, Cherokee Prairies
- MLRA 131, Southern Mississippi Valley Alluvium
- MLRA 107, Iowa and Missouri Deep Loess Hills
- MLRA 113, Central Claypan Area

[b] Soil pH in a dilute salt solution as described in Buchholz et al. (1983)

[c] not determined

of nitrate-N, phosphorus, and potassium concentration levels. The Illinois samples were sub-samples of soils used in previous studies (Sudduth and Hummel, 1991; Birrell and Hummel, 2001; Price et al., 2003) and the Missouri soils included 16 soils used by Coggeshall et al. (2005) and 4 soils collected from a long-term cropping system research site (Kitchen et al., 2005). The soil samples were screened using a 2-mm sieve and oven-dried before extraction. Soil pH, organic matter (OM), and cation exchange capacity (CEC) were determined in the University of Missouri Soil and Plant Testing Laboratory following documented procedures (Brown and Rodriguez, 1983).

Soil nutrient extraction

Soil extracts were obtained with a multiple element extractant, the Kelowna solution, according to methods previously reported (Van Lierop, 1986; 1988; Van Lierop and Gough, 1989). A 30-g soil sample was weighed using a standard 2-g soil scoop 15 times and transferred into a 500 mL glass bottle. Soil extractant (300 mL) was added to obtain a 10:1 solution-to-soil ratio by volume.

Figure 7.2. Reciprocating shaker (left) and filtering device (right) for soil nutrient extraction.

As shown in Figure 7.2, the mixtures of soil and solution were shaken on a reciprocating shaker at about 140 cpm (cycles/min) for 5 min and then filtered through Whatman No. 42 filter paper. All soil extracts were titrated to pH 4.0 with 1M NaOH.

Measurement of NPK concentrations in soil extracts using sensor array

To minimize the effects of potential drift and hysteresis that might occur during continuous measurement, the test sequence within each replication was split into three groups, each including normalization solutions, soil extract samples, and validation solution samples. The thirty-seven soil extracts were randomized, and then divided into three groups of 12, 13, and 12 samples.

At the beginning of the test of each group, the four normalization solutions of known NPK concentration level combinations (0.1-0.1-1, 20-0.1-1, 0.1-20-1, and 0.1-0.1-50 mg/L for N, P, and K ions, respectively) were tested in a random order. Five other mixed solution samples (0.1-5-50, 1-20-10, 5-0.1-50, 20-1-3, and 20-20-1 mg/L of N, P, and K ions, respectively) were inserted into each group of randomized soil extracts as validation samples. Immediately after collection of the normalization data, each expanded group (which included a total of either 17 or 18 samples) was analyzed. After testing of the expanded groups, the four normalization solutions were re-tested to verify that sensor response remained unchanged during the test period. Thus, for each replication, the test sequence consisted of normalization samples before and after each expanded group of samples. Three days were required for the test, as each replication of the test sequence took approximately six hrs to complete.

The normalized EMF data obtained from each sensor were used in conjunction with calibration equations previously developed in the mixed solution tests to predict concentrations of NPK ions in soil extracts and validation samples. Sub-samples of the extracted solutions were analyzed in a commercial soil testing laboratory (A&L Great Lakes Laboratories, Fort Wayne, Ind.) using the Lachat FIA system for NO_3-N and the ICP analyzer for P and K measurements to determine actual concentrations in the samples. The instruments for NPK analysis were separately calibrated with Kelowna solution to reduce any differences in the absorbance between the background solution and the sample matrix. The analyses of the sub-samples included an additional 8 randomly selected duplicates for investigating reproducibility of the Lachat analyzer and ICP spectrophotometer. The NPK values measured in the soil extract samples with the sensor array were compared with those determined by the laboratory instruments using linear regression analysis.

For a comparison of the ISE sensor array method to standard soil testing methods, sub-samples of the 37 soils and 8 randomly selected duplicates were provided to the same soil testing laboratory for extraction and analysis. Soil NO_3-N was extracted with 1M KCl and analyzed with a Lachat analyzer based on a 5:1 (25 ml of solution: 5 g of soil v/v) solution-to-soil ratio and a 30-min extraction time. Soil P and K were extracted using the Mehlich III solution based on a 10:1 (20 ml of solution: 2 g of soil v/v) solution-to-soil ratio and a 5-min extraction time, and the concentrations were determined by the ICP spectrophotometer. To investigate the efficiency of NPK extraction by the Kelowna extractant, additional sub-samples of the 37 soils were extracted in the commercial laboratory using the Kelowna extractant, and then analyzed using the same instrumentation described above for the standard methods.

RESULTS AND DISCUSSION

Development of Single Solution Calibration Equations

N calibration

A typical response profile (Fig. 7.3) of an N ISE to the rinsing solution and seven nitrate solutions with different concentrations ranging from 0.1 to 20 mg/L shows repeatable and consistent sensor response when tested in sequence, lowest to highest and then highest to lowest. In addition, the response of the nitrate electrode was repeatable across three replicate measurements, exhibiting consistent sensitivity to different nitrate concentrations.

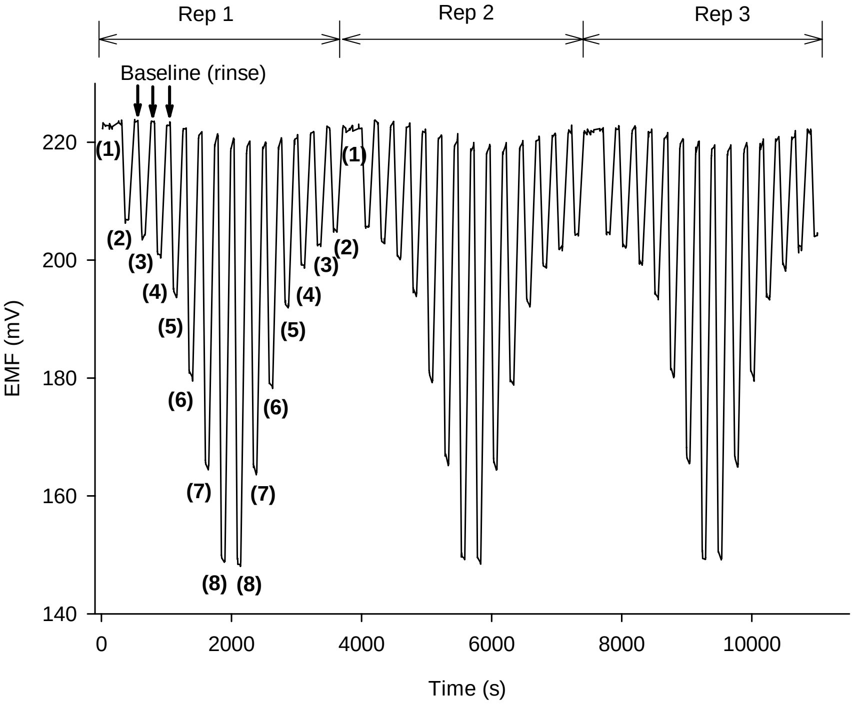


Figure 7.3. Response profiles of an N electrode to different NO_3-N concentrations: (1) 10^{-6}M KNO_3, (2) 0.1, (3) 0.5, (4) 1, (5) 2, (6) 5, (7) 10, and (8) 20 mg/L NO_3-N.

The baseline EMF in the rinse solution containing 10^{-6} M KNO_3 was affected by the concentration of the solution in which the electrode was previously immersed. For example, when the electrode was previously tested in solution of high concentration, the next baseline EMF was slightly lower. The baseline EMF droop of the sensor continued as solutions of higher concentration were sequentially tested.

The direct reading EMF responses (Fig. 7.4) of the five nitrate electrodes differed across the range of nitrate solution concentration levels tested. All five nitrate electrodes had different EMF values at the same nitrate concentrations. It seemed that calibration equations should be separately built for each electrode. Data normalization techniques were explored in search of an overall calibration equation which could be used for prediction of nitrate content using sensing outputs of any nitrate electrode.

Use of two methods, one-point normalization (Fig. 7.5a), which offsets the readings of each the five nitrate electrodes by forcing the value measured in a 20 mg/L solution of one replication to be 150 mV, and baseline correction (Fig. 7.5b), reduced the variability of response among the five electrodes as compared to the initial EMF data (Fig. 7.5).

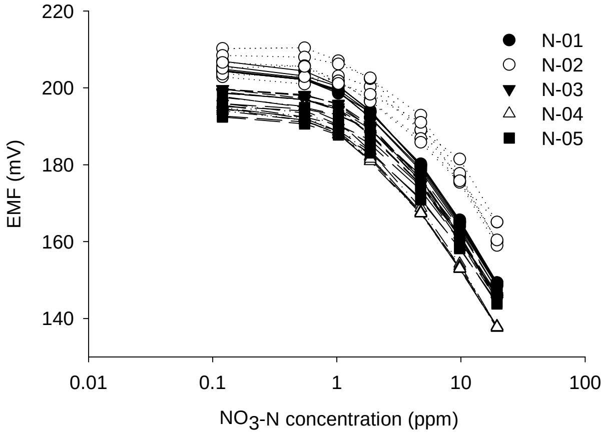


Figure 7.4. Response curves of five N electrodes to different NO_3-N concentrations in single ion solutions.

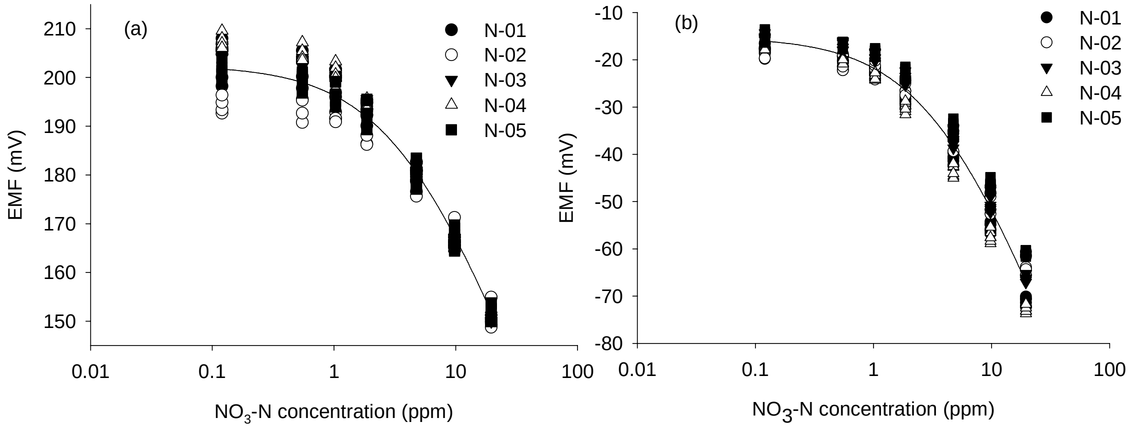


Figure 7.5. Response of five N electrodes to different NO_3-N concentrations obtained using (a) one-point normalization and (b) baseline correction methods.

However, high standard deviations in EMF values were observed at low nitrate concentrations when using the one-point normalization. In addition, even though the baseline correction provided improved reproducibility, there was still a high variability in responses among the electrodes, particularly at higher concentrations, with standard deviations of ~ 15 mV. This variability might be attributed to differences in sensitivity among the electrodes.

Therefore, in addition to baseline correction, a two-point normalization method that not only compensates for different sensitivities, but also for offsets, was used to obtain standardized responses of the five nitrate electrodes and develop an overall calibration equation (Fig. 7.6). Thus, sensor response variability among the five nitrate electrodes was significantly reduced as compared to the variability without 2-point normalization (Fig. 7.4).

A comparison (Fig 7.7) of EMF standard deviations measured with the ISEs for three replicate measurements at different concentrations when using different normalization methods clearly shows that the 2-point normalization was the most effective in reducing the response variability to obtain a representative response curve for the nitrate electrode. The response curves illustrated in each graph (Figs. 7.5 and 7.6) were developed based on logarithmic nonlinear equations using SIGMA Plot 9.0.

In summary, from this investigation, baseline correction was effective in removing short-term potential drifts of each electrode between measurements and two-point normalization was useful not only for adjusting the response of an individual electrode to a standardized response but also for compensating for changes in the sensitivity of an electrode over a larger time period (e.g., between days or replications).

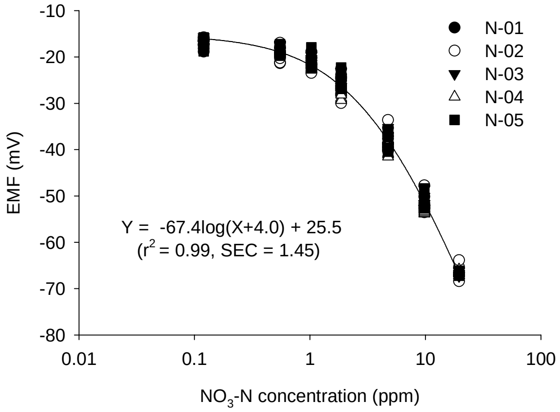


Figure 7.6. Response of five N electrodes to different NO_3–N concentrations obtained using both baseline correction and 2-point normalization methods.

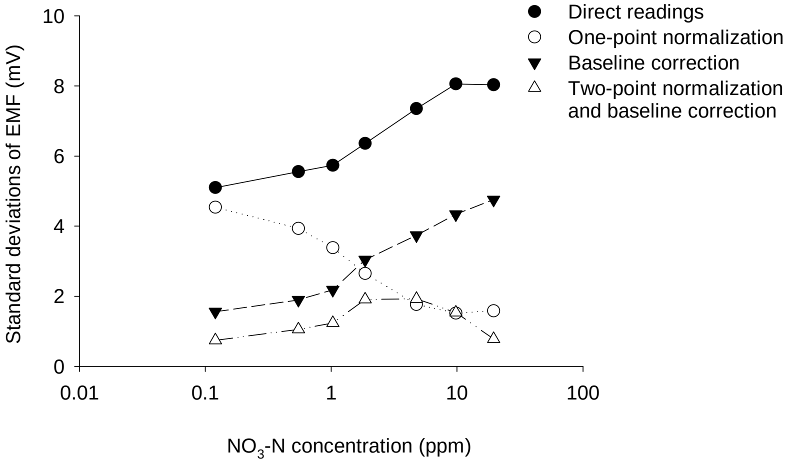


Figure 7.7. Comparison of standard deviations in EMF obtained at different concentration levels using different normalization methods.

P and K calibration

As observed with the responses of the nitrate ISEs, the P (Fig. 7.8a) and K (Fig. 7.8b) electrodes exhibited repeatable and consistent sensor response when tested in sequence, during three replicate measurements.

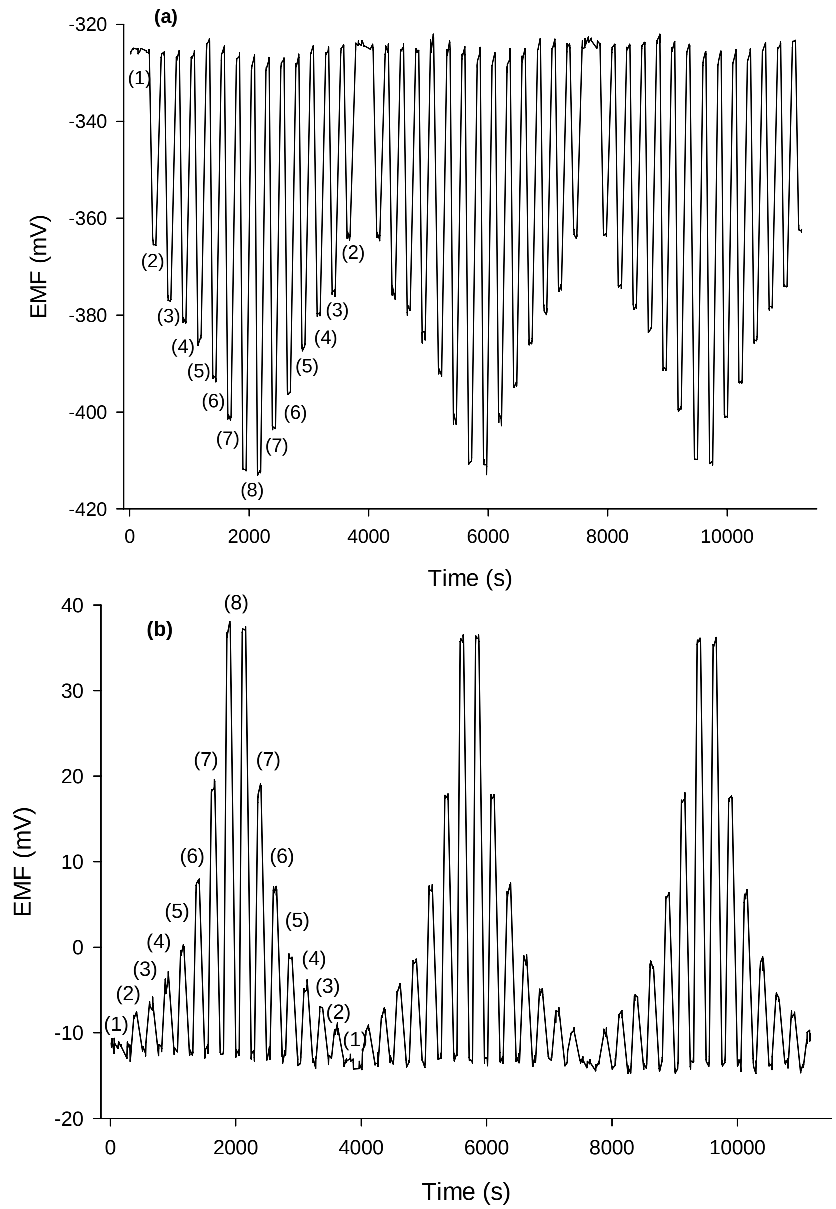


Figure 7.8. Response profiles of P electrode (a) and K electrode (b) to varying P and K concentrations: (1) 10^{-6}M KNO3, (2) 0.1 and 1, (3) 0.5 and 2 (4) 1 and 3, (5) 2 and 5, (6) 5 and 10, (7) 10 and 20, and (8) 20 and 50 mg/L for P and K, respectively.

Figures 7.9 and 7.10 compare two response curves obtained with initial EMF readings and normalized EMF readings for P and K electrodes, respectively. It is evident that the baseline correction and 2-point normalization techniques compensated for the different sensitivities and offsets of the five electrodes effectively. In the K electrodes, one of the tested five electrodes, K-04 (Fig. 7.10a) showed poor repeatability at low concentrations and the lowest concentration point for 2-point normalization was difficult to choose. Thus, the EMF data measured with the K-04 electrode were deleted from the dataset used in building the overall calibration equation.

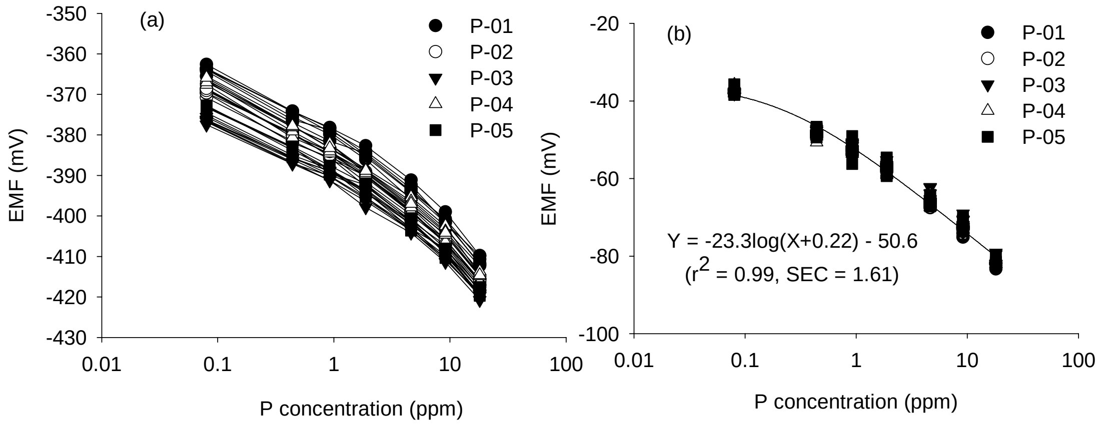


Figure 7.9. Response curves of (a) five P electrodes and (b) normalized responses to different phosphorus concentrations.

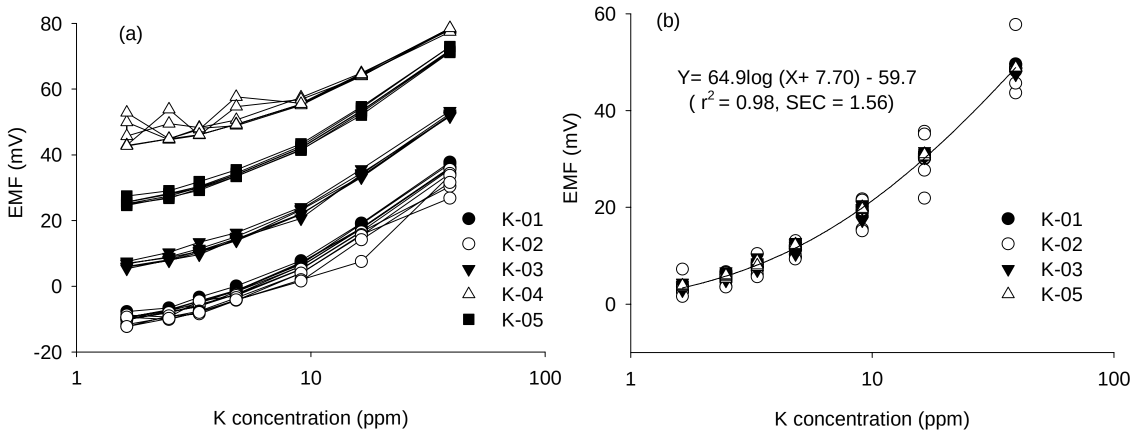
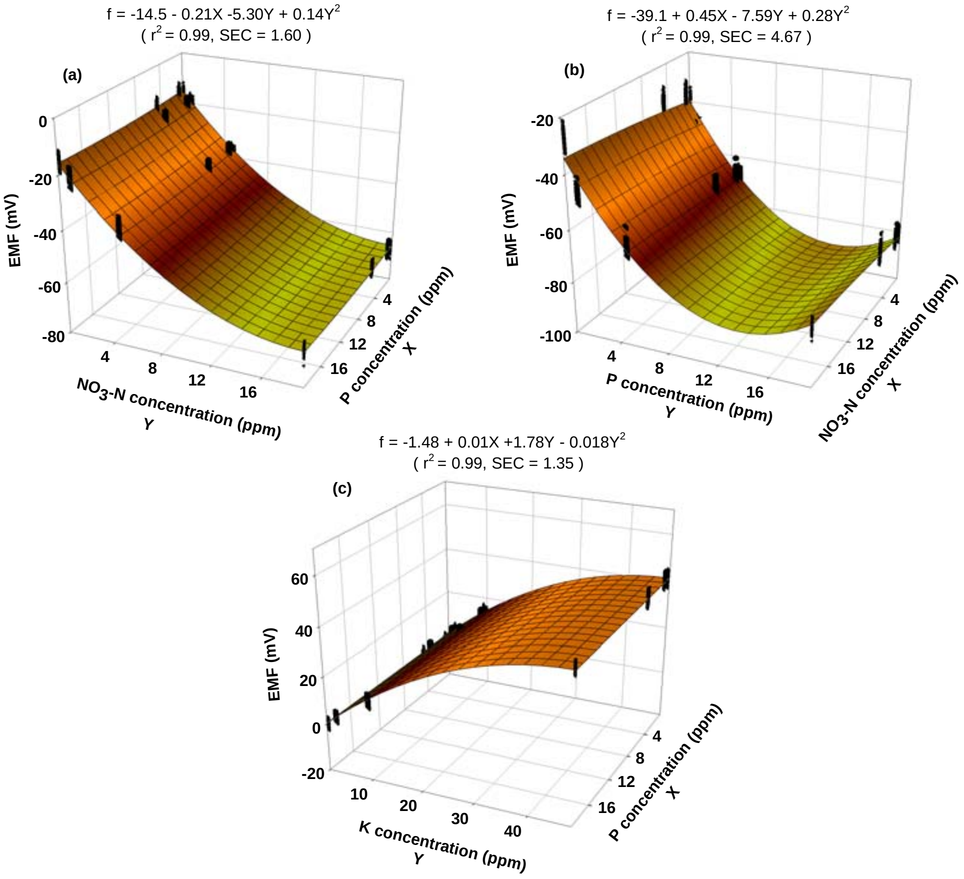


Figure 7.10. Response curves of (a) five K electrodes and (b) normalized responses to different potassium concentrations.

Development of Mixed Solution Calibration Equations

Investigation of interactive effects between ions

An investigation of interactive effects of NPK ions on electrode response was conducted with 64 solutions containing four different concentration levels of NPK ions titrated to pH 4.0. Figures 7.11 and 7.12 graphically show how the presence of three ions in solution affected the EMF responses of individual NPK sensors. The three-dimensional response surfaces (Fig. 7.11) of the three different electrode types to mixtures of four different levels of NPK ions were obtained based on fitting using a least squares method to find the best surface for each sensor.


$f = -14.5 - 0.21X -5.30Y + 0.14Y^2$
($r^2 = 0.99$, SEC = 1.60)

$f = -39.1 + 0.45X - 7.59Y + 0.28Y^2$
($r^2 = 0.99$, SEC = 4.67)

$f = -1.48 + 0.01X +1.78Y - 0.018Y^2$
($r^2 = 0.99$, SEC = 1.35)

Figure 7.11. Response surfaces of N (a), P (b), and K (c) electrodes to mixtures of NPK ions with different concentrations.

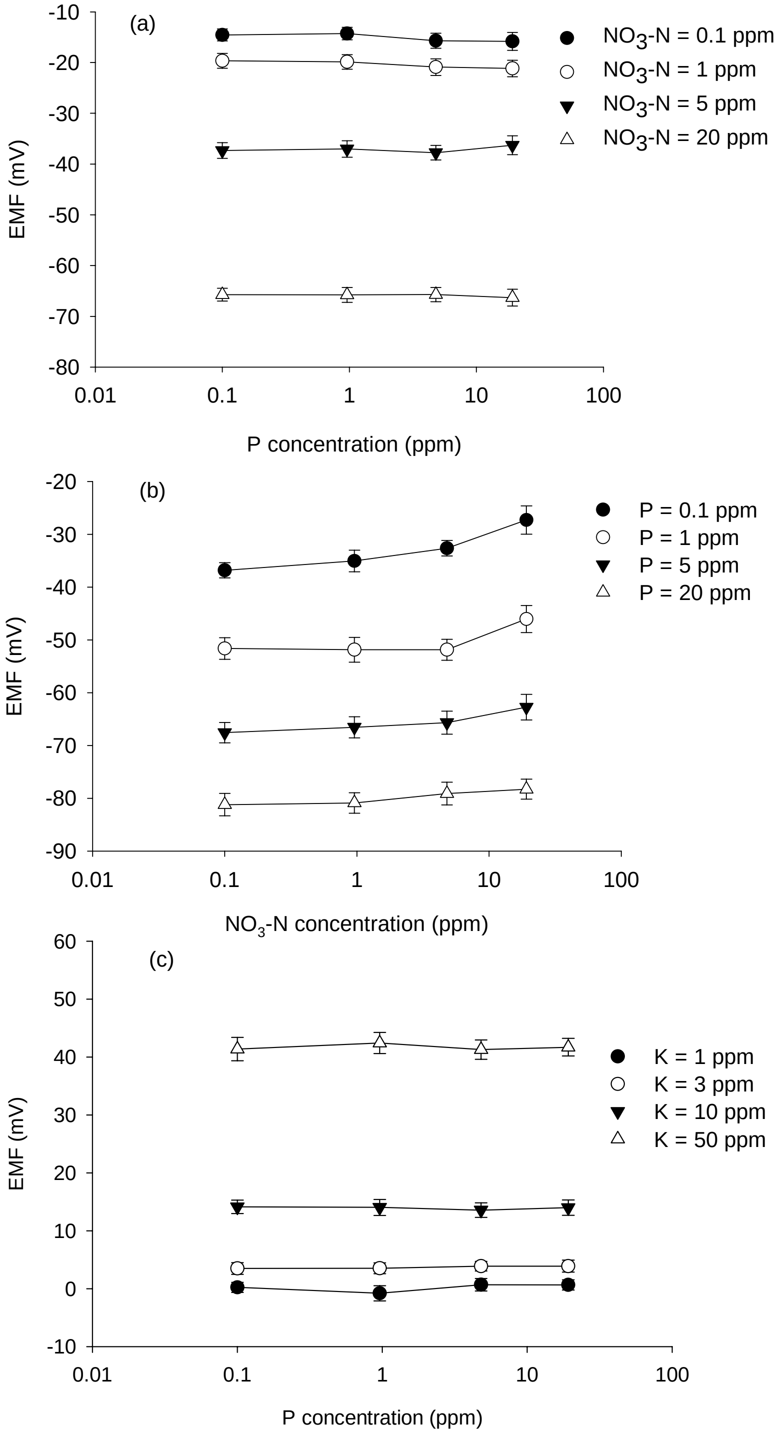


Figure 7.12. Effects of NPK ions on electrode response: (a) N ISEs, (b) P ISEs, and (c) K ISEs.

As expected, the nitrate and potassium electrodes (Fig. 7.11a and 7.12a for N, and Fig. 7.11c and 7.12c for K) were sensitive to different nitrate and potassium concentrations, respectively. The shapes of the response surfaces are different, however, because the nitrate ISE is an anion-sensitive sensor whereas the potassium electrode is a cation-sensitive sensor.

Figure 7.12 shows that the presence of phosphate ions at different concentrations in solution does not interfere with EMF responses of the nitrate and potassium electrodes. The phosphate electrodes (Fig. 7.11b) exhibited a sensitive response to different phosphate concentrations. Moreover, as shown in Figure 7.12b, the responses of the P electrodes appeared to be influenced by the presence of high concentrations of nitrate-N ($\geq$ 5mg/L) in mixtures, yielding an EMF change of about 5 ~ 10 mV, thereby resulting in reduced P sensitivity at high nitrate concentrations.

The results of SAS GLM analysis of the significance of the three ions on sensing responses of the N, P, and K electrodes are shown in Tables 7.2, 7.3, and 7.4, respectively. All of the general linear models for the NPK electrodes, when using logarithmic scale NPK values as predictor variables and normalized EMF values as response variables, provided good fits with high coefficients of determination ($r^2 > 0.97$).

The GLM results show that although the effects of electrode and replication for each primary ion were considerably reduced as compared to those obtained without baseline correction and 2-point normalization (data not shown), they were still significant. This might be because the calibration equations relating electrode response to analyte concentration are non-linear. However, since the F values of electrode, replication, and

Table 7.2. Results of GLM procedure testing the significance of NPK ions on responses of N electrodes.

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	23	376293.7107	16360.5961	6026.46	<.0001
Error	936	2541.0467	2.7148		
Corrected Total	959	378834.7574			
	R-Square	Coeff Var	Root MSE	Mean	
	0.993292	-4.759655	1.647663	-34.61728	

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Electrode	4	353.5015	88.3754	32.55	<.0001*
rep	2	67.2992	33.6496	12.39	<.0001*
electrode*rep	8	58.7193	7.3399	2.70	0.0060*
LgN	1	189590.5	189590.5	69836.1	<.0001*
LgP	1	38.7558	38.7558	14.28	0.0002*
LgK	1	0.1566	0.1566	0.06	0.8102
LgN*LgN	1	60139.82	60139.8	22152.6	<.0001*
LgP*LgP	1	2.7716	2.7716	1.02	0.3126
LgK*LgK	1	0.8134	0.8134	0.30	0.5842
LgN*LgP	1	2.7498	2.7498	1.01	0.3145
LgP*LgK	1	0.1884	0.1884	0.07	0.7923
LgN*LgP*LgK	1	14.5732	14.5732	5.37	0.0207*

electrode*replication were much lower than those of the primary ions, it was expected that accurate calibration equations could be developed without including these terms.

For the nitrate electrodes (Table 7.2), as expected, the N ion was the most significant variable affecting the sensing responses. The two-way interaction terms including the pairs of NPK ions did not significantly affect the sensor responses. Even though the P ion had a significant effect, it was thought that the model describing the relationship between multiple ions and EMF readings of the nitrate electrodes could be established with only the first and the second order N terms, because the F value for the P variable effect was much smaller than those for nitrate.

Table 7.3. Results of GLM procedure testing the significance of NPK ions on responses of P electrodes.

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	23	277754.8473	12076.2977	3222.62	<.0001
Error	867	3248.9574	3.7474		
Corrected Total	890	281003.8048			

R-Square	Coeff Var	Root MSE	Mean
0.988438	-3.388176	1.935809	-57.13424

Source	DF	Type III SS	Mean Square	F Value	Pr > F
electrode	4	604.69080	151.17270	40.34	<.0001*
rep	2	132.88992	66.44496	17.73	<.0001*
electrode*rep	7	203.68617	29.09802	7.76	<.0001*
LgN	1	1522.38339	1522.38339	406.26	<.0001*
LgP	1	88473.05388	88473.05388	23609.5	<.0001*
LgK	1	11.10275	11.10275	2.96	0.0856
LgN*LgN	1	787.23410	787.23410	210.08	<.0001*
LgP*LgP	1	1288.10600	1288.10600	343.74	<.0001*
LgK*LgK	1	3.41733	3.41733	0.91	0.3399
LgN*LgP	1	130.41280	130.41280	34.80	<.0001*
LgP*LgK	1	0.00371	0.00371	0.00	0.9749
LgN*LgK	1	65.16875	65.16875	17.39	<.0001*
LgN*LgP*LgK	1	18.87678	18.87678	5.04	0.0251*

As presented in Table 7.3, the P electrodes were significantly influenced by both P and N ions. Therefore, the EMF response function of the P electrodes could be well modeled using terms consisting of the P and N variables.

The effect of N and P ions on the K electrodes was not significant, but a two-way interaction term of N x P had a significant effect with an F value of 10.33 (Table 7.4). Overall, the K electrode was significantly affected by the primary ion, K, in the 2nd order form, suggesting that the response curve could be modeled based on polynomial regression using the 2nd order term of the K ion.

Table 7.4. Results of GLM procedure testing the significance of NPK ions on responses of K electrodes.

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	24	254490.8122	10603.7838	6030.64	<.0001
Error	935	1644.0262	1.7583		
Corrected Total		959	256134.8384		

R-Square	Coeff Var	Root MSE	Mean
0.993581	8.912236	1.326015	14.87859

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Electrode	4	75.87598	18.96900	10.79	<.0001*
rep	2	30.75211	15.37605	8.74	0.0002*
electrode*rep	8	31.12474	3.89059	2.21	0.0245*
LgN	1	1.29709	1.29709	0.74	0.3906
LgP	1	6.52869	6.52869	3.71	0.0543
LgK	1	3.11578	3.11578	1.77	0.1835
LgN*LgP	1	18.16614	18.16614	10.33	0.0014*
LgN*LgK	1	0.00501	0.00501	0.00	0.9575
LgP*LgK	1	6.52349	6.52349	3.71	0.0544
LgN*LgN	1	1.13970	1.13970	0.65	0.4210
LgP*LgP	1	3.39153	3.39153	1.93	0.1652
LgK*LgK	1	21936.37506	21936.37506	12475.8	<.0001*
LgN*LgP*LgK	1	6.12437	6.12437	3.48	0.0623

Effect of baseline correction on sensor reproducibility

It is generally thought that continuous measurement with ion-selective electrodes in a series of solutions is limited by electrode response drift and hysteresis. Therefore, minimizing or controlling the drift and hysteresis is important to obtain precise results so that the sensor readings are reproducible (Ammann, 1986). According to technical information regarding the use of ion-selective electrodes (IUPAC, 1994), drift is defined as a slow non-random change with time in the EMF of an ion-selective electrode in a solution of constant composition. Also, hysteresis, electrode memory, is considered to be a kinetic process occurring when there is a difference between the EMF readings first observed in a solution having concentration level A, and a second observation of the EMF in the same solution after exposing the electrode to a different solution with concentration level B.

Under our experimental conditions the electric potentials of three different types of sensors were measured repeatedly in a series of 64 mixed solutions along with rinse solution for about 5 ~ 6 hours during each replication. As shown in Figure 7.13, drift was observed in the baseline potentials of N and K electrodes for at least some of the replications. The drift may have occurred due to incomplete washing of the electrodes due to the limited number of rinses, a change in liquid junction potential, and/or ambient temperature change (about 1.0 ~ 3.5 °C) during the test.

Three replications of the typical EMF response of each of the three NPK electrode types to varying NPK concentrations without (Figs. 7.14(left)) and with (Figs. 7.14(right)) baseline correction are illustrated. Baseline correction was accomplished by subtracting the baseline EMF value in the proceeding rinse solution from the electrode direct EMF response. The baseline correction improved reproducibility of both N and K electrodes, which utilize ion-selective membrane technology. However, as observed in Figure 7.13b, the baselines of the P electrodes, which utilize cobalt rod technology, did not drift, implying that the use of baseline correction does not affect the reproducibility of the P electrodes (Fig. 7.14b). Although there was no evident influence of baseline correction on the responses of P electrodes, the baseline correction method was applied to data obtained from all of the N, P, and K electrodes to maintain a consistent approach for analysis.

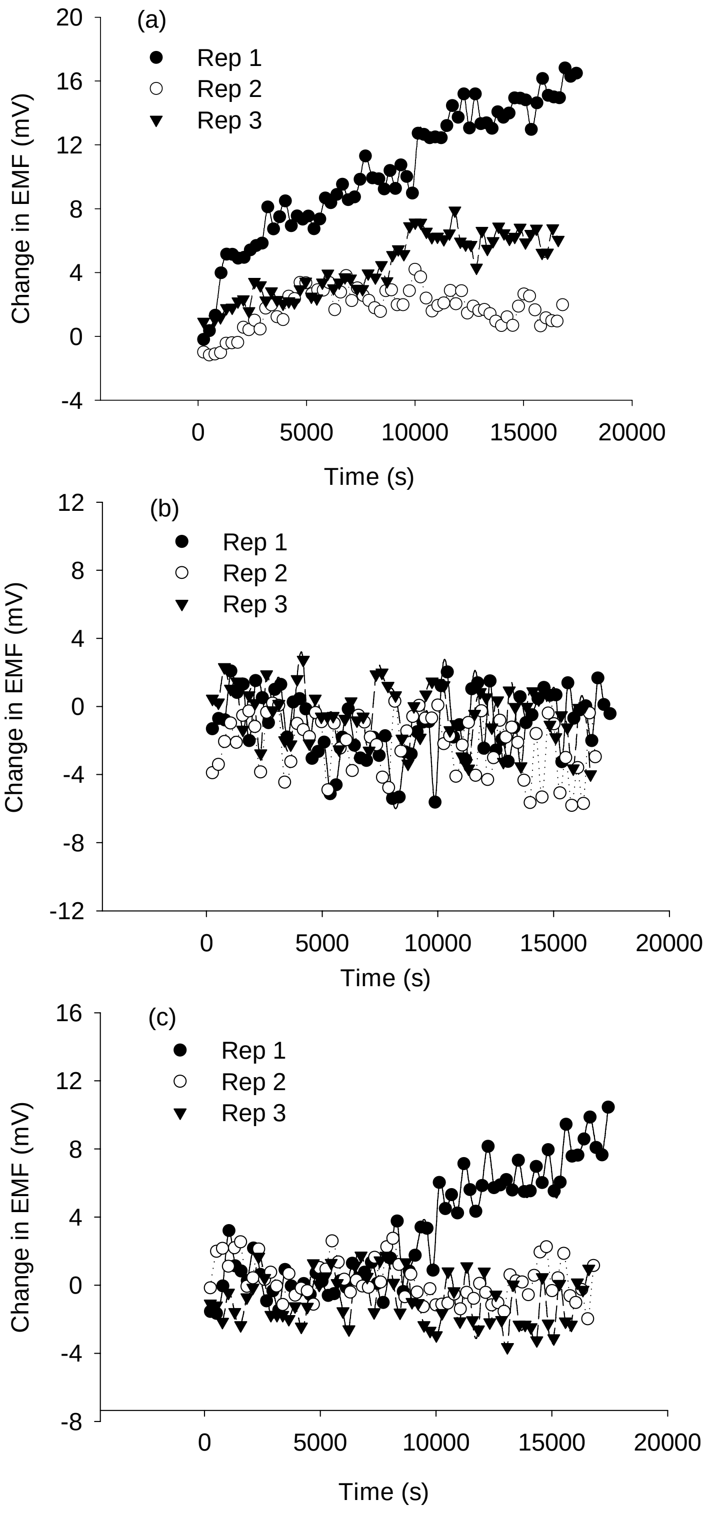


Figure 7.13. Change in baseline EMF over time for N (top), P (middle), and K (bottom) electrodes.

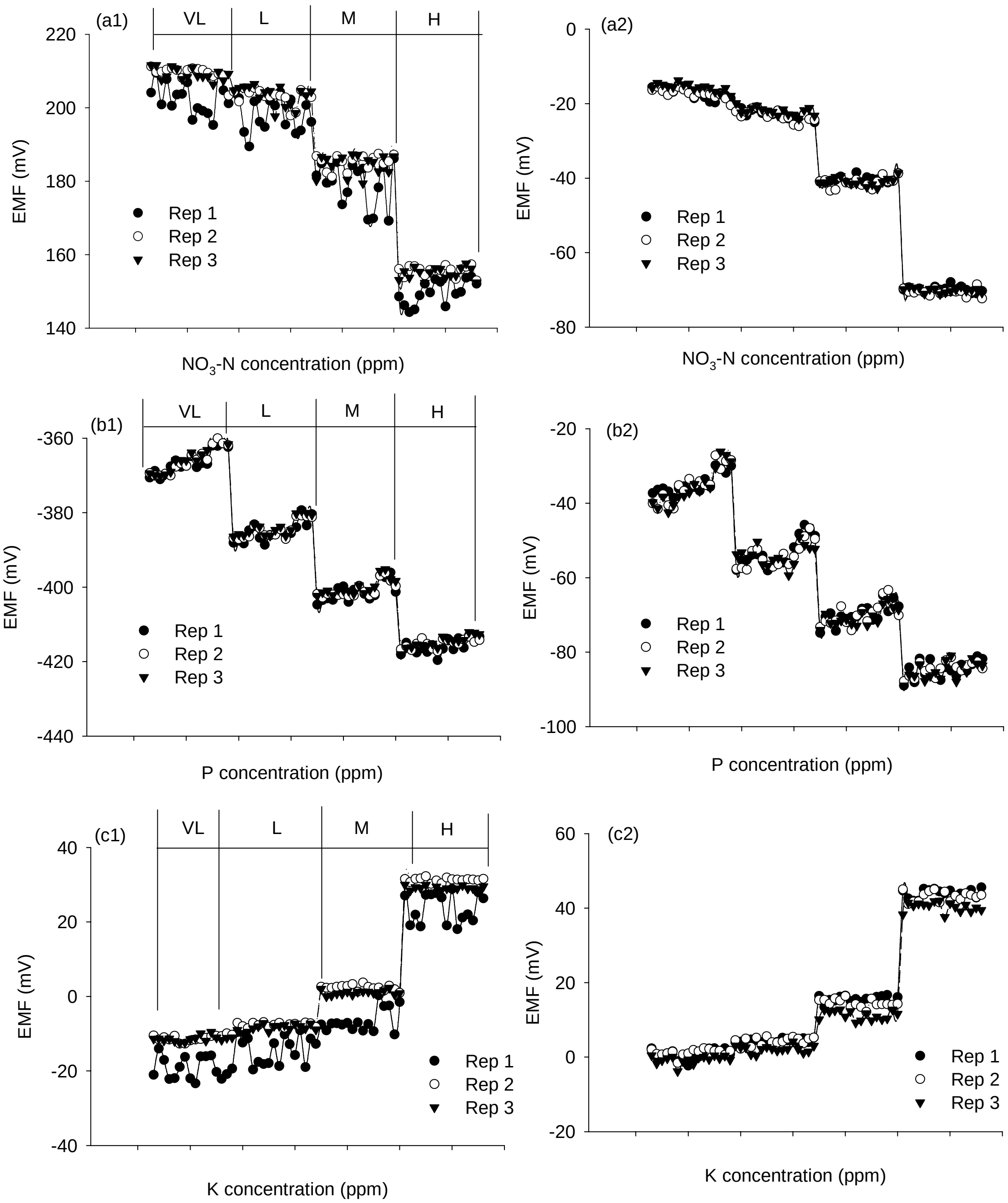


Figure 7.14. Effect of baseline correction (a1,b1, c1: without, a2, b2, c2: with) on sensing reproducibility of N (a1,a2), P (b1, b2), and K (c1, c2) electrodes measured at different concentration levels (very low (VL, 0.1, 0.1, and 1 mg/L), low (L, 1,1, and 3 mg/L), medium (M, 5,5, and 10 mg/L), and high (H, 20,20, and 50 mg/L for N, P, and K ions, respectively)).

Development of NPK calibration equations using mixed solutions

The extended Nernst equation (7.2) was transformed for nonlinear regression analysis into the following equation consisting of ionic activity as a response variable and electric potential as an independent variable:

$$a_i = 10^{\left(\frac{EMF - E_S - E_J}{S}\right)} - \sum K_{ij} a_j^{Zi/Zj} \tag{7.3}$$

For the N and K electrodes, based on the above equation, the ionic activity term and selectivity term can be simply replaced by concentrations of the corresponding ions, i.e., N and K, and interference terms, i.e., K_{SN} and K_{SK} for N and K, respectively:

$$N = 10^{\left(\frac{EMF_N - E_{oN}}{S_N}\right)} - K_{SN} \tag{7.4}$$

$$K = 10^{\left(\frac{EMF_K - E_{oK}}{S_K}\right)} - K_{SK} \tag{7.5}$$

where:

N and K = N and K concentrations

EMF_N and EMF_K = electric potentials measured with N and K electrodes

S_N and S_K = sensitivity slopes

E_{oN} and E_{oK} = sums of standard potential and liquid junction potential for N and K electrodes

K_{SN} and K_{SK} = interference terms for N and K electrodes.

Since significant effects of both P and N ions on responses of the P electrodes were found (Table 7.3), nitrate effects were added to the concentration and sensitivity terms in the following equation:

$$EMF_P = E_{oP} + (S_P + K_{N1}N)\log_{10}(P + K_{N2}N + \sum K_{ij}a_j^{Zi/Zj}) \qquad (7.6)$$

$$P = 10^{\left(\frac{EMF_P - E_{oP}}{S_P + K_{N1}N}\right)} - K_{N2}N - K_{SP} \qquad (7.7)$$

where:

P = phosphorus concentration

EMF_P = electric potential measured with P electrode

$K_{N1}*N$ and $K_{N2}*N$ = interference terms due to N ion

S_P = sensitivity slope

E_{oP} = sum of standard potential and liquid junction potential

K_{SP} = interference term by other ions.

The SAS Non-Linear Regression Procedure (NLIN) was used to determine model parameters for the three equations (7.4, 7.5, and 7.7) by means of an iterative approach. The estimates of parameters for the NPK calibration equations using the SAS NLIN regression procedure are shown in Tables 7.5, 7.6, and 7.7 for the N, P, and K sensors, respectively. The root mean square errors (RMSE) for the NPK sensors were 0.66, 1.61, and 1.53 mg/L, respectively. The coefficients of determination for the three equations were > 0.97**.

Table 7.5. Estimates of calibration equation parameters for N ISEs using SAS NLIN regression analysis.

Source	DF	Sum of Squares	Mean Square	F Value	Approx Pr > F
Model	2	56536.8	28268.4	64110.2	<.0001
Error	957	422.0	0.4409		
Corrected Total	959	56958.8			

Parameter	Estimate	Approx Std Error	Approximate 95% Confidence Limits	
E_{oN}	33.8184	1.9437	30.0040	37.6329
S_N	-72.4749	1.2387	-74.9058	-70.0440
K_{SN}	4.5845	0.1901	4.2114	4.9576

Table 7.6. Estimates of calibration equation parameters for P ISEs using SAS NLIN regression analysis.

Source	DF	Sum of Squares	Mean Square	F Value	Approx Pr > F
Model	4	42980.3	10745.1	4145.26	<.0001
Error	886	2296.6	2.5921		
Corrected Total	890	45277.0			

Parameter	Estimate	Approx Std Error	Approximate 95% Confidence Limits	
E_{oP}	-40.1444	1.0172	-42.1409	-38.1479
S_p	-33.2840	0.7426	-34.7415	-31.8266
K_{SP}	1.2008	0.1493	0.9077	1.4939
K_{N1}	0.0973	0.0102	0.0772	0.1173
K_{N2}	-0.0400	.00866	-0.0570	-0.0230

Table 7.7. Estimates of calibration equation parameters for K ISEs using SAS NLIN regression analysis.

Source	DF	Sum of Squares	Mean Square	F Value	Approx Pr > F
Model	2	211949	105975	45440.9	<.0001
Error	957	2231.9	2.3321		
Corrected Total	959	214181			

Parameter	Estimate	Approx Std Error	Approximate 95% Confidence Limits	
E_{oK}	-102.3	4.9688	-112.1	-92.5516
S_k	83.2520	2.5138	78.3187	88.1853
K_{SK}	15.3599	0.9357	13.5236	17.1963

Model Validation

The results of comparing the predictive capability of a set of calibration equations based on data obtained with single ion solutions with a set of calibration equations based on data collected using mixed solutions are shown in Figure 7.15. One replication of the data obtained with the 64 mixed solutions was used as a validation dataset.

At low and medium concentration levels of NPK ions (i.e. $\leq$ 5 mg/L NO_3-N and P, and $\leq$ 10 mg/L K), the two different sets of calibration equations provided good prediction capability showing mean prediction errors between the measured and actual values of $\pm$2 mg/L. However, at high concentrations (i.e., 20 mg/L NO_3-N and PO_4-P, and 50 mg/L K), the error increased to $\pm$ 8 mg/L. In general, the variation in the predicted values of the NPK sensors became higher as sample concentrations increased. This problem might be related to the fact that the responses of ion-selective electrodes are linearly proportional to the logarithm of ionic concentration rather than the concentration itself.

Linear regression analyses comparing the sensor NPK values from different calibration equations to actual values determined by analytical instruments (Table 7.8) show that strong relationships ($r^2 \geq 0.94^{**}$) were obtained and the N and K values determined using either of the calibration equations were very similar to the actual concentration values. However, even though high coefficients of determination were found in the P measurement, the regression slope obtained with the separate calibration equation was relatively low (0.84). As shown in Figure 7.15, the decreased slope might be attributed to poor prediction capability at a high concentration (20 mg/L P). This problem might be explained by an interactive effect of nitrate in the mixed solutions on the P electrode response. As found earlier, the responses of the P electrodes were reduced when the solution contained high concentrations of nitrate-N.

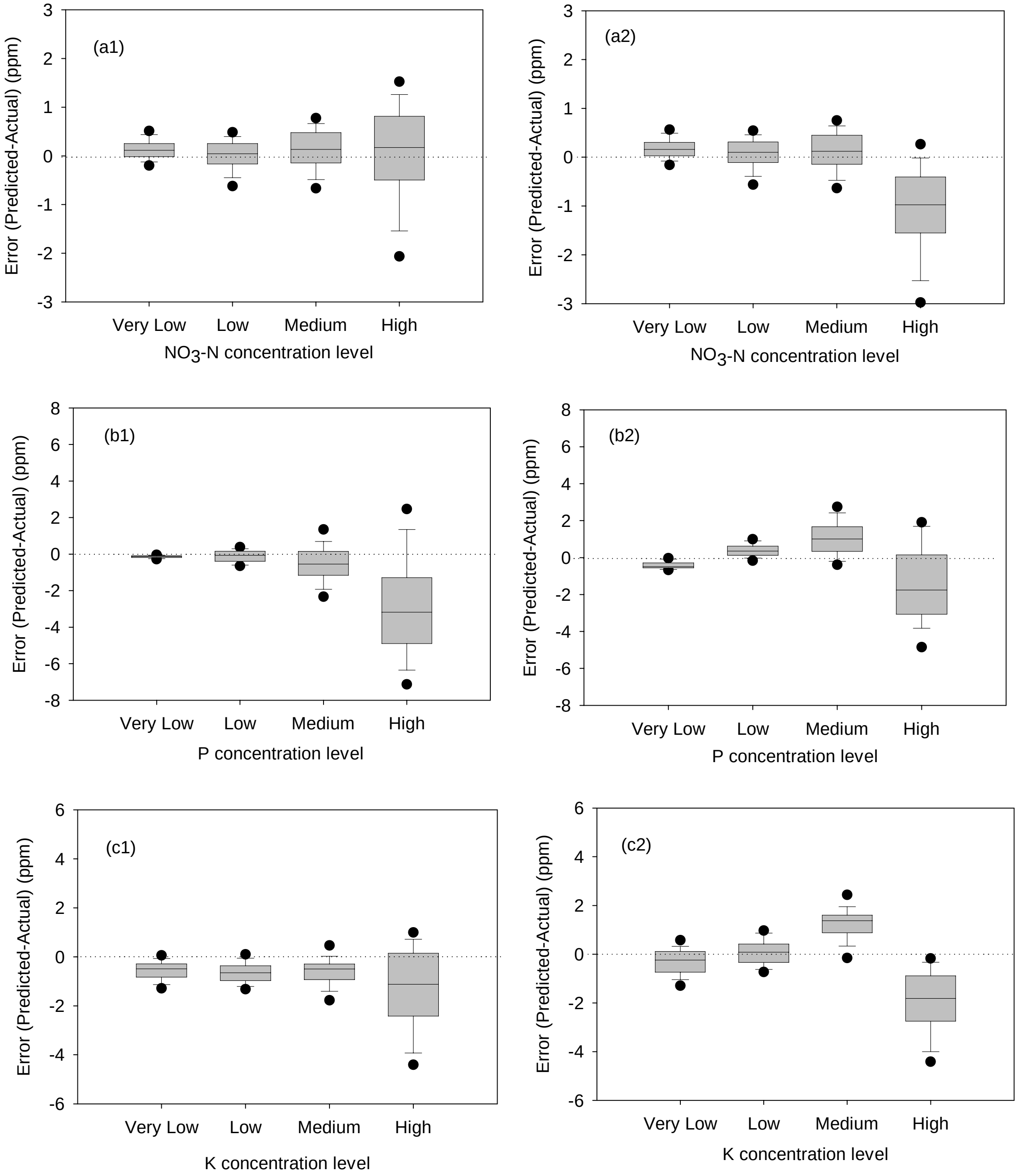


Figure 7.15. Comparison of variability in NPK concentrations predicted from separate (a1,b1,c1) and mixed (a2,b2,c2) calibration equations at four different concentration levels: (a1,a2) nitrate-N, (b1,b2) phosphorus, and (c1,c2) potassium measurements.

Table 7.8. Comparison between regression equations obtained with single NPK ion solutions and with mixed NPK solutions.

Ion	Dataset	Predicted value(Y) vs. Actual value(X)	Coefficient of determination (r^2)	SEP[c]
NO_3-N	S[a]	Y = 0.99X + 0.09	0.99	0.58
	M[b]	Y = 0.93X + 0.24	0.99	0.54
P	S	Y = 0.84X + 0.04	0.94	1.47
	M	Y = 0.91X + 0.44	0.96	1.33
K	S	Y = 0.99X + 0.09	0.99	0.98
	M	Y = 0.94X + 0.56	0.99	1.14

[a] S = single ion solution data.
[b] M = mixed solution data.
[c] SEP = standard error of prediction in mg/L.

The use of mixture calibration equations for P measurement improved the regression results as compared to those obtained with separate calibration equations (Table 7.8). Therefore, it was concluded that NPK calibration equations obtained from mixed solution tests would be more efficient than those developed with single ion solution tests due to the better prediction of P ions in the mixtures of NPK ions.

Soil Extract Tests

Validation Tests with Known Samples

The validation results of the sensor array in the soil extract tests using five known mixtures containing different NPK concentrations are shown in Table 7.9. The values determined by the nitrate and potassium electrodes were in good agreement with the actual values, yielding almost 1:1 relationships between the predicted (Y) and actual (X) values: Y = 0.97X + 1.13 (r^2 = 0.98**) for nitrate ISEs, and Y = 1.00X + 1.16 (r^2 = 0.99**) for potassium ISEs. The P electrodes also showed a slope near unity (Y = 1.02X + 0.36). However, as shown in Table 7.9, a high variation in prediction values (maximum standard deviation of 8.38 mg/L) was observed at the highest P concentration of 20 mg/L, yielding a lower coefficient of determination (r^2) of 0.88**.

This validation (Table 7.9) shows that the array of N, P, and K electrodes, in conjunction with the developed calibration equations, allowed the mixtures of NPK ions to be accurately analyzed, indicating that the electrodes, in combination with the normalization and calibration procedures, provided consistent data during the soil extract test.

Table 7.9. Comparison of actual and ISE-predicted concentrations for five validation samples.

	Actual concentration, mg/L			Predicted concentration, mg/L		
sample	NO_3-N	P	K	NO_3-N	P	K
1	0.21	4.56	37.10	0.79 ±0.45	6.26 ±2.51	38.4 ±1.50
2	0.97	17.90	8.09	2.44 ±0.89	18.2 ±6.53	10.1 ±0.57
3	4.95	0.21	36.60	6.18 ±0.65	-0.3 ±0.14	37.9 ±1.61
4	18.36	0.93	2.69	18.37 ±1.62	1.36 ±0.40	3.93 ±0.46
5	18.25	17.80	1.48	19.3 ±1.69	21.7 ±8.38	1.96 ±0.35

Reproducibility of laboratory instruments

Figure 7.16 shows the differences in concentrations of NPK for eight duplicate soil extract and soil samples, respectively, obtained with the Lachat and ICP analyzers for N, and P and K ions, respectively.

The Lachat analyzer provided NO_3-N values with maximum absolute differences of 0.3 mg/L and 25 mg/L for soil extract and soil samples, respectively. When using the ICP spectrophotometer, differences in P and K measurements for the soil extract check samples were about 0.3 mg/L and 0.4 mg/L, whereas those for soil samples were 10 mg/L and 25 mg/L, respectively. When considering a dilution ration of 10:1(solution: soil), the differences were higher than those for the soil extract samples, i.e., 2.5, 1.0, and 2.5

mg/L for N, P, and K, respectively, which might be attributed to variations in nutrient amounts extracted and weighed among sub-samples.

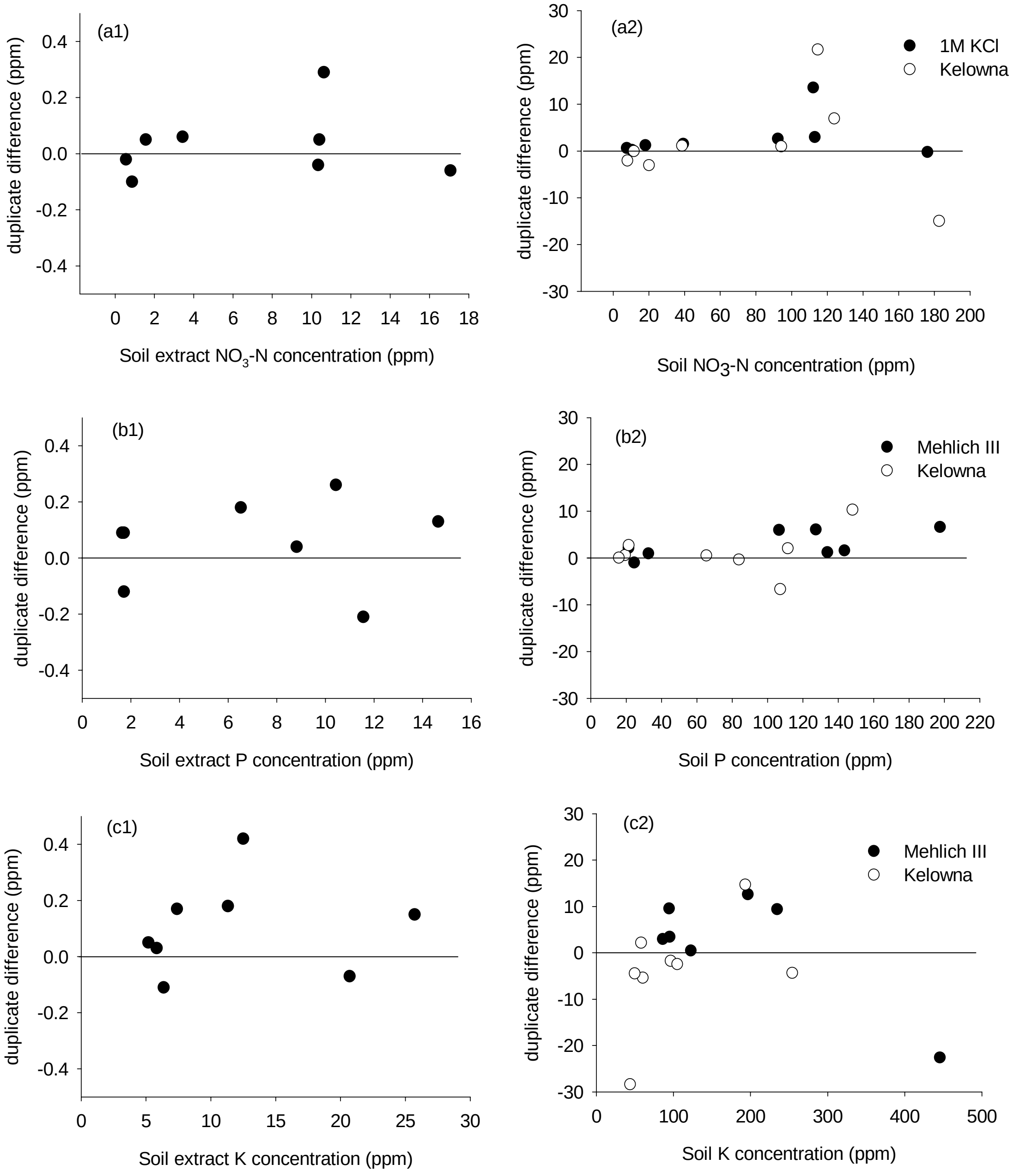


Figure 7.16. Investigation of laboratory instrument repeatability using duplicate soil extract (left: a1, b1, and c1 for N, P, and K, respectively) and (right: a2, b2, and c2 for N, P, and K) samples.

From this investigation, it was found that the Lachat and ICP analyzers for NPK analysis might provide measurement errors within 0.3 mg/L and 25 mg/L for soil extract and soil samples, respectively. According to instrument specifications, detection limits of the Lachat and ICP analyzers were 0.5 mg/L, 0.5 mg/L, and 1 mg/L for NO_3-N, P, and K analysis.

Comparison of solution NPK determinations by ISE and by standard instruments

Figures 7.17, 7.18, and 7.19 show the regression relationships between soil extract NPK values in soil extracts determined by individual NPK sensors and by standard instruments, i.e., the Lachat analyzer for N and the ICP spectrophotometer for P and K measurements. The regression results for the NPK sensors when the responses measured with all five electrodes were combined are presented in Figure 7.20.

When comparing the amounts of nitrate-N in soil extracts determined by the N ISEs to the Lachat analyzer values (Fig. 7.17 and Fig. 7.20a), strong linear relationships ($r^2 > 0.92^{**}$) were observed with a slope near 1. However, on average, a relatively high offset of 2 mg/L was obtained.

Highly significant relationships ($r^2 > 0.94^{**}$) were found between potassium amounts measured with the K ISEs and ICP analyzer (Fig. 7.19, and Fig. 7.20c). Since the regression slopes were close to 1 and there were only relatively small y-intercepts of < 1 mg/L, it was expected that there was little difference in potassium quantity estimated by the two methods.

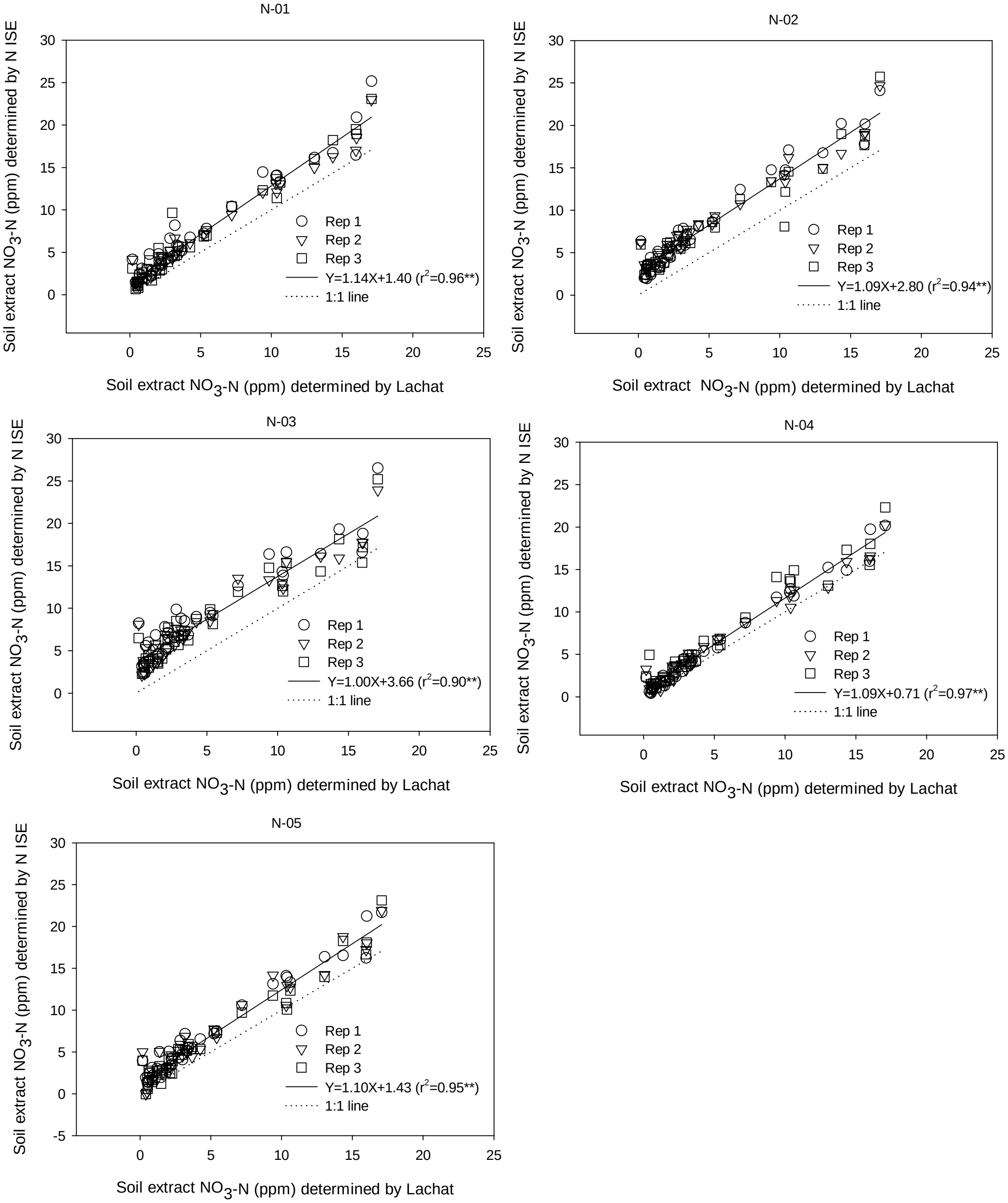


Figure 7.17. Relationships between soil extract NO_3-N determined by individual N ISEs and Lachat.

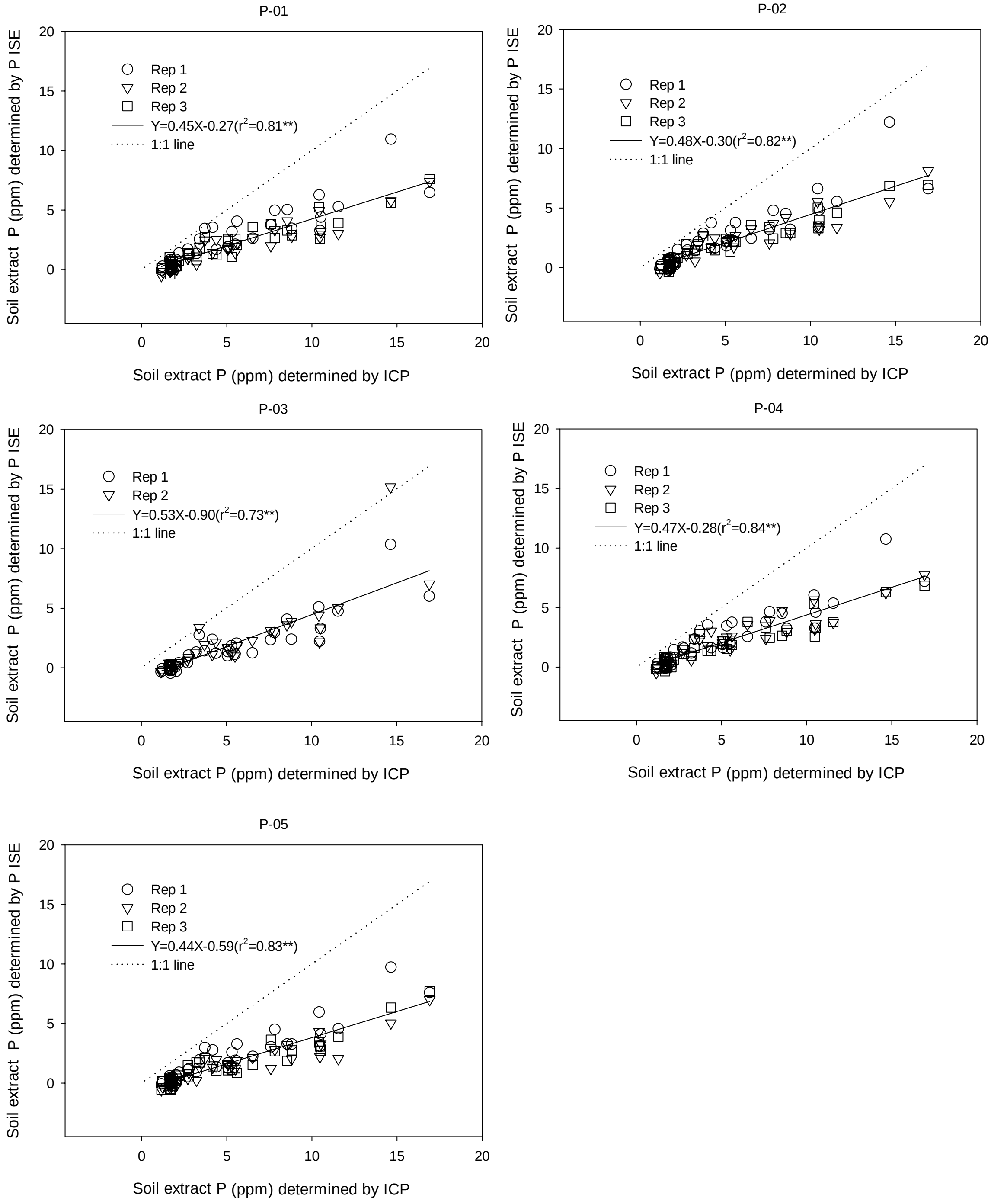


Figure 7.18. Relationships between soil extract P determined by individual P ISEs and ICP.

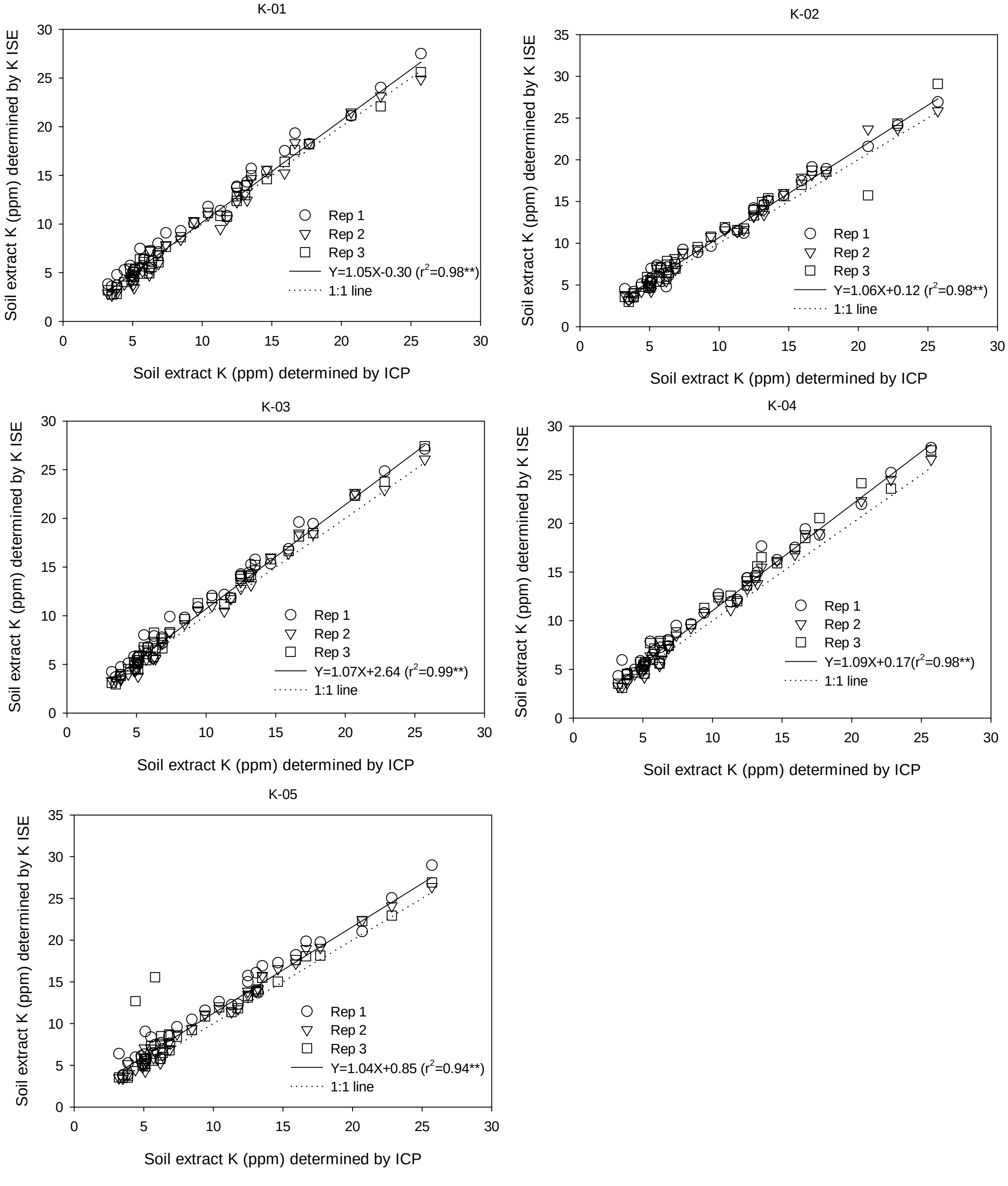


Figure 7.19. Relationships between soil extract K determined by individual K ISEs and ICP.

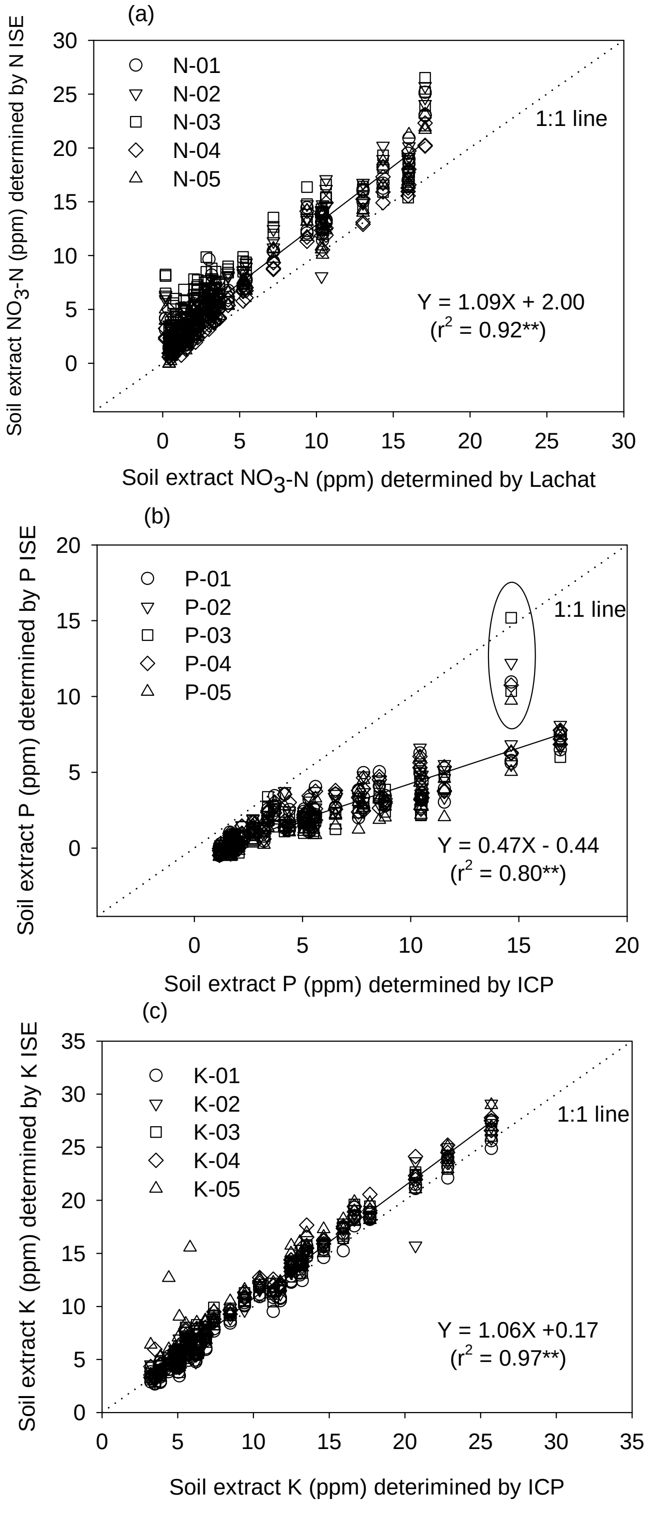


Figure 7.20. Relationships between (a) NO_3-N, (b) P, and (c) K determined by five ISEs and by standard instruments, i.e., Lachat for N and ICP for P and K.

On the other hand, as shown in Figure 7.18 and 7.20b, on average, the regression slope of the phosphorus relationship was only 0.47 with a coefficient of determination of 0.80**, indicating that the average ISE-P is 53% lower P than the ICP-P. A literature review revealed that, since the ICP can measure other P forms in addition to orthophosphate-P, the P measured with an ICP has been shown to be up to 50% higher than P measured with colorimetric methods (Mallarino, 2003; Pittman et al., 2005). Engblom (1999) reported that the ICP also yielded higher P concentrations than did the colorimeter whereas the measurements with cobalt electrodes predicted the lowest concentrations among three methods (ICP, colorimetric, and cobalt ISE).

Possible causes responsible for the lower P estimations with the cobalt electrodes are difficult to explain. However, first, it is probable that the cobalt electrode responded to only orthophosphate ions. Second, there might be a change in sensitivity of the P electrode in soil extracts as compared to that measured in pure mixtures of NPK ions. This is supported by validation results for the mixtures of NPK ions randomly tested within a group of soil extract and validation solution samples where the regression slope between ISE-P and ICP-P for the mixtures of NPK was close to 1 (Table 7.9). Moreover, in a study proposing cobalt as a phosphate-sensitive material (Xiao et al., 1995), the sensitivity of cobalt electrodes changed significantly depending on what biochemical reagents for P sensing were included in the extractants tested, such as ATP (disodium adenosine 5’-triphosphate), ADP (disodium adenosine 5’-diphosphate), and AMP (disodium adenosine 5-monophosphate).

The cobalt electrodes showed several problems in these tests. For example, since one of the five cobalt electrodes (P-03) showed inconsistent responses throughout the 3rd replication, the data were excluded from the regression (Fig. 7.18). In addition, as shown in Figure 7.20b, all five of the electrodes showed an inconsistent response to one soil extract sample (circled), Drummer #13 (Table 7.1), in the 1st replication as compared to those measured in the 2nd and 3rd replications.

Efficiency of NPK extraction using Kelowna solution

The results of extraction of 37 soils by Kelowna solution and standard extractants for analyses of N, P, and K ions are shown in Figures 7.21a, 7.21b, and 7.21c, respectively. The nitrate-N amounts extracted from the test soils with the Kelowna solution were comparable to those obtained with 1M KCl, yielding an almost 1:1 relationship and only a small y-intercept of 0.72 with a high coefficient of determination of 0.99**.

There was a strong relationship between phosphorus amounts extracted with the Kelowna and the Mehlich III extractants ($r^2 = 0.98$**) when using the 37 soils having a pH range of 4.1 to 6.9 (Table 7.1). However, the Kelowna solution extracted 26% less P than did the Mehlich III extractant. These results are different from those reported in previous research (Van Lierop, 1988), which showed that P amounts extracted with Kelowna from 40 soils with $pH < 7.0$ were similar to those obtained with Bray P_1 solution. According to other researchers (Mehlich, 1984; Mallarino, 1997), P extracted with the Mehlich III test is similar to P extracted with Bray P_1, therefore, it was expected that the amounts extracted with the Kelowna and Mehlich III be would also be similar.

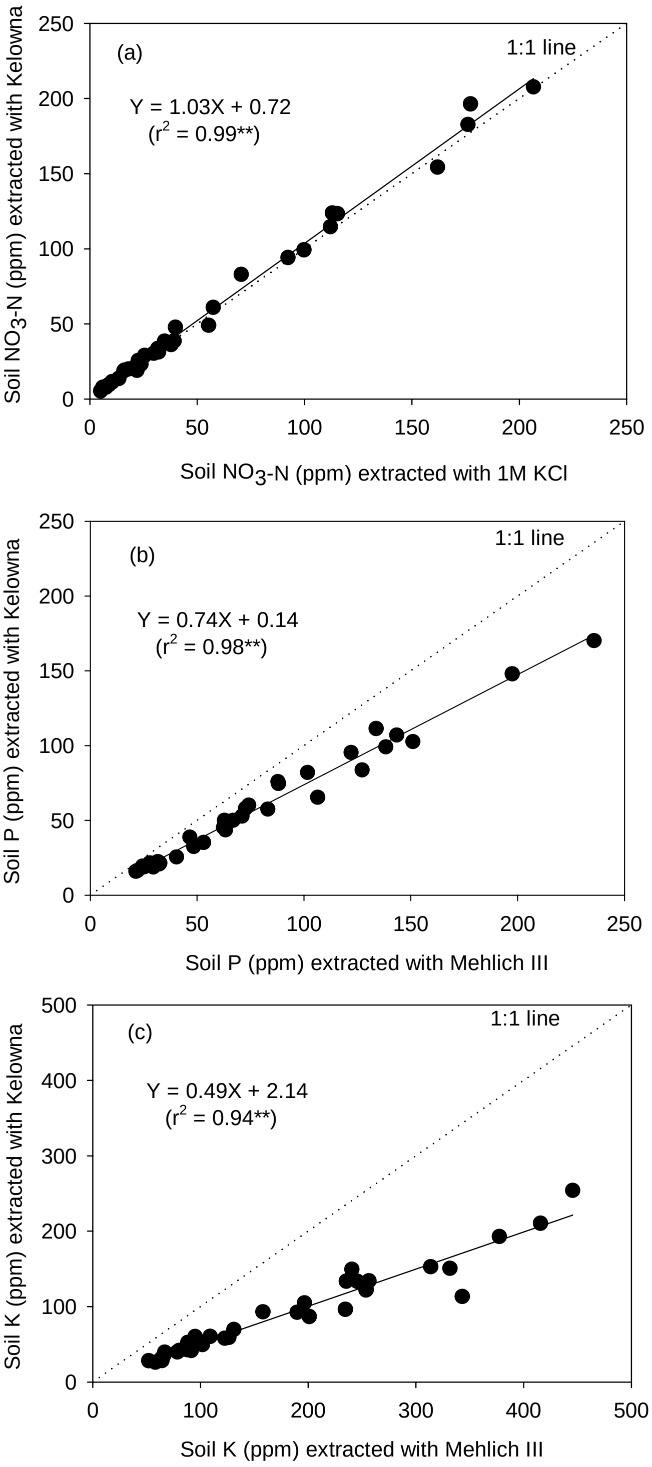


Figure 7.21. Relationships between soil (a) NO$_3$-N, (b) P, (c) K extracted with Kelowna and with standard extractants, i.e., 1M KCl for N and Mehlich III for P and K extraction.

The Kelowna solution extracted 51 % less K from the soils, as compared to that obtained with the Mehlich III extractant with a highly significant relationship (r^2 = 0.94**). The potassium amounts extracted with the Kelowna are lower than those found previously by Van Lierop and Gough (1989), who reported that Kelowna extracted about 20 % less K than did the 1M NH_4OA_C using sixty soils from various regions of British Columbia. According to Mehlich (1984), K obtained with Mehlich III is similar to K measured with 1M NH_4OA_C.

In spite of differences in extraction efficiency for P and K between the Kelowna and Mehlich III, the Kelowna extractant could still be used for the simultaneous extraction of NPK ions because the relationships between the Kelowna and Mehlich III for extraction of P and K were linear with high coefficients of determination ($r^2 \geq 0.94$**).

Comparison of soil NPK determinations by ISE and by standard methods

Figures 7.22, 7.23, and 7.24, respectively, illustrate comparisons of nitrate, phosphorus, and potassium concentrations in soil (volume basis) determined by using the three NPK electrodes and Kelowna extractant with those obtained by standard laboratory analysis methods. The regression results for NPK sensors when the responses measured with all five electrodes were combined are shown in Figure 7.25.

Soil NO_3-N concentrations obtained with 1M KCl and Lachat analyzer ranged from 5.1 to 206.6 mg/L. In the comparison of soil NO_3-N levels determined by the standard and the ISE methods (Figs. 7.22 and 7.25a), the regression slopes were close to 1 with high coefficients of determination ($r^2 > 0.86$**). However, the y-intercepts were relatively high ranging from 8.9 to 39.3 mg/L.

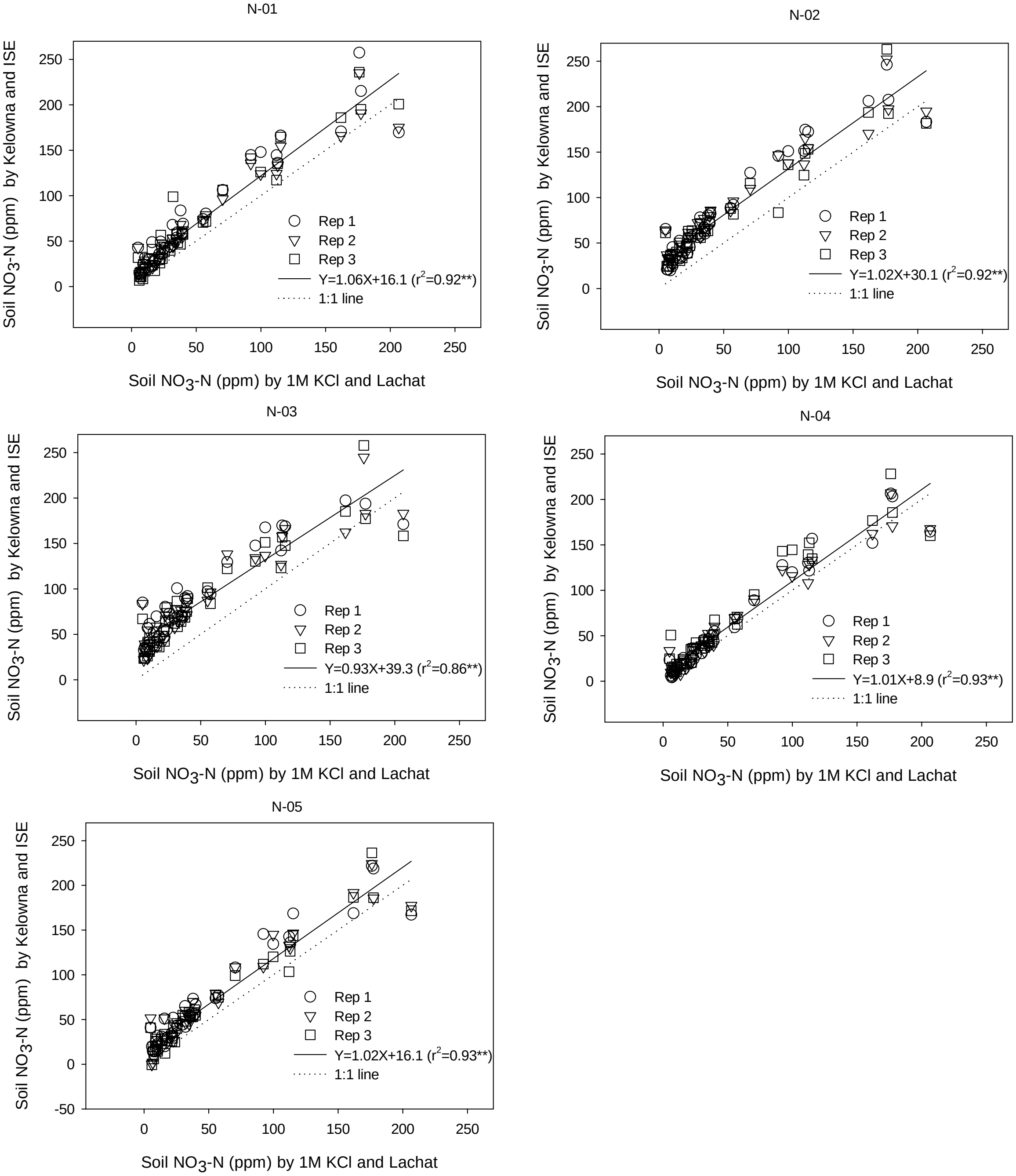


Figure 7.22. Relationships between soil NO_3-N determined by individual N ISEs and Kelowna and by Lachat and 1M KCl.

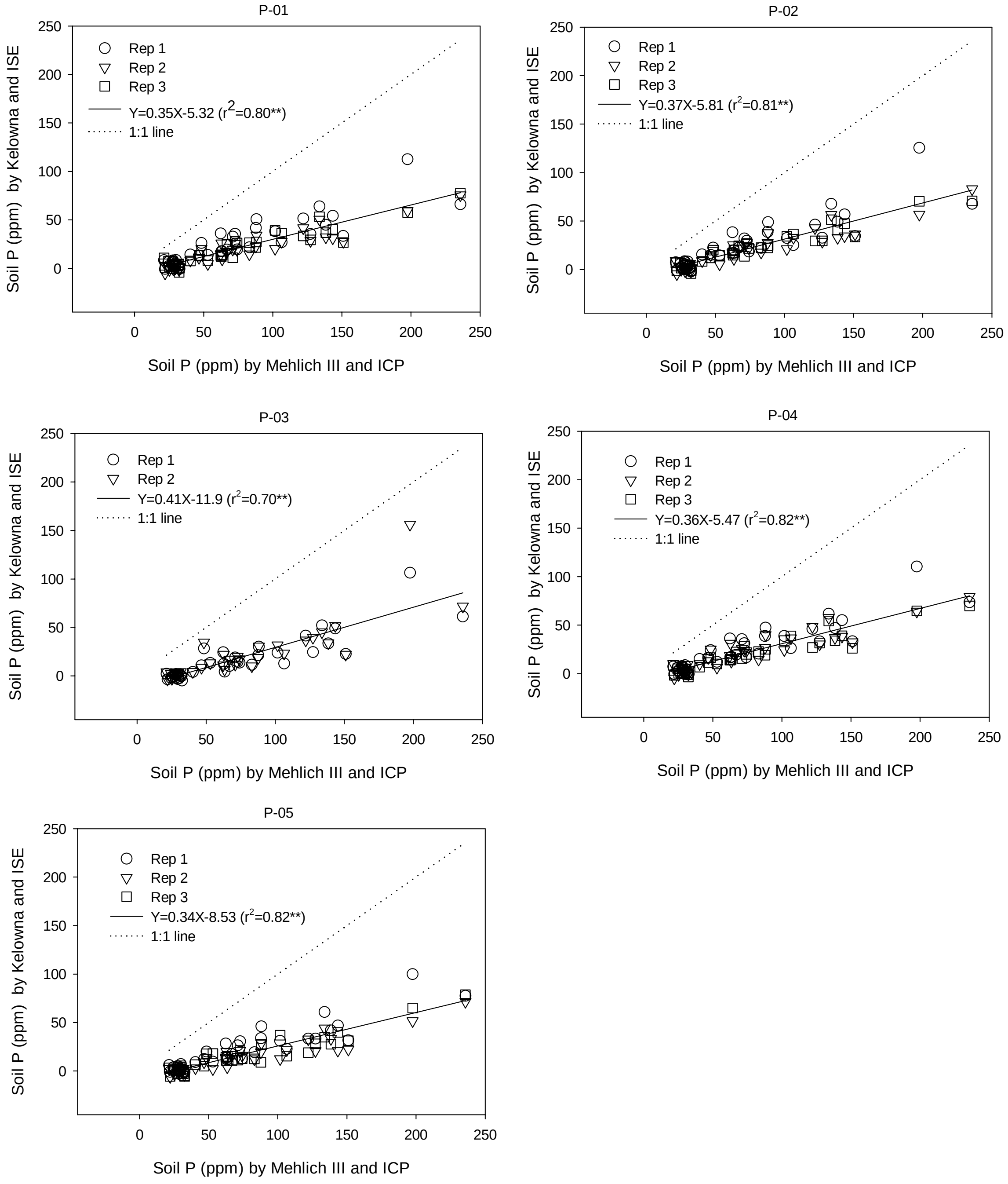


Figure 7.23. Relationships between soil P determined by individual P ISEs and Kelowna and by ICP and Mehlich III.

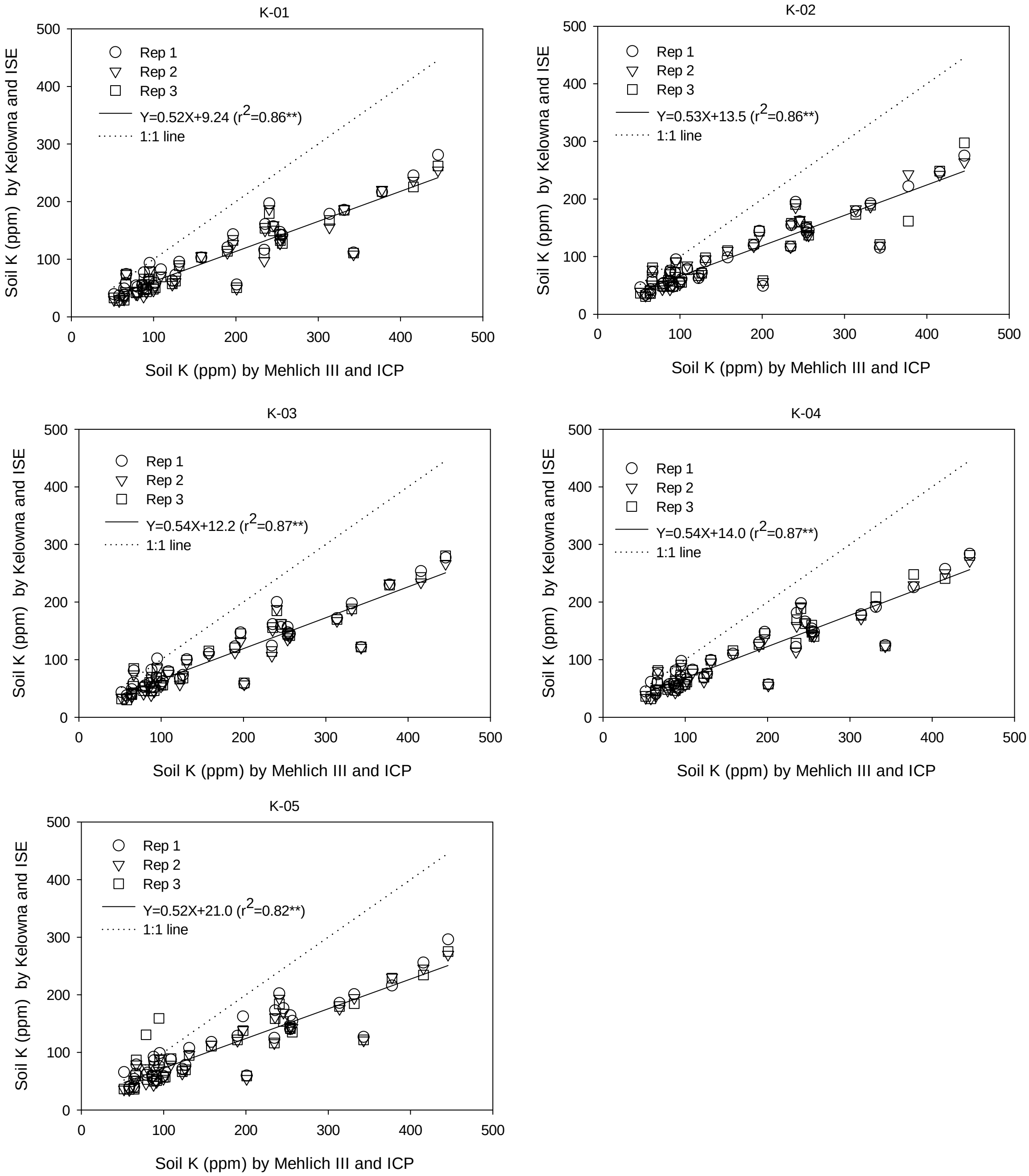


Figure 7.24. Relationships between soil K determined by individual K ISEs and Kelowna and by ICP and Mehlich III.

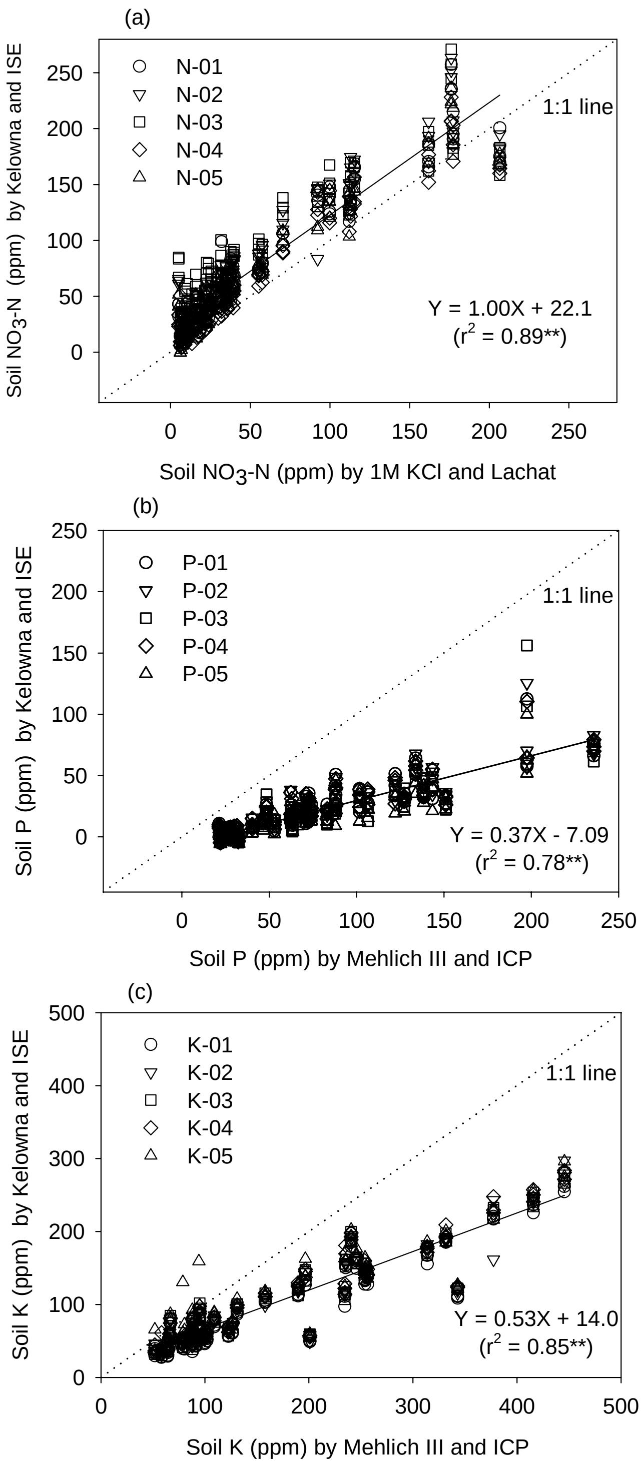


Figure 7.25. Relationships between (a) nitrate, (b) phosphorus, and (c) potassium determined by Kelowna and five ISEs, and by standard extractants and analyzers.

Soil P levels obtained with Kelowna and five P electrodes measured (Fig. 7.23 and Fig. 7.25b), on average, 63% lower P than those for the ICP analyzer with Mehlich III extractions. However, a strong relationship ($r^2 = 0.78^{**}$) was observed between the two methods. Such low P estimates might be due to the fact that, as found in previous sections, the P levels in solution determined by the P electrodes were 53% less than those obtained with the ICP, and the Kelowna solution extracted about 26% less P than did the Mehlich III solution. Thus, the regression slope of 0.37 can be explained by multiplying a slope of 0.74 for extraction efficiency by another slope of 0.47 for measurement. This explanation of the relationship between our measurement and soil testing results indicates that the experiments were carried out under good quality control.

In the comparison between soil potassium concentrations determined by the ISE method using five potassium electrodes and Kelowna solution, and by standard methods (Fig. 7.24 and Fig. 7.25c), a significant relationship ($r^2 = 0.85^{**}$) also existed between the two tests, but due to a decrease in K extraction efficiency by the Kelowna solution (about 50%), the ISE method measured 47% less K than did the standard method.

In summary, the N and K electrodes showed good prediction ability for determination of N and K in soil extracts. The Kelowna solution did not influence the measurement of nitrate in soils with nitrate electrodes due to similar extraction efficiency between the Kelowna and 1M KCl extractions, suggesting that the nitrate electrodes, in conjunction with the Kelowna solution, are feasible for predicting nitrate-N concentrations in soils. However, the ISE-K values for the tested soils were lower than the ICP-K values due to decreased K extractions by Kelowna solution. The ISE-P values were much lower than those obtained with standard methods both due to decreased P estimates in the soil extracts and reduced P extraction by the Kelowna extractant. In spite of differences in P and K concentrations determined by ion-selective electrode and standard methods, the K and P electrodes, in conjunction with the Kelowna solution, would be a promising approach because strong linear relationships existed between the two methods and the differences could easily be addressed by applying calibration factors.

CONCLUSIONS

A sensor array of three different ion-selective electrodes, based on TDDA-NPOE and valinomycin-DOS membranes, and cobalt rod, was evaluated for the simultaneous determination of nitrate-N, phosphate, and potassium ions in soil. Soil extract samples were obtained from 37 different Missouri and Illinois soils with the Kelowna soil extractant. The relationships between the NPK amounts obtained with the electrodes and Kelowna solution and with standard soil tests were investigated using linear regression analysis.

In mixed solutions, the TDDA-NPOE-based nitrate and valinomycin-DOS-based potassium ion-selective electrodes were significantly influenced only by their primary ions. The cobalt-rod-based phosphate ion-selective electrodes were significantly affected by both phosphate and nitrate ions showing reduced sensitivity in the presence of high nitrate-N concentrations (≥ 5 mg/L).

The calibration models for each type of electrode in separate or mixed solutions based on the Nikolskii-Eisenman equation resulted in high coefficients of determination $> 0.97^{**}$ when baseline correction and 2-point normalization were used.

Nitrate and potassium electrodes were able to measure nitrate-N and potassium ions in Kelowna – soil extracts, with nearly1:1 relationships and high coefficients of determination ($r^2 > 0.92^{**}$) between the amounts obtained with the ion-selective electrodes and with standard instruments, i.e., the Lachat and ICP analyzers for nitrate-N and potassium analysis, respectively. However, the cobalt rod-based P electrodes predicted, on average, 53 % less soil extract P than did the ICP spectrophotometer ($r^2 = 0.80^{**}$).

In a comparison of the amount of soil NO_3-N obtained with the Kelowna solution and five nitrate ISEs and with 1M KCl and Lachat analyzer, a significant relationship ($r^2 = 0.89^{**}$) was observed, showing the regression slope of near 1 and the y-intercept of about 20 mg/L.

The levels of soil P extracted with the Kelowna solution and measured with the P electrodes were 63 % less than the levels of P extracted with the Mehlich III solution and measured with the ICP analyzer, with a coefficient of determination of 0.78**. This difference in values between the two methods might be attributed to the low estimates of solution P by the cobalt electrode (53 % less as compared to the ICP) and reduced P extraction due to the use of Kelowna (26 % less as compared to the Mehlich III).

A significant linear relationship ($r^2 = 0.85^{**}$) was observed between potassium levels in Kelowna extractions measured with the potassium ISEs and those extracted by Mehlich III solution and analyzed by the ICP. However, the potassium ISE and Kelowna solution showed about 47 % lower soil potassium levels than did the ICP and Mehlich III, because the levels of soil potassium extracted with the Kelowna extractant were about 50 % less than those obtained with the Mehlich III solution.

Due to highly significant relationships in measured values for NPK between the ISE and standard methods, it was concluded that the ISE method that uses three different sensors (TDDA-NPOE-based nitrate ISE, valinomycin-DOS-based potassium ISE, and cobalt rod-based phosphate ISE) in conjunction with the Kelowna soil extractant, could be used for simultaneous determination of soil NPK concentrations.

CHAPTER 8
CONCLUSIONS

CONCLUSIONS OF THE STUDY

A sensor array of three different ion-selective electrodes (ISEs) was developed to simultaneously measure soil macronutrients (N, P, and K). Conclusions based on the results reported in this study are:

- The sensitivity and selectivity of PVC membrane-based ion-selective electrodes with tetradodecylammonium nitrate (TDDA) and valinomycin for nitrate and potassium analysis, respectively, and of cobalt rod-based phosphate ion-selective electrodes were satisfactory for measuring N, P, and K ions over typical ranges of soil concentrations. The rapid response time and a wide sensitivity range of the electrodes allowed samples to be analyzed within 15 s and without the need to dilute samples, characteristics useful for real-time soil sensing.
- The Kelowna multiple-ion extractant (0.25M CH_3COOH + 0.015M NH_4F) was usable for simultaneous extraction of soil NPK ions, showing strong linear relationships between the amounts of NPK extracted with the Kelowna solution and with standard soil extracting solutions (i.e., 1M KCl for NO_3-N and Mehlich III for P and K) from 37 Missouri and Illinois acid soils.
- The nitrate and potassium ion-selective electrodes measured NO_3-N and K ions in Kelowna-based soil extracts with approximately 1:1 relationships

between the values determined by the ion-selective electrodes and by standard laboratory instruments. Furthermore, owing to a significant relationship with a nearly 1:1 regression slope, the nitrate ISE method, used in conjunction with the Kelowna extractant, provided results in close agreement with the standard method using the Lachat analyzer and 1M KCl extractant. However, the Kelowna-K amounts obtained with the potassium ISEs were about 50% lower than the Mehlich III-K concentrations measured with the ICP spectrophotometer due to decreased K extraction by the Kelowna solution.

- Soil P values obtained with the Kelwona extractant and cobalt P ISEs were much lower (about 63%) than those extracted with the Mehlich III extractant and analyzed with the ICP spectrometer due to both a lower P extraction by the Kelowna solution and lower estimates of P concentrations in the extract by the cobalt P ISEs. Nevertheless, the high coefficient of determination obtained between the ISE and standard methods supports the conclusion that a calibration relating the ISE results to standard methods of soil phosphorus sensing can be developed.
- After further development, this sensor array could be employed in a real-time soil analysis system based on automatic soil sampling and nutrient extraction, thereby allowing fast on-site measurements of macronutrients at a high sampling intensity.

SUGGESTIONS FOR FUTURE STUDY

Based on the results obtained from this study, the following are recommendations for future work:

- For field use of the system, further investigations needed include the development of calibration methods suitable for field operation and of optimum methods for rinsing and conditioning electrodes for continuous use so that the sensors can provide reliable and repeatable responses in the field.
- Phosphorus measurement is achieved by pH adjustment of samples to remove the effect of pH on phosphorus forms, which would require pH monitoring and control for practical use. Therefore, integrating a pH sensor into the system would be needed, and further studies on the development of calibration models that account for pH change are required for accurate P estimations without need to control pH. The use of known equilibrium constants for the reaction of phosphates in solution would make it possible to obtain a relationship between results obtained with and without pH adjustments.
- Further studies on the decreased sensitivity of the cobalt P electrodes in soil extracts are needed to improve the predictive ability of the soil P sensor. A possible approach might be to use soil extract samples for calibration, thereby compensating for the reduced sensitivity.
- To develop a multi-ion ISFET sensor based on these NPK sensors, further studies are needed, including the effect of the miniaturization of the

electrodes on sensing performance and the integration of the ISFET into a FIA (Flow Injection Analysis) system.

- The effects of extraction time and moist soils on the extraction efficiency of the Kelowna solution should be investigated for real-time extraction.
- Since the Kelowna solution is not currently used in the US Midwest, further investigations on the correlation between Kelowna and standard soil extractants, as well as the correlation between Kelowna-extractable NPK and plant uptake, would increase the potential for adoption of the developed system.

APPENDIX A. OPERATION AND SPECIFICATIONS OF AN AUTOMATED TEST STAND

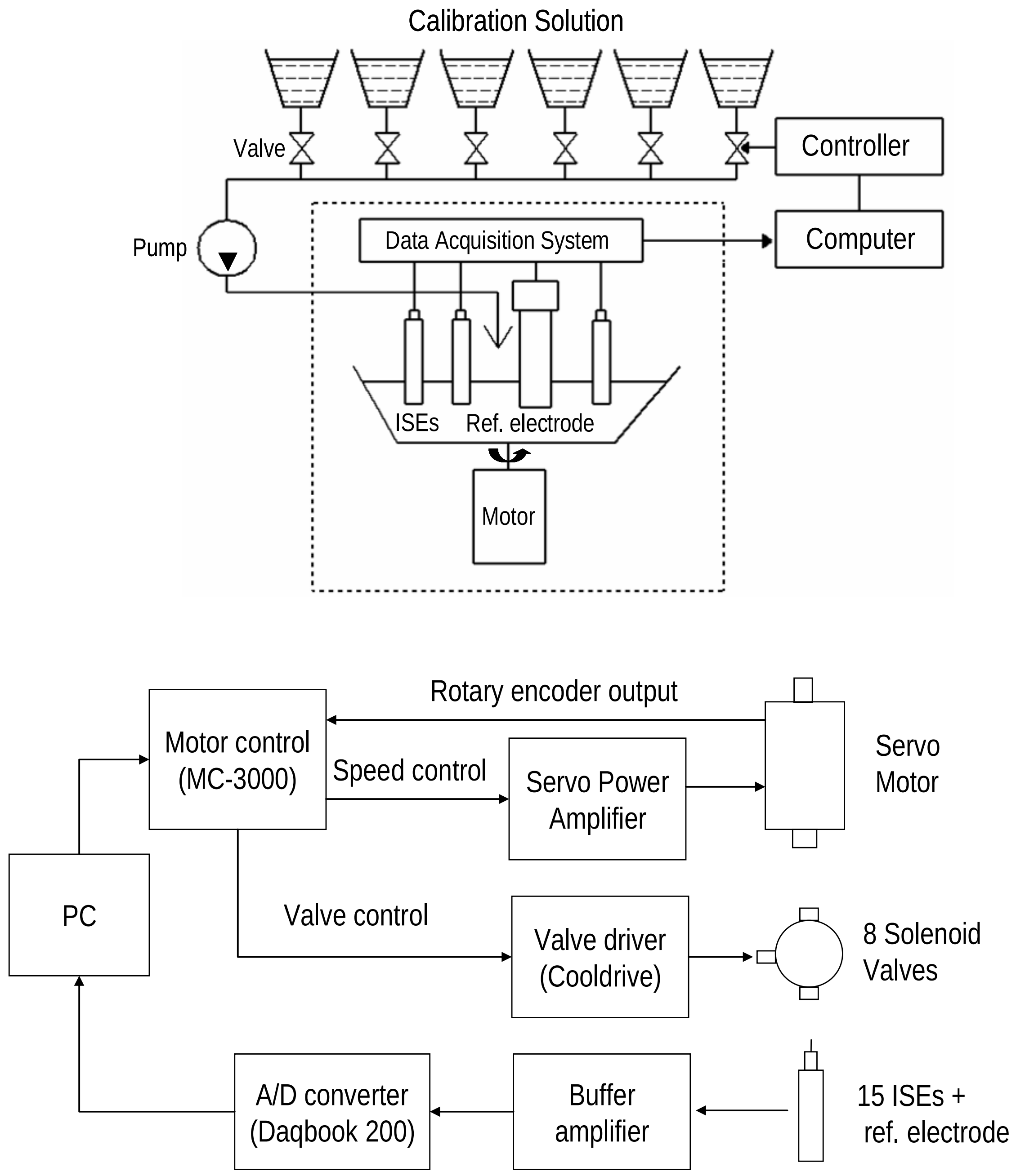


Figure A.1. Schematic representation of automated test stand (upper) and block diagram for controlling the test stand (lower).

Table A.1. Specifications of components of the test stand.

Name	Specifications	Manufacturer
Servo Motor	- Model : GMX-6MP013A - built-in rotary encoder - Motor rpm: 410 - Power: 24 VDC	Matsushita (Japan)
Motor controller	- Model: MC-3000 - ISA-bus based data transfer - PWM modulation: 20 kHz - Velocity : $32*10^6$(counts/sec) - Encoder : 312.5 kHz	Servomotive Corporation (Worcester, Mass.)
Solenoid valve	- Model : 98300-02 - Three-way direct lift - Response time: 20 ms - Max : 30 psi - Power: 12 VDC	Cole-Parmer Instrument Co. (Chicago, Ill.)
Valve driver	- Model : Cooldrive 360D5X12 - Power input: 12 VDC - Holding voltage: 5 VDC - Output: Solenoid coil 34 Ohms	Neptune Research Inc. (West Caldwell, N.J.)
Peristaltic pump	- Materflex multichannel - Model : 7520-25 - Motor rpm: 6 to 600, - Power : 100 to 130 VAC	Cole-Parmer Instrument Co. (Chicago, Ill.)
A/D converter	- Model: Daqbook 200 - Parallel port-based data acquisition - 16 channels - 100kHz A/D convert	IO Tech (Cleveland, Ohio)

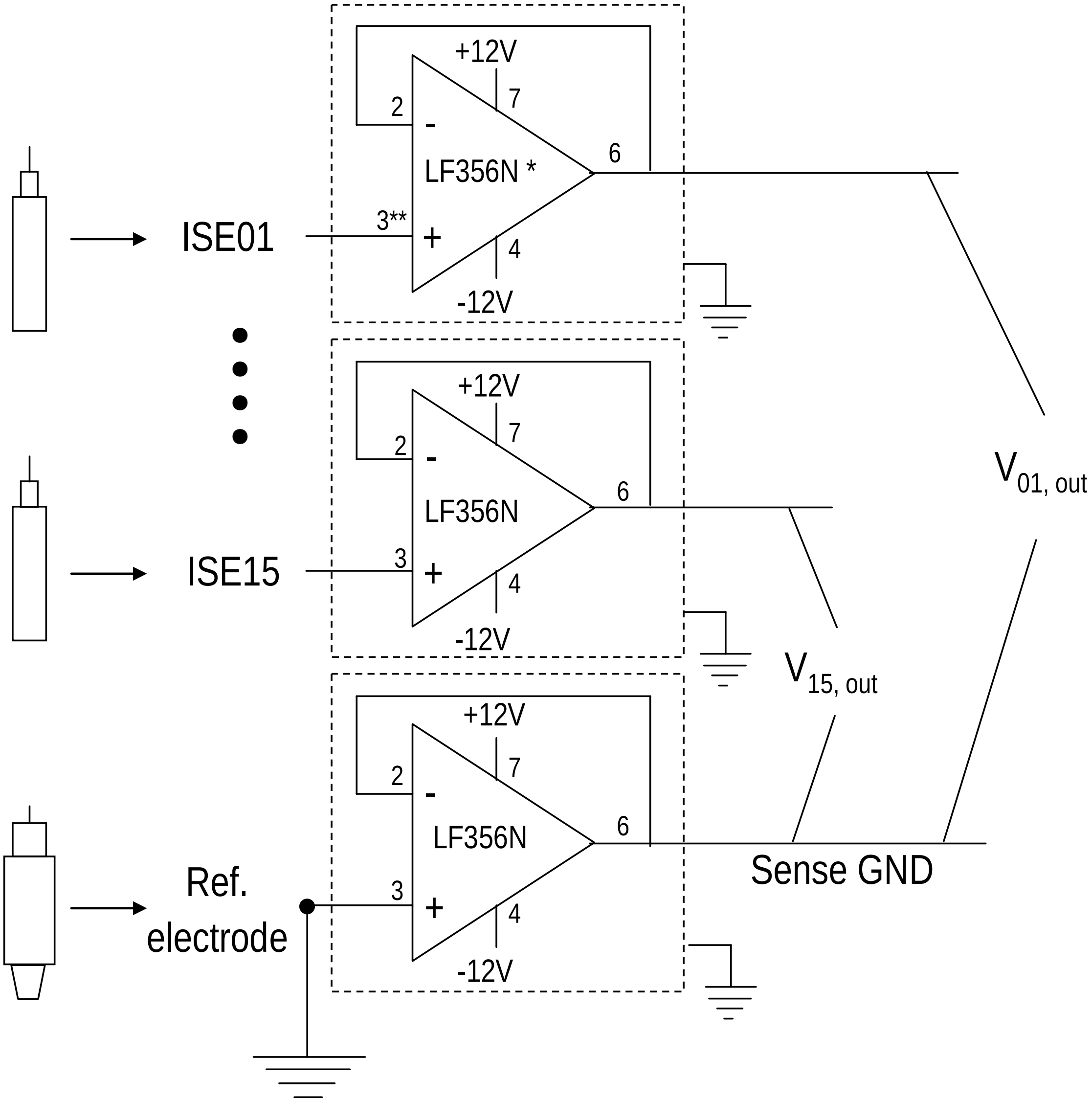
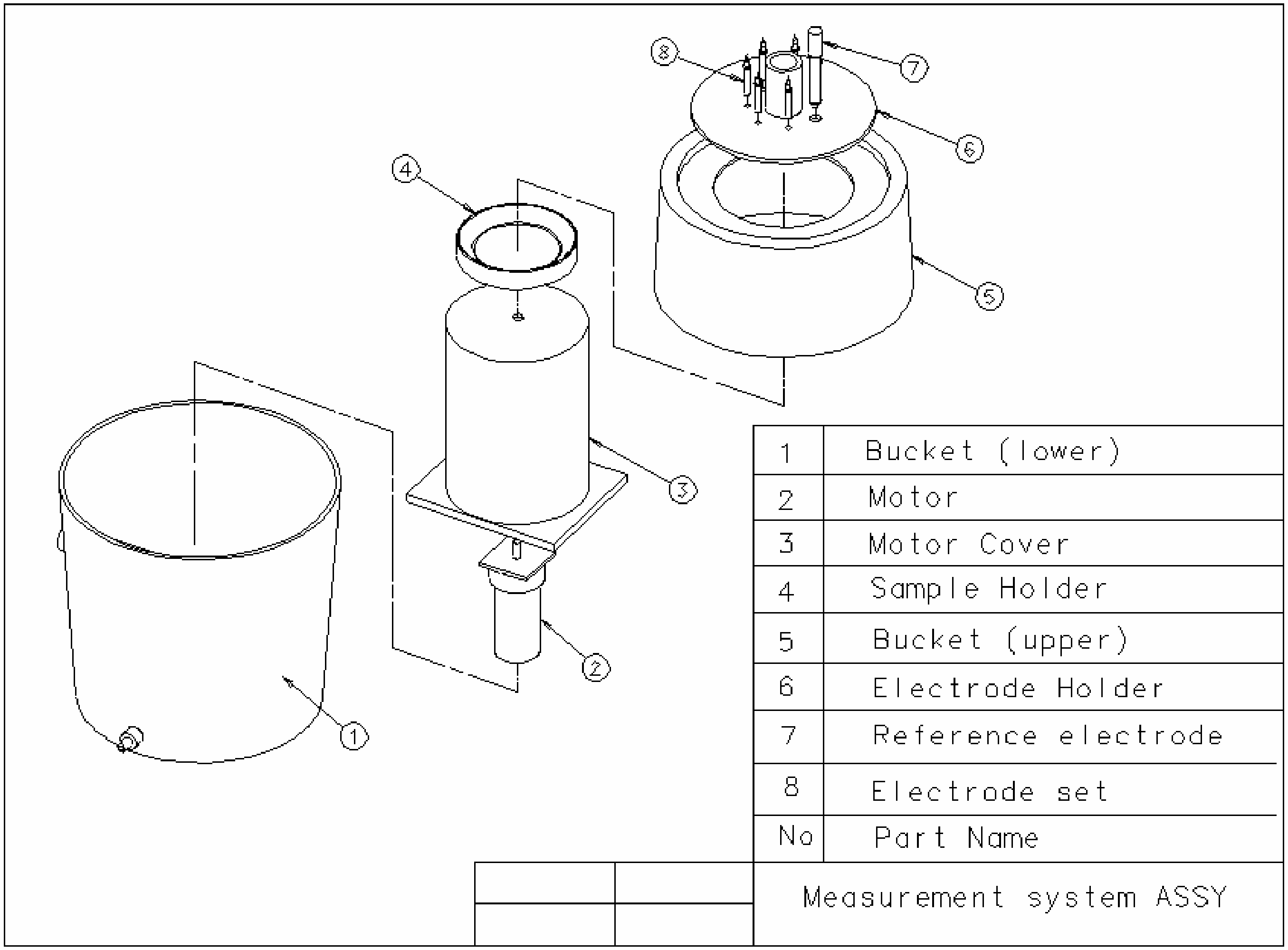


Figure A.2. Circuit diagram for voltage source buffering and impedance transformation

*Note:

- LF356N OP amplifier (10^{12}ohms input impedance, 3 pF input capacitance, <8nA bias current, National Semiconductor, Santa Clara, Calif.)

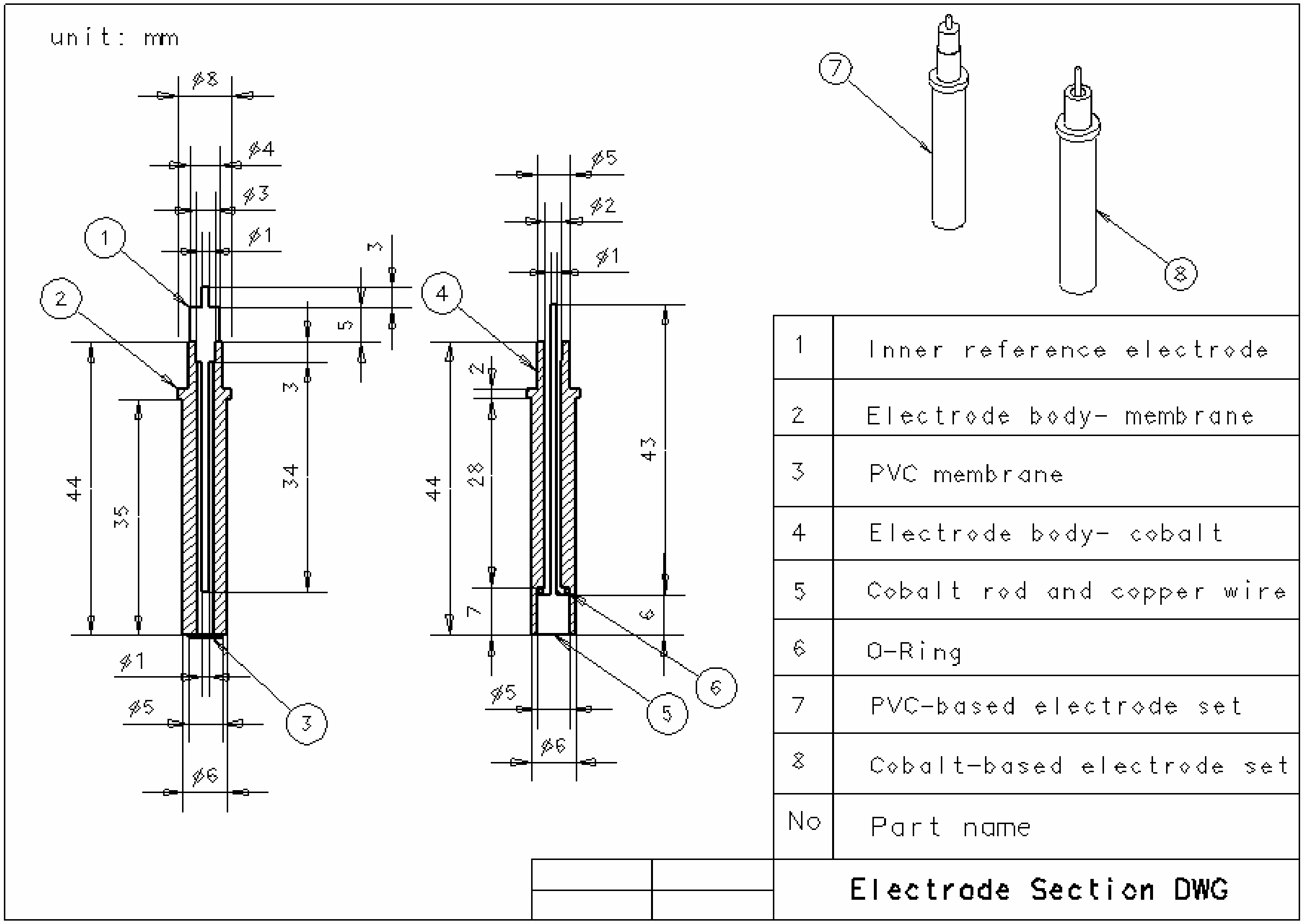
- ISE input (pin3) was wired directly to the ISE to reduce current leakage to the ground plane of the circuit board.



No	Part Name
1	Bucket (lower)
2	Motor
3	Motor Cover
4	Sample Holder
5	Bucket (upper)
6	Electrode Holder
7	Reference electrode
8	Electrode set

Measurement system ASSY

Figure A.3. Components of automated measurement system to empty and fill sample solution.



No	Part name
1	Inner reference electrode
2	Electrode body- membrane
3	PVC membrane
4	Electrode body- cobalt
5	Cobalt rod and copper wire
6	O-Ring
7	PVC-based electrode set
8	Cobalt-based electrode set

Electrode Section DWG

Figure A.4. Drawing of PVC membrane-based (left) and cobalt rod-based (right) electrodes.

APPENDIX B. FLOW CHARTS FOR TEST STAND PROGRAM

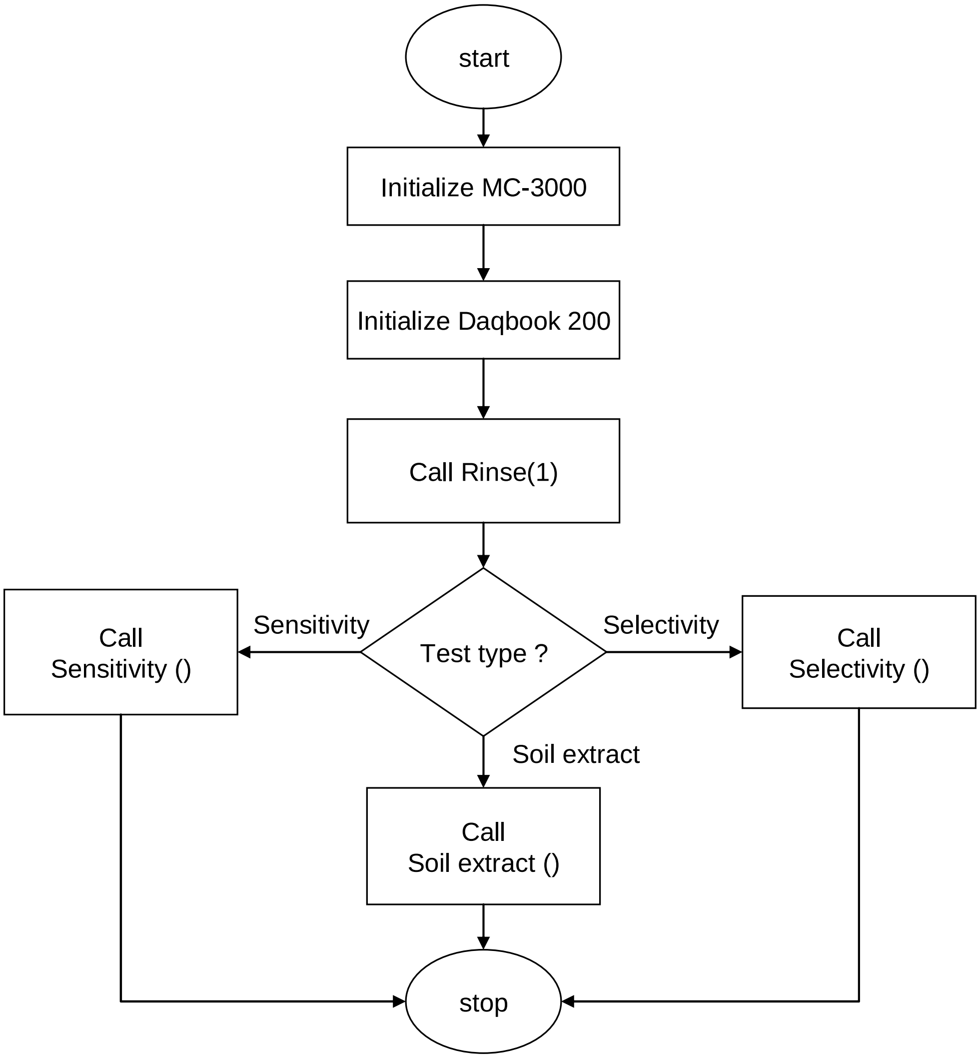


Figure B.1. Flow chart for main program.

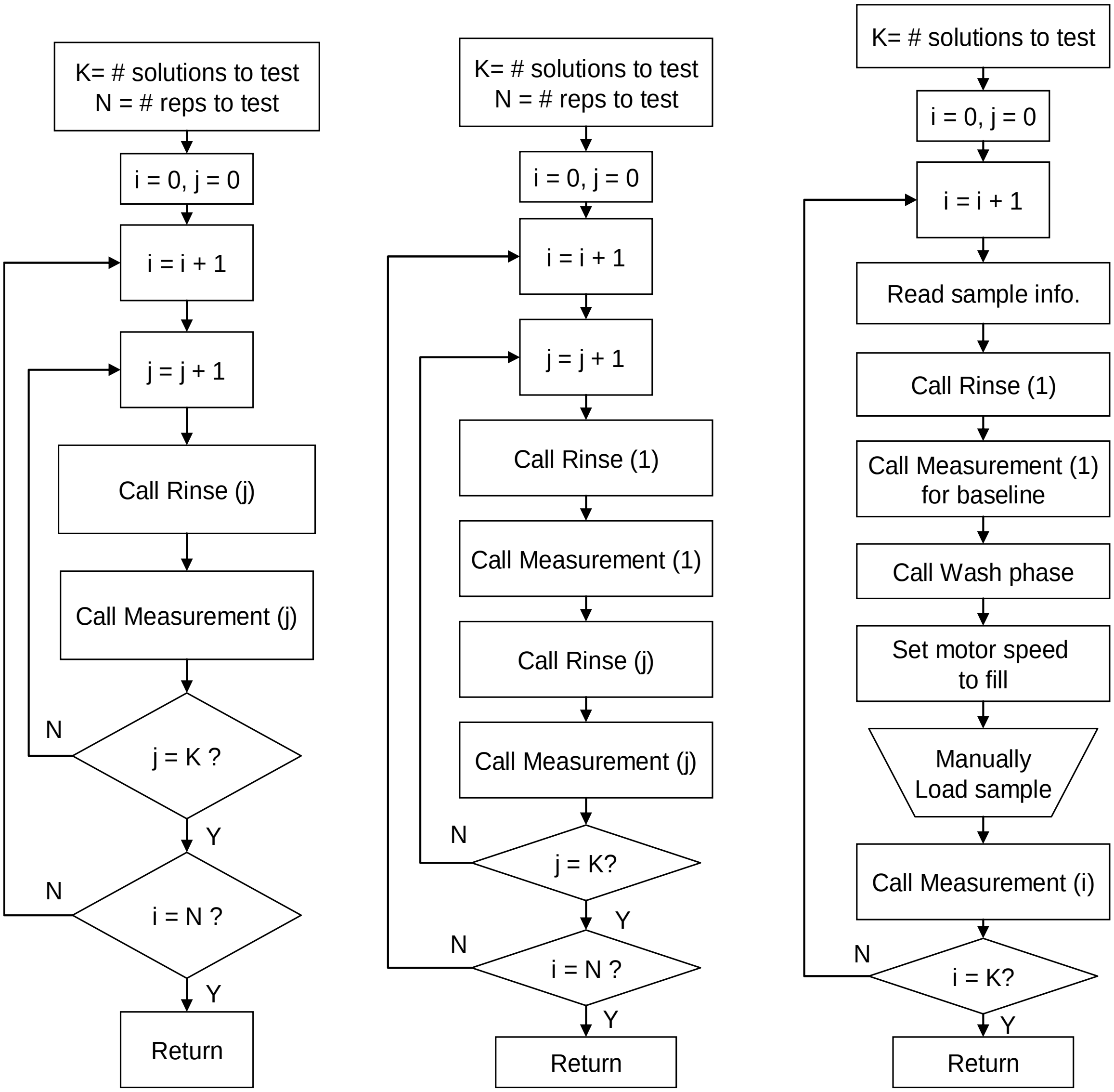


Figure B.2. Flow charts for three different tests, sensitivity (left), selectivity (center), and soil extract (right).

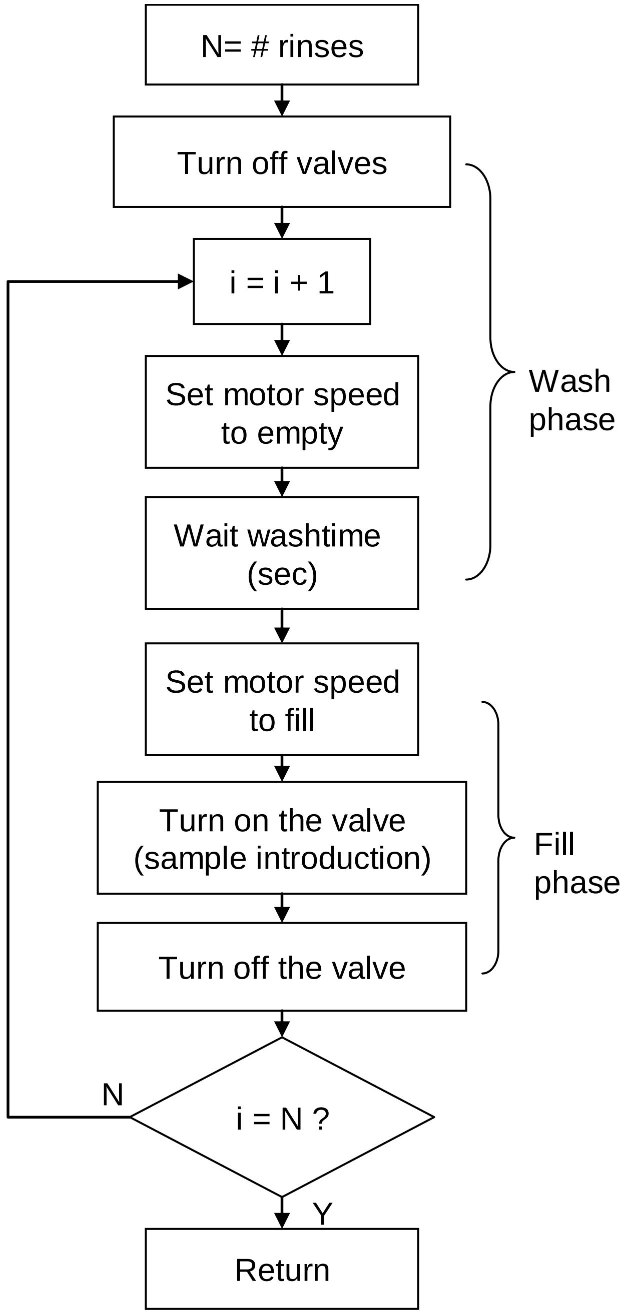


Figure B.3. Control flow of subprogram RINSE to wash electrodes and fill sample solution into the sample holder.

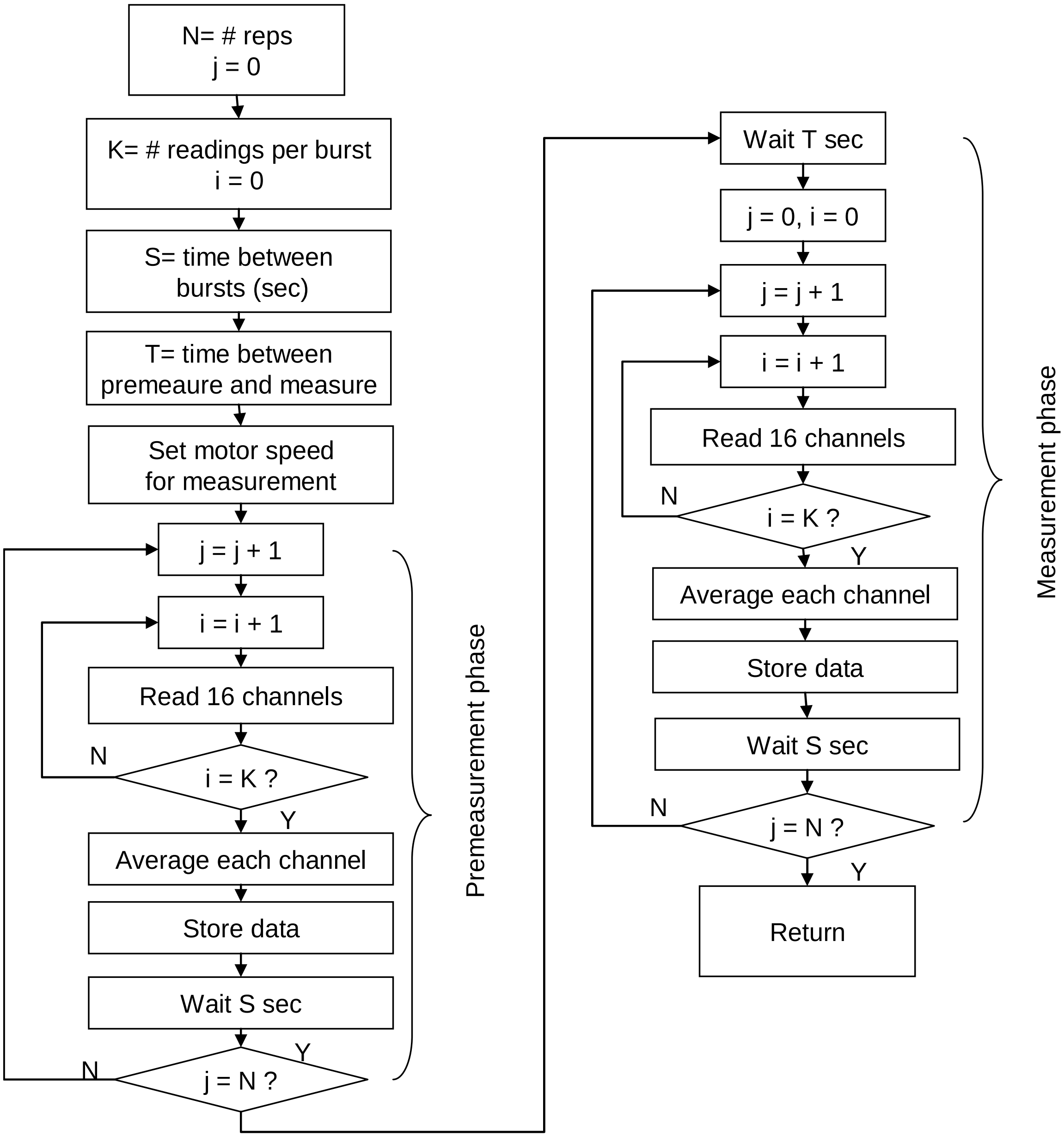


Figure B.4. Flow chart of subprogram MEASUREMENT to collect EMF data from 16 electrodes.

APPENDIX C. RAW DATA TAKEN FROM SENSITIVITY AND SELECTIVITY TESTS

Table C.1. EMF data taken from sensitivity tests of N electrodes in DI water.

DI water

Test 1(6/13/2003)		TDDA-NPOE-A			TDDA-NPOE-B			MTDA-NPOE-A			MTDA-NPOE-B			MTDA-TOTM-A		
	Conc. (M)	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3
	NaNO3	Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV		
Rep 1	0.000001	305.66	303.21	308.77	*drifts	313.53	307.76	313.15	315.85	305.58	315.34	317.41	313.53	299.00	304.21	317.05
	0.00001	308.01	306.29	309.76		313.93	308.17	304.46	307.71	297.28	307.52	310.07	306.40	291.10	296.62	310.58
	0.0001	245.86	240.27	242.97		253.41	247.50	253.40	255.35	245.52	256.69	256.67	253.77	237.94	243.42	255.43
	0.001	185.05	179.24	180.90		194.59	188.89	190.83	191.98	182.65	194.46	194.06	191.03	175.13	180.95	193.65
	0.01	121.75	114.59	117.56		132.79	126.25	128.19	131.02	119.35	130.69	130.47	127.80	112.61	117.21	130.26
	0.1	64.43	57.14	60.16		77.04	69.74	70.19	73.24	62.42	73.24	72.50	70.33	56.73	60.66	72.32
Rep 2	0.000001	302.98	301.71	306.18		300.66	298.51	308.68	314.66	301.79	310.40	313.93	310.78	295.74	301.85	314.26
	0.00001	309.80	308.77	313.41		312.04	307.04	306.10	311.40	298.92	309.14	311.98	308.30	293.62	299.45	312.57
	0.0001	247.49	241.55	244.18		254.59	249.34	254.98	257.24	246.97	258.00	257.37	255.29	240.51	245.14	257.50
	0.001	185.88	179.10	180.71		195.69	189.64	191.88	192.85	183.07	195.05	193.99	191.31	176.82	182.26	194.30
	0.01	121.66	115.99	117.03		133.29	126.42	127.36	132.11	119.32	130.40	129.63	127.23	112.66	116.74	130.14
	0.1	64.52	58.92	60.10		77.72	70.27	70.38	74.59	62.07	72.83	72.13	70.09	57.49	59.99	72.41
Rep 3	0.000001	303.56	300.84	303.61		301.39	298.36	309.07	314.15	301.47	310.20	313.63	310.33	298.39	301.85	314.23
	0.00001	307.94	308.29	313.17		311.92	304.26	304.13	305.61	296.59	308.11	309.93	306.95	294.19	298.49	311.86
	0.0001	247.09	240.60	246.94		253.63	248.43	254.51	256.42	246.09	256.93	258.47	254.27	239.58	244.34	256.31
	0.001	186.22	179.67	182.63		198.43	189.62	192.60	193.37	184.10	195.38	194.92	192.22	177.07	181.21	193.99
	0.01	121.00	115.54	116.79		133.80	125.36	127.93	127.78	118.05	129.91	129.76	126.25	111.77	117.35	129.01
	0.1	65.11	59.15	60.00		78.66	70.15	70.96	70.34	61.61	72.59	72.45	70.01	57.11	60.72	71.69

Test 2 (6/16/2003)		TDDA-NPOE-A			TDDA-NPOE-B			MTDA-TOTM-B			MTDA-NPOE-B			MTDA-TOTM-A		
	Conc. (M)	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3
	NaNO3	Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV		
Rep 1	0.000001	325.36	317.87	* drifts	308.76	306.11	300.06	294.03	300.56	* broken	311.52	314.64	311.08	306.40	302.38	298.33
	0.00001	313.19	311.03		303.12	300.35	295.10	284.93	290.14		302.34	305.35	302.83	296.76	292.89	287.93
	0.0001	256.06	247.21		240.85	241.35	234.46	230.27	236.29		250.93	250.74	246.36	242.99	238.27	233.25
	0.001	197.81	186.09		180.46	181.53	174.32	167.79	173.57		188.59	188.61	184.52	181.47	176.16	171.52
	0.01	128.21	123.54		116.17	117.51	110.56	102.77	109.79		123.76	123.66	122.70	116.32	110.98	106.38
	0.1	74.42	71.47		64.74	67.97	59.17	48.71	55.54		70.37	70.19	69.76	64.35	56.95	53.49
Rep 2	0.000001	315.86	317.17		307.66	295.40	297.42	292.34	298.95		308.58	313.39	311.49	305.57	301.50	295.92
	0.00001	311.30	312.79		302.76	295.80	294.17	285.19	290.33		301.50	305.21	304.46	297.30	291.47	287.38
	0.0001	250.56	249.45		241.26	240.62	234.86	230.26	236.32		251.31	251.02	252.12	243.18	237.80	233.56
	0.001	189.99	188.79		181.40	182.42	176.18	168.31	174.60		188.84	189.06	190.04	181.85	176.48	172.36
	0.01	124.28	123.45		116.77	118.86	110.35	102.22	108.84		123.08	123.74	124.35	116.28	109.96	105.98
	0.1	71.87	71.42		64.33	68.19	59.48	50.16	57.61		70.52	71.52	73.62	65.11	58.34	53.84
Rep 3	0.000001	316.46	321.22		309.42	298.93	301.06	295.99	302.80		311.58	316.37	317.17	308.22	303.71	298.96
	0.00001	311.04	314.87		304.07	298.20	295.33	286.04	291.69		302.85	306.70	307.46	298.32	292.56	288.47
	0.0001	250.24	250.81		242.30	241.73	236.55	231.25	237.65		252.43	252.02	254.94	244.64	239.62	235.45
	0.001	189.77	190.64		182.62	184.14	177.27	169.70	176.96		190.88	191.26	193.83	182.89	178.43	173.56
	0.01	124.39	125.18		117.21	120.16	112.82	104.26	110.01		124.99	125.49	127.85	117.11	112.09	107.48
	0.1	70.49	71.78		65.00	68.45	60.10	50.68	57.54		71.34	72.06	74.78	65.00	59.01	54.80

Table C.2. EMF data taken from sensitivity tests of N electrodes in 0.01M $CuSO_4$ solution.

0.01M CuSO4

Test 1(7/1/2003)		**TDDA-NPOE-A**			**TDDA-NPOE-B**			**MTDA-NPOE-A**			**MTDA-NPOE-B**			**MTDA-TOTM-A**		
	Conc. (M)	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3
	NaNO3	Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV		
Rep 1	0.000001	286.65	280.42	* drifts	295.20	295.02	293.33	210.56	212.27	199.87	218.64	218.72	218.37	189.69	196.29	211.62
	0.00001	276.98	270.26		283.54	286.86	282.24	214.86	217.04	204.57	222.80	222.90	222.50	191.14	197.93	212.26
	0.0001	232.71	225.54		238.67	242.76	236.75	212.51	215.00	202.78	219.97	219.50	216.08	186.43	193.28	207.78
	0.001	173.20	166.58		178.73	182.85	176.80	186.58	186.47	172.99	190.15	190.42	178.53	160.75	165.43	181.01
	0.01	116.19	109.18		122.07	125.30	119.86	123.77	124.45	112.04	129.14	128.32	119.98	106.09	109.33	124.63
	0.1	64.32	57.42		69.38	73.81	68.00	71.23	71.84	59.92	76.11	75.55	67.30	54.31	57.41	71.38
Rep 2	0.000001	285.87	279.96		293.56	289.54	292.48	207.40	211.69	199.56	217.86	216.89	220.94	187.15	194.51	207.60
	0.00001	275.77	268.99		282.98	283.90	281.43	213.27	215.84	203.24	221.38	220.57	222.86	189.06	196.29	208.51
	0.0001	232.79	226.33		238.50	241.89	237.07	211.42	214.56	202.51	219.23	218.07	215.56	185.55	192.47	205.47
	0.001	172.42	165.92		178.97	183.00	177.00	185.67	186.00	173.02	188.51	188.42	176.42	161.30	165.92	180.29
	0.01	116.84	110.18		122.15	125.63	120.53	123.96	125.46	112.15	129.44	128.35	119.69	106.42	109.51	124.22
	0.1	64.26	59.11		69.67	74.03	67.64	71.60	72.28	60.91	76.26	75.72	67.05	54.58	57.59	71.56
Rep 3	0.000001	287.46	281.81		295.31	290.99	293.19	209.71	213.95	202.42	219.44	217.84	222.96	188.70	194.35	208.10
	0.00001	277.28	270.74		283.70	285.51	282.32	213.91	218.18	205.98	223.31	222.66	224.71	189.78	195.70	209.78
	0.0001	234.20	227.18		239.54	243.09	238.29	212.83	215.93	203.99	220.31	219.12	216.99	185.64	192.69	205.72
	0.001	173.54	166.35		179.25	183.21	178.31	185.64	186.79	173.54	188.31	187.92	177.33	162.68	166.90	180.40
	0.01	116.74	110.96		122.62	126.67	120.78	124.63	125.61	113.87	129.11	128.67	119.52	106.39	109.80	124.27
	0.1	65.47	60.00		70.07	74.89	69.28	71.47	72.76	61.55	75.82	75.85	67.37	55.54	57.89	70.62

Test 2 (6/25/2003)		**TDDA-NPOE-A**			**TDDA-NPOE-B**			**MTDA-TOTM-B**			**MTDA-NPOE-B**			**MTDA-TOTM-A**		
	Conc. (M)	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3
	NaNO3	Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV		
Rep 1	0.000001	290.99	291.67	290.80	286.07	287.81	280.14	190.57	197.99	* broken	217.21	229.32	220.13	206.03	202.29	196.23
	0.00001	284.80	286.33	284.49	279.71	281.63	273.90	192.36	199.52		221.75	232.93	224.07	208.35	204.28	198.20
	0.0001	244.71	247.18	244.41	239.93	242.58	233.88	188.08	196.16		219.45	223.98	215.89	203.07	199.89	193.50
	0.001	184.12	186.70	184.57	179.75	181.82	173.89	161.77	175.74		196.81	187.30	177.98	180.88	174.29	170.84
	0.01	127.76	130.65	127.86	123.06	125.85	117.10	105.46	120.55		129.58	129.58	121.15	127.11	119.71	116.49
	0.1	78.52	81.41	78.97	73.71	76.79	68.14	56.19	71.13		79.99	80.31	71.95	79.47	70.96	67.21
Rep 2	0.000001	290.53	293.02	291.58	286.26	282.53	279.96	192.32	199.84		212.34	230.97	221.61	207.20	203.75	197.62
	0.00001	283.59	286.29	284.35	279.95	281.07	274.48	192.89	200.14		218.11	232.72	223.69	208.93	204.93	198.22
	0.0001	245.10	248.22	245.47	240.40	242.81	234.59	190.10	197.72		217.49	225.08	216.94	204.84	201.60	195.16
	0.001	184.35	187.77	185.23	180.11	182.47	174.43	163.08	176.32		191.55	187.55	179.48	181.75	175.91	172.54
	0.01	127.97	131.48	128.68	123.46	125.77	118.09	106.73	121.32		130.21	130.11	121.80	127.68	119.80	117.09
	0.1	77.73	80.46	78.05	73.29	76.79	68.02	54.70	68.77		78.90	79.08	70.73	78.13	68.64	66.01
Rep 3	0.000001	289.89	292.51	291.76	286.45	283.39	280.54	192.57	199.06		215.89	230.83	221.96	206.85	203.08	196.68
	0.00001	284.02	286.97	284.71	279.46	280.70	273.39	193.18	200.11		220.19	233.09	224.31	208.26	203.87	198.05
	0.0001	244.97	248.09	245.71	240.16	243.40	235.42	190.48	198.10		218.19	225.39	217.04	205.05	201.63	195.20
	0.001	184.48	188.27	185.23	180.08	182.97	174.82	163.92	176.73		189.71	186.78	180.06	182.45	175.99	172.27
	0.01	128.80	131.99	129.29	124.12	127.21	119.11	107.85	121.26		130.87	130.25	123.02	127.98	120.64	117.71
	0.1	78.81	82.73	80.09	74.08	78.13	69.46	58.07	71.91		80.52	80.66	73.13	79.07	71.05	67.65

Table C.3. EMF data taken from sensitivity tests of N electrodes in Kelowna extractant.

Kelowna

Test 1(8/17/2003)		TDDA-NPOE-A			TDDA-NPOE-B			MTDA-NPOE-A			MTDA-NPOE-B			MTDA-TOTM-A		
	Conc. (M)	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3
	NaNO3	Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV		
Rep 1	0.000001	231.73	* drifts	218.21	231.13	229.48	231.36	209.97	209.36	201.40	214.84	214.44	214.73	193.86	195.40	210.81
	0.00001	233.95		207.55	222.42	223.18	223.48	209.24	206.28	198.06	213.83	210.72	212.55	189.21	192.37	206.94
	0.0001	209.67		187.74	203.72	207.52	203.97	202.02	196.51	188.88	207.30	200.95	203.16	179.06	183.03	197.53
	0.001	160.98		134.63	149.52	155.33	149.02	150.59	145.22	138.75	157.99	150.48	151.86	131.10	135.82	148.74
	0.01	96.89		76.63	90.71	96.80	91.03	92.27	86.43	79.93	98.98	91.41	93.33	72.99	77.19	90.26
	0.1	50.50		24.60	38.31	45.02	39.22	39.41	34.83	28.02	46.72	39.16	41.46	23.45	24.78	38.28
Rep 2	0.000001	239.62		217.91	230.27	226.35	231.45	213.44	211.21	204.76	219.18	213.24	218.13	192.69	194.91	210.51
	0.00001	236.62		208.41	222.13	222.00	223.29	210.00	208.18	201.65	217.22	209.42	214.78	188.88	191.36	206.77
	0.0001	215.80		187.77	203.52	207.64	204.56	201.87	198.02	192.26	208.73	200.05	204.86	179.14	183.62	196.85
	0.001	158.17		134.69	149.12	155.35	150.05	150.35	146.39	140.05	158.95	149.55	153.42	131.22	135.52	148.53
	0.01	97.48		75.94	90.56	96.93	91.48	91.52	87.67	80.49	100.44	91.04	94.05	73.05	77.88	90.52
	0.1	45.37		25.03	38.97	46.18	40.11	39.75	36.28	29.81	48.77	38.96	42.70	24.09	25.76	38.36
Rep 3	0.000001	240.51		217.11	229.97	225.70	231.61	211.59	212.24	204.80	219.42	213.12	217.81	192.24	194.82	209.69
	0.00001	235.24		206.95	222.48	221.38	224.37	209.01	209.14	201.65	216.83	209.36	215.64	188.11	192.26	206.49
	0.0001	215.46		187.58	203.39	208.06	203.95	201.26	198.70	191.73	209.19	200.45	205.20	179.67	184.04	196.80
	0.001	157.30		133.44	149.42	155.59	150.73	150.17	146.90	140.72	158.91	149.43	153.84	130.14	135.96	148.42
	0.01	102.26		75.70	90.60	97.16	92.18	91.76	88.80	81.67	99.95	90.14	94.31	73.27	77.75	90.18
	0.1	49.46		25.04	40.68	48.11	42.76	41.05	37.36	30.60	49.14	40.55	44.87	25.15	27.82	39.30

Test 2(8/19/2003)		TDDA-NPOE-A			TDDA-NPOE-B			MTDA-TOTM-B			MTDA-NPOE-B			MTDA-TOTM-A		
	Conc. (M)	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3
	NaNO3	Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV		
Rep 1	0.000001	226.94	229.00	233.85	* drifts	218.01	217.41	183.39	183.71	* broken	210.21	211.38	212.03	197.59	188.39	186.03
	0.00001	218.20	218.35	219.94		209.63	205.77	180.17	179.35		206.64	206.61	206.04	193.79	183.77	180.29
	0.0001	202.56	202.86	201.42		196.07	188.70	172.05	171.26		199.76	198.27	195.67	186.20	176.87	170.76
	0.001	151.02	155.08	151.46		145.08	137.77	128.01	128.51		154.66	151.05	146.86	140.15	132.72	125.45
	0.01	93.20	97.20	93.56		87.17	80.17	69.71	70.36		95.70	91.16	87.27	84.03	75.61	67.00
	0.1	41.76	48.05	43.16		35.91	28.80	17.51	19.12		45.04	40.12	36.25	34.54	22.45	14.79
Rep 2	0.000001	228.35	228.45	233.37		216.24	220.05	187.05	185.82		213.96	212.75	213.02	200.42	193.52	187.94
	0.00001	223.19	222.48	224.51		213.05	213.75	184.15	182.81		211.96	209.76	209.09	197.64	189.57	183.44
	0.0001	206.08	205.08	204.42		198.63	193.97	175.77	174.94		204.24	200.37	198.43	189.39	181.67	174.22
	0.001	152.14	155.85	152.47		146.44	140.62	128.82	129.68		156.44	150.99	146.33	142.53	134.70	125.42
	0.01	92.75	97.68	94.37		88.30	81.13	70.12	69.90		96.82	90.80	86.66	84.23	76.14	67.39
	0.1	41.79	47.98	43.77		36.69	30.12	18.20	18.77		44.80	39.67	35.65	34.78	23.87	15.21
Rep 3	0.000001	230.13	231.36	236.20		218.79	222.76	188.39	186.80		214.97	213.73	214.19	203.31	194.98	188.58
	0.00001	223.49	224.15	225.79		215.02	214.48	184.83	183.21		212.62	209.72	210.12	199.61	189.48	184.80
	0.0001	206.85	206.99	205.48		200.11	195.01	176.71	175.16		205.31	201.30	198.93	191.06	182.36	174.87
	0.001	153.20	157.69	153.74		148.60	141.00	130.45	130.39		157.80	151.30	147.29	143.56	135.14	127.01
	0.01	93.70	99.28	94.96		90.27	83.05	70.73	71.45		97.28	91.24	87.86	86.81	76.35	68.61
	0.1	42.08	48.53	43.65		38.52	30.47	19.63	17.98		45.12	40.18	35.88	35.96	26.59	16.91

Table C.4. EMF data taken from selectivity tests of N electrodes in DI water.

DI water

	Test 1 (8/31/2003)		TDDA-NPOE-A			TDDA-NPOE-B			MTDA-NPOE-A			MTDA-NPOE-B			MTDA-TOTM-A		
	Ions	Conc. (M)	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3
			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV		
Rep 1	$NaNO_3$	0.01	84.88	78.14	71.21	96.37	108.40	106.79	85.28	85.80	73.79	86.31	89.67	95.33	68.35	72.04	92.50
	$NaNO_3$	0.1	30.24	25.62	18.58	42.09	55.00	52.46	33.17	32.74	19.61	32.52	36.21	41.43	15.56	17.34	39.04
	$NaNO_3$	0.01	85.25	77.04	70.57	94.94	107.28	105.38	86.67	85.87	74.11	86.13	89.22	95.47	68.80	71.92	92.55
	$NaHCO_3$	0.1	227.23	223.67	223.40	241.90	242.73	257.04	179.93	181.27	168.53	183.72	186.59	194.96	153.36	156.96	176.68
	$NaNO_3$	0.01	86.86	79.79	72.36	95.32	108.06	107.00	87.22	86.21	76.03	86.97	90.51	96.67	68.20	71.49	94.44
	NaCl	0.1	167.64	156.54	156.61	176.52	184.31	191.77	133.39	134.28	123.02	135.22	137.90	146.30	110.81	114.63	137.88
	$NaNO_3$	0.01	87.73	79.67	73.72	96.16	108.66	108.48	86.80	85.05	75.38	86.08	90.00	97.00	68.41	71.77	94.12
	NaBr	0.1	87.88	76.60	71.68	93.84	107.99	108.88	66.51	69.48	59.31	70.56	74.45	81.84	49.23	51.65	75.85
Rep 2	$NaNO_3$	0.01	89.57	79.70	72.71	97.09	107.50	108.38	86.85	84.33	76.05	85.70	91.63	96.48	68.73	72.32	95.02
	$NaNO_3$	0.1	35.28	25.17	19.12	42.46	54.62	53.83	33.74	30.76	23.35	32.49	37.28	42.39	17.82	17.08	40.88
	$NaNO_3$	0.01	88.56	77.25	71.14	95.46	106.52	107.24	87.64	84.73	76.66	85.37	91.08	96.16	67.75	70.05	94.26
	$NaHCO_3$	0.1	230.06	223.24	223.87	241.61	241.34	257.51	180.90	181.28	171.65	183.84	188.53	196.48	153.32	156.16	178.07
	$NaNO_3$	0.01	90.42	79.66	73.70	97.16	108.01	108.10	88.82	84.70	78.92	86.44	92.72	98.15	70.02	71.76	96.13
	NaCl	0.1	168.11	154.52	155.34	175.82	183.22	190.09	133.85	134.28	125.10	135.96	139.72	147.31	111.87	114.48	139.08
	$NaNO_3$	0.01	89.99	79.63	73.30	96.97	107.94	108.48	87.94	84.44	77.08	85.47	90.70	96.77	68.79	70.24	95.21
	NaBr	0.1	88.73	76.79	72.57	94.77	106.62	106.90	68.78	69.26	61.28	70.99	76.72	81.81	51.94	52.21	75.97
Rep 3	$NaNO_3$	0.01	90.70	78.39	72.37	98.14	107.51	108.74	87.51	84.08	77.44	85.51	93.14	97.19	69.72	70.61	95.42
	$NaNO_3$	0.1	35.89	25.09	17.98	42.49	54.16	53.49	33.73	30.57	23.87	32.09	38.71	43.07	17.49	17.51	41.57
	$NaNO_3$	0.01	88.67	76.78	71.06	96.13	106.74	107.18	87.46	83.52	77.12	85.36	91.95	97.00	69.12	70.67	94.62
	$NaHCO_3$	0.1	229.24	221.13	221.89	240.93	239.85	256.19	180.31	180.57	171.80	183.74	189.60	196.51	153.28	156.02	177.94
	$NaNO_3$	0.01	90.38	79.69	72.73	97.18	108.25	107.85	88.92	84.59	79.03	86.34	93.87	98.63	69.95	71.34	95.81
	NaCl	0.1	168.04	154.24	153.20	175.85	182.76	190.77	135.09	133.79	125.76	136.14	141.33	148.35	111.98	114.24	140.48
	$NaNO_3$	0.01	92.53	80.48	74.56	96.01	107.48	107.80	88.91	84.76	78.63	85.55	91.42	96.69	70.40	72.29	95.86
	NaBr	0.1	94.00	77.85	72.86	93.14	106.29	105.84	71.29	69.58	63.34	70.68	75.94	81.40	52.43	53.31	78.54

	Test 2 (8/31/2003)		TDDA-NPOE-A			TDDA-NPOE-B			MTDA-TOTM-B			MTDA-NPOE-B			MTDA-TOTM-A		
	Ion	Conc. (M)	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3
			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV		
Rep 1	$NaNO_3$	0.01	106.10	100.83	96.20	91.39	99.92	106.06	72.57	77.04	* broken	86.39	90.55	92.35	84.00	76.42	75.04
	$NaNO_3$	0.1	53.31	49.85	43.29	37.14	50.56	53.62	17.45	23.09		35.16	38.18	43.37	32.55	22.36	21.23
	$NaNO_3$	0.01	106.92	101.57	92.66	88.70	101.32	105.42	68.21	74.46		86.09	88.70	93.91	81.62	73.46	72.84
	$NaHCO_3$	0.1	245.89	251.92	250.33	241.59	243.37	259.00	152.99	159.27		181.04	186.11	192.92	167.18	159.60	158.74
	$NaNO_3$	0.01	103.44	104.21	97.34	93.98	108.00	111.91	69.14	77.59		86.14	90.48	96.71	84.08	75.83	76.90
	NaCl	0.1	183.38	185.37	183.88	178.64	184.68	193.88	113.05	116.64		135.30	139.11	147.06	126.45	119.34	119.38
	$NaNO_3$	0.01	99.95	104.22	96.71	93.98	108.15	111.18	68.91	78.89		84.85	88.41	95.02	82.40	74.89	74.90
	NaBr	0.1	102.37	106.82	100.77	97.14	109.44	110.81	51.47	58.51		70.71	74.92	81.71	67.19	57.73	58.81
Rep 2	$NaNO_3$	0.01	98.38	107.62	98.72	95.42	109.86	115.19	67.90	78.96		84.37	88.19	93.36	82.80	75.02	76.01
	$NaNO_3$	0.1	45.95	54.73	44.62	42.91	59.06	61.97	15.46	25.96		32.41	35.91	42.37	33.03	23.92	24.77
	$NaNO_3$	0.01	96.68	105.71	95.44	94.03	109.38	112.95	67.26	78.06		84.31	86.98	93.93	81.97	75.61	76.25
	$NaHCO_3$	0.1	239.74	255.80	252.31	244.82	246.03	262.91	152.47	159.18		182.06	186.12	192.92	167.23	160.93	160.52
	$NaNO_3$	0.01	97.92	107.62	98.46	96.07	113.42	119.96	69.14	80.52		85.71	89.48	95.40	84.32	76.55	78.15
	NaCl	0.1	178.62	186.96	183.44	179.44	189.11	198.20	112.44	119.05		135.18	138.14	145.43	125.73	119.81	121.22
	$NaNO_3$	0.01	96.49	108.56	97.77	95.62	114.43	116.52	66.89	81.73		83.82	87.50	94.14	82.33	75.75	77.62
	NaBr	0.1	98.09	108.26	101.13	95.99	114.21	113.27	50.45	63.50		70.36	73.85	80.60	66.24	59.51	58.56
Rep 3	$NaNO_3$	0.01	96.22	107.34	100.33	96.20	114.68	122.02	68.22	79.98		83.04	87.13	93.30	83.41	75.47	76.97
	$NaNO_3$	0.1	42.94	56.00	47.55	43.52	62.50	67.66	16.04	28.92		31.86	34.98	41.47	33.74	24.13	25.31
	$NaNO_3$	0.01	94.26	107.81	97.04	95.47	112.13	116.77	68.49	78.99		83.87	86.84	94.38	82.66	75.05	76.85
	$NaHCO_3$	0.1	237.21	258.33	253.33	245.64	252.16	267.62	152.46	161.24		183.21	186.41	192.42	169.48	163.28	161.47
	$NaNO_3$	0.01	96.07	110.56	99.38	97.55	118.35	126.63	68.30	82.08		84.75	89.40	95.65	84.63	77.05	79.42
	NaCl	0.1	176.63	187.29	183.74	179.57	194.67	199.10	111.53	120.97		134.45	138.37	145.25	126.73	120.92	120.81
	$NaNO_3$	0.01	95.20	108.37	98.54	96.59	117.95	117.53	67.70	81.84		83.04	87.28	93.79	82.39	74.99	76.98
	NaBr	0.1	97.00	108.58	99.59	94.77	116.78	114.17	50.97	62.84		69.80	73.96	80.80	66.61	59.66	60.93

Table C.5. EMF data taken from selectivity tests of N electrodes in 0.01M $CuSO_4$ solution.

0.01M CuSO4

	Test 1(8/27/2003)		TDDA-NPOE-A			TDDA-NPOE-B			MTDA-NPOE-A			MTDA-NPOE-B			MTDA-TOTM-A		
	Ions	Con. (M)	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3
			Measued voltage, mV			Measued voltage, mV			Measued voltage, mV			Measued voltage, mV			Measued voltage, mV		
Rep 1	$NaNO_3$	0.01	83.82	82.06	73.58	92.14	99.36	98.88	92.19	87.17	81.35	94.20	89.71	94.53	80.38	75.64	95.60
	$NaNO_3$	0.1	34.03	32.86	24.54	42.65	50.23	48.35	42.86	37.27	32.91	44.03	39.95	45.42	33.23	25.84	45.59
	$NaNO_3$	0.01	82.81	80.86	71.80	91.22	97.36	96.33	91.41	85.64	80.47	93.11	89.02	95.62	79.14	74.16	93.30
	$NaHCO_3$	0.1	170.60	167.25	165.81	181.25	180.62	190.25	145.07	141.46	137.44	147.06	143.29	152.69	128.98	124.55	145.34
	$NaNO_3$	0.01	83.51	81.89	72.85	91.65	98.38	98.84	91.97	85.33	82.38	92.46	88.21	94.73	80.39	75.51	93.86
	NaCl	0.1	90.77	89.88	82.69	97.77	104.05	104.58	80.48	75.95	72.75	82.75	77.95	85.86	68.12	61.15	82.04
	$NaNO_3$	0.01	80.61	78.71	70.06	89.08	95.75	95.68	88.90	82.52	79.27	90.76	84.38	92.29	76.45	70.85	94.09
	NaBr	0.1	33.97	31.60	22.64	40.96	48.84	49.19	41.01	34.97	32.03	43.79	37.51	45.08	32.15	22.44	47.25
Rep 2	$NaNO_3$	0.01	79.64	77.96	67.80	87.43	93.62	97.07	89.13	82.93	78.83	92.36	84.38	93.25	75.69	67.79	93.54
	$NaNO_3$	0.1	31.48	30.61	20.60	38.84	46.78	48.39	40.78	33.91	30.36	43.23	35.62	44.52	30.04	21.15	44.41
	$NaNO_3$	0.01	78.55	77.83	67.48	87.83	93.56	97.73	89.61	82.61	78.25	91.00	84.39	93.06	75.91	68.87	92.11
	$NaHCO_3$	0.1	169.79	167.48	165.17	180.39	180.35	190.84	145.33	140.72	137.35	147.73	143.06	152.74	128.03	123.96	144.28
	$NaNO_3$	0.01	83.13	80.85	72.92	89.94	96.51	100.15	89.95	82.95	82.53	91.39	84.96	94.14	78.50	70.74	93.06
	NaCl	0.1	89.19	88.45	80.05	95.61	101.61	105.96	80.16	74.61	71.11	82.87	76.55	86.19	66.96	57.93	83.80
	$NaNO_3$	0.01	81.59	81.02	70.73	89.54	96.56	99.79	89.35	82.82	79.99	91.14	85.55	94.02	78.84	71.31	95.54
	NaBr	0.1	32.62	31.83	21.79	40.34	47.89	52.68	40.40	34.44	31.16	43.71	36.20	45.23	31.57	23.57	47.75
Rep 3	$NaNO_3$	0.01	80.38	79.76	70.17	89.13	95.80	100.21	89.89	83.29	80.77	92.92	85.63	94.86	78.62	71.12	94.96
	$NaNO_3$	0.1	33.74	33.20	24.53	40.89	49.14	53.45	41.93	34.87	33.15	43.69	38.27	47.32	34.04	24.61	47.45
	$NaNO_3$	0.01	81.19	79.34	69.99	88.83	95.30	100.10	91.05	83.27	80.18	91.09	85.80	94.08	78.32	70.97	93.17
	$NaHCO_3$	0.1	169.52	167.64	165.44	179.25	178.50	191.71	144.65	139.98	136.17	146.67	141.87	151.90	125.85	122.45	144.55
	$NaNO_3$	0.01	82.13	83.13	73.56	90.44	97.49	99.90	90.87	83.84	81.76	91.81	85.14	94.69	78.83	71.58	94.35
	NaCl	0.1	88.19	87.76	79.05	94.30	101.41	103.48	80.41	74.90	70.85	82.43	76.08	85.51	65.47	57.84	82.36
	$NaNO_3$	0.01	81.04	79.84	69.43	88.94	94.83	98.06	88.06	82.25	78.93	89.38	83.64	92.70	77.50	69.37	92.82
	NaBr	0.1	33.04	33.50	23.30	40.52	48.28	52.15	40.47	34.40	32.22	43.10	36.62	46.54	32.54	24.53	47.77

	Test 2 (8/28/2003)		TDDA-NPOE-A			TDDA-NPOE-B			MTDA-TOTM-B			MTDA-NPOE-B			MTDA-TOTM-A		
	Ions	Con. (M)	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3
			Measued voltage, mV			Measued voltage, mV			Measued voltage, mV			Measued voltage, mV			Measued voltage, mV		
Rep 1	$NaNO_3$	0.01	100.84	96.27	91.52	87.26	101.36	96.44	68.79	76.04	*broken	86.08	90.62	94.59	84.86	72.97	72.99
	$NaNO_3$	0.1	52.56	47.07	41.68	37.77	51.01	48.60	20.24	27.15		36.47	39.90	45.58	37.18	24.88	24.56
	$NaNO_3$	0.01	101.74	96.82	90.21	86.79	98.80	98.84	68.12	76.95		85.87	89.18	94.64	84.79	74.26	73.45
	$NaHCO_3$	0.1	189.17	183.68	186.22	177.49	180.19	188.44	117.87	122.26		139.60	144.32	150.61	131.80	122.56	123.42
	$NaNO_3$	0.01	103.27	99.48	93.10	87.30	102.87	102.74	68.35	79.22		85.01	90.15	94.69	84.44	73.95	72.89
	NaCl	0.1	111.12	106.88	99.85	93.94	104.36	108.36	56.17	63.04		75.27	80.69	86.55	73.14	61.52	61.46
	$NaNO_3$	0.01	106.07	101.13	94.76	88.10	102.19	102.48	69.63	79.80		86.09	92.09	95.34	85.77	75.12	75.51
	NaBr	0.1	55.61	52.68	45.58	39.42	55.59	54.08	22.75	32.99		37.96	43.65	48.00	39.63	27.88	28.50
Rep 2	$NaNO_3$	0.01	105.39	100.27	93.51	87.77	105.88	102.74	68.08	78.61		85.65	92.38	94.87	84.43	74.13	75.63
	$NaNO_3$	0.1	55.30	49.83	41.82	37.43	56.73	50.96	19.31	28.14		35.36	41.77	44.33	37.45	24.83	25.01
	$NaNO_3$	0.01	103.94	99.12	91.46	87.30	104.10	101.67	68.09	75.97		85.32	91.53	93.36	84.84	72.22	74.08
	$NaHCO_3$	0.1	193.69	187.55	186.64	176.63	187.45	192.34	119.00	124.83		140.44	147.09	151.63	133.27	123.86	126.18
	$NaNO_3$	0.01	106.42	102.11	94.05	87.57	106.31	105.25	69.17	79.91		85.51	92.27	93.40	84.32	72.81	75.65
	NaCl	0.1	111.52	107.23	99.71	92.92	108.68	109.16	55.56	64.77		74.98	81.73	85.47	73.37	60.59	62.61
	$NaNO_3$	0.01	105.12	101.81	94.03	88.41	104.76	103.10	67.73	77.94		85.46	91.64	94.29	83.63	72.41	73.29
	NaBr	0.1	54.51	51.43	43.36	38.00	56.74	52.89	19.32	29.41		35.34	42.01	44.29	37.03	25.15	25.57
Rep 3	$NaNO_3$	0.01	106.12	101.36	91.85	87.13	108.92	102.58	68.87	79.31		85.47	92.52	94.63	84.09	73.76	76.40
	$NaNO_3$	0.1	54.92	50.91	41.65	36.44	58.82	50.39	16.82	27.98		34.51	41.58	43.74	36.54	24.47	24.77
	$NaNO_3$	0.01	104.56	101.14	91.59	86.50	108.15	100.00	68.39	78.09		84.42	93.17	94.25	85.15	74.03	74.28
	$NaHCO_3$	0.1	191.96	187.18	184.81	175.53	188.92	190.04	115.53	122.04		138.43	146.48	148.85	131.66	122.31	122.25
	$NaNO_3$	0.01	106.59	103.93	94.58	87.51	108.73	105.33	68.59	80.34		85.15	92.39	93.91	84.33	74.21	75.05
	NaCl	0.1	110.25	107.91	100.11	91.16	110.87	107.44	54.79	62.57		74.22	83.05	84.04	71.53	59.99	60.72
	$NaNO_3$	0.01	105.62	103.54	94.97	87.63	107.80	103.26	68.58	78.62		84.15	92.44	94.53	83.82	73.55	74.28
	NaBr	0.1	54.74	52.25	43.29	36.64	59.69	51.58	18.57	29.20		34.56	42.66	43.59	36.04	23.92	24.62

Table C.6. EMF data taken from selectivity tests of N electrodes in Kelowna extractant.

Kelowna

	Test 1 (8/26/2003)		**TDDA-NPOE-A**			**TDDA-NPOE-B**			**MTDA-NPOE-A**			**MTDA-NPOE-B**			**MTDA-TOTM-A**		
	Ions	Con. (M)	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3
			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV		
Rep 1	NaNO$_3$	0.01	79.58	74.30	70.84	85.00	109.55	103.32	78.90	80.24	66.27	86.90	80.42	81.72	68.72	62.95	81.94
	NaNO$_3$	0.1	28.70	22.58	20.09	33.59	57.56	40.29	30.28	30.35	16.61	37.69	30.12	32.13	21.82	14.65	33.79
	NaNO$_3$	0.01	77.07	73.23	69.73	84.79	106.88	91.48	81.66	80.68	68.34	86.87	80.07	83.86	69.73	62.97	82.69
	NaHCO$_3$	0.1	192.36	187.78	191.66	203.62	215.62	210.50	177.61	178.69	166.19	184.05	177.16	184.09	152.71	151.72	170.92
	NaNO$_3$	0.01	77.72	73.65	70.71	85.59	106.78	90.87	82.38	80.51	69.57	88.46	79.47	83.92	69.04	63.35	83.23
	NaCl	0.1	136.10	127.71	129.44	143.83	160.81	149.29	123.03	122.55	112.16	130.78	122.19	128.84	104.39	101.42	123.68
	NaNO$_3$	0.01	76.83	72.90	68.99	85.35	105.82	90.82	81.36	80.53	69.74	87.40	80.04	84.54	70.00	62.73	85.72
	NaBr	0.1	80.34	76.37	73.26	87.48	106.94	92.30	66.48	69.00	60.27	77.58	69.14	75.30	56.74	51.83	74.35
Rep 2	NaNO$_3$	0.01	77.35	73.61	69.10	86.77	105.35	94.74	80.40	80.01	71.38	88.62	80.47	84.45	70.78	64.08	86.34
	NaNO$_3$	0.1	27.05	24.05	20.48	35.37	55.13	41.93	30.79	30.65	21.39	38.87	28.85	34.18	21.57	13.62	36.59
	NaNO$_3$	0.01	76.31	73.24	71.22	86.40	104.78	92.26	81.36	81.55	70.88	89.82	79.71	84.52	71.06	64.86	85.09
	NaHCO$_3$	0.1	188.67	183.69	192.76	201.82	212.64	208.74	175.49	178.72	168.48	185.54	177.09	184.78	153.84	152.90	171.63
	NaNO$_3$	0.01	75.79	74.55	76.25	87.66	105.15	91.97	80.58	81.66	72.33	88.71	79.56	86.17	71.37	64.78	84.48
	NaCl	0.1	134.12	127.92	131.00	145.31	159.01	148.65	121.23	123.69	114.55	131.44	123.39	130.06	105.27	102.22	125.22
	NaNO$_3$	0.01	76.95	73.58	72.28	88.80	106.55	90.49	81.72	81.57	72.01	88.68	79.76	84.59	69.99	64.58	84.91
	NaBr	0.1	80.52	75.55	77.08	90.53	106.50	90.72	67.15	70.87	61.44	77.62	69.42	75.06	56.71	52.25	74.51
Rep 3	NaNO$_3$	0.01	77.00	73.94	72.08	88.28	105.41	92.14	80.68	81.04	72.44	88.91	79.55	85.81	71.83	64.68	85.83
	NaNO$_3$	0.1	27.60	23.69	23.83	37.00	54.32	40.44	31.46	31.12	22.44	38.55	29.81	34.83	22.12	15.94	34.88
	NaNO$_3$	0.01	77.21	74.69	71.80	88.27	103.82	90.83	82.05	82.07	73.72	89.31	80.33	86.06	72.78	64.80	85.35
	NaHCO$_3$	0.1	187.64	184.55	189.25	203.48	208.28	206.30	175.59	180.09	168.25	184.97	179.21	184.56	155.43	153.09	174.25
	NaNO$_3$	0.01	76.40	74.02	74.66	90.09	105.45	89.60	81.95	81.47	72.52	88.82	80.35	86.05	73.38	66.51	87.83
	NaCl	0.1	135.30	129.97	131.25	147.96	158.88	148.07	122.80	124.81	115.82	131.96	123.21	129.92	106.50	104.53	125.89
	NaNO$_3$	0.01	not measured			not measured			not measured			not measured			not measured		
	NaBr	0.1															

	Test 2 (8/26/2003)		**TDDA-NPOE-A**			**TDDA-NPOE-B**			**MTDA-TOTM-B**			**MTDA-NPOE-B**			**MTDA-TOTM-A**		
	Ions	Con. (M)	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3
			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV		
Rep 1	NaNO$_3$	0.01	89.57	91.05	98.57	82.47	* drifts	85.77	67.27	66.46	* broken	90.05	85.87	79.10	82.07	67.97	65.06
	NaNO$_3$	0.1	39.95	39.66	44.90	32.12		36.54	19.36	13.71		40.86	33.90	28.50	37.17	17.27	16.32
	NaNO$_3$	0.01	89.25	88.79	94.43	81.64		89.79	69.71	62.38		90.47	83.70	78.25	85.27	66.63	65.53
	NaHCO$_3$	0.1	203.61	207.08	222.42	200.12		207.91	159.98	150.14		184.34	179.70	179.31	171.28	156.35	154.97
	NaNO$_3$	0.01	90.61	90.75	97.94	80.16		88.73	72.69	66.26		89.57	82.61	76.98	86.85	67.18	64.61
	NaCl	0.1	145.22	143.79	152.91	138.05		148.24	109.41	97.29		131.40	123.52	120.78	121.23	104.31	106.52
	NaNO$_3$	0.01	90.68	89.99	97.89	79.65		90.51	71.23	63.04		89.71	82.06	77.03	82.93	67.17	68.76
	NaBr	0.1	91.66	93.02	98.26	81.63		93.63	57.07	49.07		79.34	70.76	67.76	71.53	54.32	56.79
Rep 2	NaNO$_3$	0.01	96.85	91.27	96.81	82.21		91.02	73.04	62.57		90.27	82.68	79.11	85.63	66.95	66.63
	NaNO$_3$	0.1	45.09	42.06	49.24	31.16		41.31	23.54	13.09		38.64	32.83	29.36	38.39	18.93	19.53
	NaNO$_3$	0.01	94.99	89.49	97.03	80.56		91.00	75.45	62.79		88.39	82.61	78.55	87.00	68.42	67.80
	NaHCO$_3$	0.1	209.53	204.17	221.26	199.00		208.35	162.16	149.58		183.38	179.03	180.44	170.38	157.01	156.24
	NaNO$_3$	0.01	93.93	91.78	98.85	80.31		92.22	73.54	63.81		88.96	82.99	79.40	86.91	68.67	68.19
	NaCl	0.1	150.19	144.65	154.05	137.52		149.71	110.90	97.74		129.75	123.95	122.88	120.55	105.69	108.24
	NaNO$_3$	0.01	95.17	90.10	98.94	79.64		90.37	73.51	64.23		89.14	82.02	77.81	84.99	67.36	69.09
	NaBr	0.1	94.92	94.92	100.53	83.24		97.63	61.46	49.41		78.63	71.24	69.89	72.81	55.72	57.17
Rep 3	NaNO$_3$	0.01	95.15	91.00	97.53	80.14		90.71	74.14	62.54		87.49	81.48	80.75	86.44	67.89	68.91
	NaNO$_3$	0.1	44.51	42.28	50.11	31.26		38.22	24.03	12.27		38.61	31.96	31.96	38.61	18.59	20.19
	NaNO$_3$	0.01	94.17	90.19	97.88	80.77		87.48	75.12	62.35		87.78	82.80	81.73	87.02	68.41	68.32
	NaHCO$_3$	0.1	206.91	204.16	217.90	197.58		207.26	162.25	150.55		181.50	179.22	182.96	169.49	156.65	158.08
	NaNO$_3$	0.01	93.53	91.77	96.64	80.59		88.43	75.45	64.18		87.89	82.34	82.97	87.29	68.60	70.92
	NaCl	0.1	150.17	145.66	153.84	139.00		146.01	112.00	98.54		130.00	124.17	127.96	121.89	105.02	108.71
	NaNO$_3$	0.01	92.30	90.88	97.33	80.62		89.54	71.86	63.10		88.76	81.46	82.86	85.89	68.68	69.66
	NaBr	0.1	95.42	95.06	100.93	84.21		91.13	60.42	49.06		78.68	71.25	74.05	72.91	54.43	58.23

Table C.7. EMF data taken from sensitivity tests of K electrodes in DI water.

DI water

2/7/2004		V-DOS			V-NPOE			V-DOA			TDDA-NPOE			MTDA-NPOE		
	Con.(M)	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3
	KCl	Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV		
Rep 1	0.000001	-104.53	-105.49	-123.81	* drifts	-130.33	-129.78	-105.63	-84.72	* broken	322.84	338.15	331.65	313.73	288.74	286.75
	0.00001	-92.59	-84.40	-109.47		-120.26	-115.94	-97.29	-81.40		320.05	337.45	332.71	315.77	289.98	289.23
	0.0001	-41.18	-32.24	-57.44		-67.12	-61.10	-50.40	-39.75		275.05	302.21	285.15	305.64	286.06	290.19
	0.001	13.47	29.86	-1.70		-13.11	-6.84	-1.21	14.06		223.79	249.10	239.78	246.65	233.01	241.06
	0.01	73.86	86.82	59.27		47.86	53.87	56.21	75.23		168.59	194.13	185.04	190.44	175.12	180.62
	0.1	130.17	144.35	115.72		105.07	109.81	106.70	121.47		116.25	143.53	134.55	136.87	120.99	127.26
Rep 2	0.000001	-104.25	-95.73	-125.36		-136.24	-134.80	-117.99	-90.12		328.61	348.13	340.87	322.87	294.57	295.24
	0.00001	-91.31	-72.12	-108.11		-122.00	-117.21	-105.72	-81.90		324.16	342.37	337.71	318.82	293.56	292.36
	0.0001	-36.37	-16.78	-53.95		-66.66	-61.66	-56.76	-37.37		279.16	306.40	289.58	307.91	289.75	292.83
	0.001	16.26	35.38	0.59		-12.66	-7.80	-0.59	15.21		226.23	249.95	240.69	247.95	234.41	242.17
	0.01	76.45	94.45	60.87		47.97	53.73	57.55	75.35		171.56	195.05	186.86	191.01	177.88	181.82
	0.1	135.09	151.59	117.32		107.01	109.99	108.47	121.69		119.17	143.97	136.97	137.32	121.72	126.40
Rep 3	0.000001	-100.14	-85.47	-122.96		-135.28	-134.56	-115.65	-88.91		332.51	347.88	344.90	325.49	298.52	297.55
	0.00001	-86.01	-65.07	-105.98		-121.70	-116.42	-103.94	-80.66		326.93	343.38	339.75	322.09	295.43	293.70
	0.0001	-36.98	-15.76	-53.21		-68.00	-62.25	-56.86	-37.09		280.54	304.28	290.92	308.45	290.83	292.79
	0.001	17.81	38.04	0.99		-13.13	-7.65	-0.49	16.93		228.54	249.56	241.23	248.71	235.55	242.30
	0.01	77.57	95.11	61.15		47.49	52.34	57.27	74.77		172.48	193.95	187.38	190.58	176.04	179.39
	0.1	137.43	153.22	121.05		107.20	111.23	110.44	123.51		122.08	145.13	137.62	139.89	122.78	127.02

2/16/2004	KCl	V-DOS			V-NPOE			V-DOA			TDDA-NPOE			MTDA-NPOE		
	Con. (M)	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3
		Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV		
Rep 1	0.000001	-130.11	-134.81	-145.26	-138.64	-154.56	-137.59	-145.22	-124.23	* broken	341.67	333.58	330.44	281.70	285.66	273.83
	0.00001	-107.57	-109.37	-118.85	-116.38	-131.37	-113.59	-127.59	-105.44		340.88	333.76	330.24	281.03	286.96	275.22
	0.0001	-51.87	-51.31	-60.63	-63.18	-72.29	-56.42	-76.12	-55.13		298.85	298.88	292.01	267.26	285.36	274.86
	0.001	7.07	8.30	-0.66	-9.76	-13.81	1.41	-18.16	10.38		253.11	255.30	246.60	221.63	235.51	232.28
	0.01	74.82	76.33	69.89	55.34	55.47	72.40	47.84	75.71		199.17	201.92	193.83	168.79	177.95	174.20
	0.1	131.03	133.23	126.41	98.85	114.76	131.42	97.63	122.48		145.66	150.16	139.89	115.55	123.90	119.19
Rep 2	0.000001	-125.09	-127.97	-130.85	-123.68	-145.80	-129.97	-141.63	-102.85		345.11	336.44	335.97	291.31	291.07	276.88
	0.00001	-100.40	-101.95	-107.48	-105.97	-124.99	-107.39	-123.73	-90.61		345.12	336.44	334.99	291.37	291.87	278.03
	0.0001	-46.34	-43.49	-48.80	-56.64	-65.35	-48.80	-67.49	-41.20		301.47	301.04	297.45	275.02	283.92	277.86
	0.001	12.79	14.85	11.87	-1.90	-5.66	9.66	-8.56	19.42		256.54	258.13	250.78	228.97	238.33	235.16
	0.01	78.67	81.13	77.76	57.42	62.51	74.87	57.96	83.01		200.49	203.26	195.39	172.65	182.51	176.36
	0.1	134.87	137.51	132.83	102.99	120.15	131.35	108.06	123.90		145.97	149.23	141.79	120.98	126.46	119.24
Rep 3	0.000001	-118.84	-121.28	-123.06	-118.28	-138.73	-123.96	-131.93	-96.33		349.59	339.87	340.40	299.00	295.82	281.08
	0.00001	-96.95	-96.52	-100.72	-101.75	-117.48	-103.74	-112.01	-83.14		346.49	338.57	338.37	297.76	297.51	280.89
	0.0001	-42.92	-38.30	-44.92	-51.11	-60.04	-47.26	-61.66	-35.68		303.08	302.42	299.89	280.55	287.39	280.91
	0.001	16.63	21.35	15.90	4.09	-0.99	13.32	0.79	24.87		261.27	260.18	254.72	235.00	242.07	238.80
	0.01	81.02	88.53	81.17	63.86	63.51	76.98	64.68	88.80		202.40	203.61	198.27	177.17	182.99	176.60
	0.1	not measured			not measured			not measured			not measured			not measuerd		

Table C.8. EMF data taken from selectivity tests of K electrodes in Kelowna extractant.

Kelowna

2/20/2004		V-DOS			V-NPOE			V-DOA			TDDA-NPOE			MTDA-NPOE		
	Con.(M)	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3
	KCl	Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV		
Rep 1	0.000001	-49.36	-51.56	-56.99	-49.65	-76.60	-57.40	-67.14	-53.94	*broken	224.52	167.33	211.76	207.55	197.34	179.61
	0.00001	-49.96	-52.40	-60.49	-46.20	-76.83	-56.46	-68.01	-56.47		223.12	165.99	209.71	208.50	195.15	177.77
	0.0001	-47.70	-49.32	-57.17	-43.47	-70.33	-53.71	-66.15	-54.03		216.78	158.42	203.53	203.24	189.38	175.26
	0.001	-12.34	-10.74	-17.66	-9.72	-28.67	-14.52	-28.87	-18.80		213.71	158.06	200.28	199.44	187.06	172.80
	0.01	44.20	45.58	39.63	38.31	27.33	44.22	29.11	38.45		182.64	132.18	170.48	170.41	157.55	139.17
	0.1	105.02	105.50	100.25	78.83	86.49	104.27	77.64	81.39		135.04	87.32	122.41	121.74	111.43	91.55
Rep 2	0.000001	-43.51	-46.18	-54.69	-34.47	-67.05	-49.17	-65.01	-40.68		230.38	177.03	219.95	215.01	210.37	189.02
	0.00001	-43.11	-45.96	-56.04	-37.79	-68.01	-50.40	-63.40	-46.39		228.48	174.59	216.61	212.44	202.80	186.01
	0.0001	-36.26	-37.35	-47.57	-30.15	-57.52	-41.02	-55.70	-39.62		226.59	172.05	213.67	212.97	199.30	184.83
	0.001	-4.29	-3.68	-13.08	-2.56	-22.66	-6.61	-22.27	-10.41		219.06	166.19	205.00	204.89	191.66	177.93
	0.01	52.42	56.16	46.59	42.80	34.89	51.59	34.44	46.50		190.04	143.57	177.05	176.39	163.70	146.84
	0.1	114.28	111.99	101.76	81.68	91.53	109.02	82.51	86.69		139.60	94.86	126.36	125.35	112.30	94.22
Rep 3	0.000001	-34.43	-40.04	-47.89	-26.41	-60.44	-44.35	-58.25	-37.76		235.23	185.82	221.16	218.55	207.62	191.61
	0.00001	-33.25	-37.15	-46.02	-29.09	-57.49	-41.73	-57.32	-39.44		234.38	186.15	220.50	220.87	208.08	194.02
	0.0001	-27.65	-30.43	-39.03	-20.93	-48.19	-33.43	-51.91	-32.41		231.99	182.51	220.21	220.22	204.72	193.09
	0.001	1.76	1.31	-7.13	1.24	-17.01	-2.27	-20.06	-5.44		220.93	172.61	208.77	209.87	193.33	183.56
	0.01	58.22	58.79	49.55	49.04	40.29	55.55	36.31	50.82		192.69	147.80	179.72	181.04	166.27	150.61
	0.1	118.68	117.00	108.33	87.33	99.10	114.47	84.98	92.34		143.87	99.94	129.93	130.92	116.50	99.32

5/8/2004		V-DOS			V-NPOE			V-DOA (new)			TDDA-NPOE			MTDA-NPOE		
	Con.(M)	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3
	KCl	Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV		
Rep 1	0.000001	-16.33	-21.91	-21.05	-11.30	-25.00	-32.77	-21.65	-4.94	2.09	* error due to previous selectivity tests					
	0.00001	-15.24	-20.82	-25.51	-10.12	-22.88	-30.89	-26.02	-4.66	7.30						
	0.0001	-10.42	-19.45	-18.08	-9.07	-23.14	-26.95	-15.34	-4.92	7.47						
	0.001	11.39	7.77	14.07	34.78	17.41	4.07	17.73	26.52	39.83						
	0.01	65.74	61.87	66.70	85.21	65.93	52.95	70.85	79.98	94.82						
	0.1	124.06	121.31	122.51	124.53	102.35	98.13	130.07	137.55	154.30						
Rep 2	0.000001	-17.68	-21.79	-21.20	-8.21	-28.75	-34.20	-18.54	-7.99	8.10						
	0.00001	-17.33	-23.53	-21.42	-6.91	-27.57	-31.86	-20.18	-7.23	10.27						
	0.0001	-11.57	-17.22	-14.13	1.32	-21.25	-25.19	-12.15	-0.40	11.77						
	0.001	11.23	11.17	14.23	35.64	11.83	8.57	19.67	31.21	48.58						
	0.01	64.86	62.03	65.03	82.75	63.44	55.16	71.99	84.65	99.31						
	0.1	124.83	121.41	125.24	124.50	102.81	99.10	129.23	140.43	160.30						
Rep 3	0.000001	-18.78	-21.89	-22.19	-8.14	-29.19	-35.45	-20.66	-7.86	11.74						
	0.00001	-17.86	-20.73	-21.54	-9.32	-28.22	-33.76	-21.37	-5.78	10.46						
	0.0001	-11.06	-15.35	-14.02	10.02	-20.67	-25.62	-13.41	3.78	21.96						
	0.001	14.06	9.96	16.70	43.23	11.08	7.34	18.54	35.05	55.57						
	0.01	66.29	63.35	68.79	88.51	62.77	57.06	73.11	86.19	110.92						
	0.1	125.15	123.01	124.73	137.68	104.05	100.91	133.49	146.95	167.37						

Table C.9. EMF data taken from sensitivity tests of K electrodes in Bray P1 (upper) and Mehlich III (lower) extractants.

Bray P1

3/202004		V-DOS			V-NPOE			V-DOA			TDDA-NPOE			MTDA-NPOE		
	Con.(M)	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3
	KCl	Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV		
Rep 1	0.000001	-16.94	-23.35	-27.07	* drifts	-37.11	-25.52	* drifts	* drifts	-58.97	* drifts	35.19	16.83	18.54	39.52	31.43
	0.00001	-16.59	-24.66	-28.63		-38.17	-26.00			-59.40		32.59	13.01	14.91	40.49	28.48
	0.0001	-10.31	-21.52	-25.86		-35.20	-23.70			-54.99		30.22	11.26	12.86	38.58	25.98
	0.001	11.19	0.35	-3.27		-11.77	0.74			-30.87		31.58	12.59	14.21	45.04	28.55
	0.01	60.59	48.62	44.16		36.54	49.04			16.29		30.66	11.95	14.79	45.53	27.97
	0.1	112.18	100.63	95.77		90.90	101.46			64.38		36.17	17.98	20.36	51.41	34.20
Rep 2	0.000001	-6.72	-26.41	-30.75		-40.06	-27.75			-55.39		31.04	13.63	14.83	47.44	28.05
	0.00001	-6.75	-24.77	-29.68		-39.08	-25.90			-54.31		30.40	12.53	15.13	47.57	28.30
	0.0001	-1.03	-21.25	-25.25		-34.64	-22.15			-50.67		29.61	12.15	13.79	44.62	27.36
	0.001	18.48	1.03	-4.42		-12.51	2.93			-29.38		30.16	12.38	13.84	43.83	27.51
	0.01	68.31	49.83	45.15		38.59	53.58			18.30		31.32	14.19	15.91	43.99	29.91
	0.1	117.49	101.44	96.47		93.75	106.26			65.57		36.64	23.04	21.65	48.63	35.08
Rep 3	0.000001	-0.36	-24.56	-28.59		-37.34	-19.94			-55.56		32.92	18.80	18.15	43.36	30.80
	0.00001	0.08	-22.88	-27.28		-36.01	-17.93			-54.46		32.38	16.80	17.79	42.45	30.25
	0.0001	4.40	-19.23	-23.77		-32.31	-13.39			-51.18		31.50	15.05	15.88	41.37	29.34
	0.001	25.88	3.94	-0.71		-7.02	10.59			-26.95		33.68	18.20	18.60	41.58	32.41
	0.01	72.93	52.09	46.88		43.42	59.12			19.42		33.07	21.96	18.22	42.03	32.52
	0.1	123.13	105.34	99.57		96.98	112.80			68.43		39.66	30.18	24.88	48.11	38.23

Mehlich III

3/2/2004		V-DOS			V-NPOE			V-DOA			TDDA-NPOE			MTDA-NPOE		
	Con.(M)	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3
	KCl	Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV		
Rep 1	0.000001	27.70	30.80	18.77	* drifts	8.41	27.94	* drifts	* drifts	38.15	-5.00	-22.52	-18.72	-10.15	25.76	-5.81
	0.00001	28.23	30.81	18.41		9.75	28.38			40.68	-5.26	-20.98	-18.26	-10.06	25.43	-5.89
	0.0001	27.56	31.07	18.38		10.56	28.82			41.85	-6.42	-21.83	-19.72	-10.64	24.83	-5.37
	0.001	32.25	36.74	23.32		16.19	34.61			48.10	-6.81	-21.23	-20.27	-10.77	23.66	-5.73
	0.01	53.76	59.85	46.36		43.46	60.70			71.98	-6.44	-19.71	-20.10	-10.34	23.20	-5.09
	0.1	91.24	99.46	85.04		88.07	101.92			115.90	-5.73	-15.86	-17.96	-8.54	25.45	-3.52
Rep 2	0.000001	28.26	31.49	18.65		13.23	30.53			43.35	-8.51	-18.89	-20.86	-10.84	22.49	-5.13
	0.00001	29.17	31.98	20.38		15.19	32.20			44.95	-6.87	-17.10	-18.66	-10.18	22.76	-4.25
	0.0001	29.60	32.44	20.64		14.52	31.12			44.51	-7.87	-17.29	-19.57	-10.54	21.85	-4.45
	0.001	33.72	36.39	24.86		19.65	35.83			46.18	-7.89	-17.59	-21.43	-10.97	21.58	-4.23
	0.01	55.71	59.96	47.62		45.33	61.58			70.57	-7.47	-17.14	-20.70	-10.01	21.55	-4.46
	0.1	91.54	97.66	85.97		91.92	103.59			112.71	-6.27	-15.19	-17.64	-7.88	23.31	-1.48
Rep 3	0.000001	25.18	26.46	15.72		9.85	29.63			35.73	-10.98	-20.16	-26.78	-15.50	15.48	-7.49
	0.00001	26.54	27.23	16.41		10.52	29.34			38.38	-9.31	-19.63	-25.53	-15.24	15.21	-6.69
	0.0001	26.74	26.13	15.90		8.87	27.97			38.86	-8.94	-19.35	-26.22	-16.08	14.26	-7.97
	0.001	30.77	30.52	20.88		13.72	31.93			43.93	-9.73	-19.04	-27.66	-16.80	13.54	-7.95
	0.01	54.66	54.98	44.44		41.66	59.39			70.86	-6.96	-17.53	-24.21	-14.53	15.05	-5.17
	0.1	91.39	96.69	82.86		86.53	102.22			112.85	-5.26	-11.96	-21.94	-13.05	16.34	-0.79

Table C.10. EMF data taken from selectivity tests of K electrodes in DI water.

		DI water															
		4/25/2004	V-DOS			V-NPOE			V-DOA			TDDA-NPOE			MTDA-NPOE		
	Ions	Con.(M)	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3
			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV		
Rep 1	KNO_3	0.01	60.12	*drifts	* drifts	41.27	42.22	56.05	70.54	66.58	65.50	55.59	51.50	48.35	51.94	57.73	60.23
	KNO_3	0.1	113.48			35.18	36.12	49.09	121.96	117.91	117.31	4.31	-0.82	-3.97	0.89	3.89	8.32
	KNO_3	0.01	60.10			42.15	44.25	56.17	69.61	65.77	64.48	55.65	50.16	47.85	52.21	56.94	62.94
	$Mg(NO_3)_2$	0.1	-87.64			-78.67	-110.24	-81.66	-110.81	-109.79	-92.47	-6.89	-10.73	-15.56	-10.27	-7.80	-0.99
	KNO_3	0.01	56.93			37.27	43.34	52.25	65.68	62.27	61.44	52.19	47.68	44.75	48.51	53.09	59.29
	$Ca(NO_3)_2$	0.1	-94.82			-86.17	-115.36	-90.33	-117.21	-116.10	-99.47	-5.68	-10.13	-12.56	-8.47	-5.91	0.66
	KNO_3	0.01	55.94			36.26	43.63	51.28	64.63	61.61	60.40	51.03	46.10	46.21	47.32	52.13	58.17
	$NaNO_3$	0.1	-90.76			-91.47	-112.59	-93.53	-111.27	-110.71	-96.46	3.88	-0.97	-3.44	1.16	3.34	9.57
	KNO_3	0.01	59.91			39.82	49.76	54.10	68.51	65.51	63.80	53.76	50.10	47.49	51.21	55.78	61.79
	$LiNO_3$	0.1	-90.65			-87.70	-101.76	-86.76	-99.30	-100.79	-94.16	4.90	-0.30	-2.67	1.22	3.71	10.80
	KNO_3	0.01	59.09			38.93	49.25	53.00	67.33	64.42	63.21	54.19	48.11	47.37	50.13	55.06	60.85
	$Al(NO_3)_3$	0.1	-91.89			-84.26	-109.76	-89.73	-113.24	-112.02	-98.69	-7.53	-12.17	-14.99	-10.39	-9.07	-2.78
	KNO3	0.01	54.83			34.79	45.95	49.25	63.31	60.70	61.93	49.16	44.92	42.93	46.43	50.84	56.59
	NH_4NO_3	0.1	14.41			-9.24	-2.19	2.05	14.93	12.84	14.98	2.29	-1.95	-4.52	0.83	2.02	7.41
	KNO_3	0.01	59.09			39.41	51.70	53.12	66.91	64.52	64.84	53.98	48.87	46.71	50.63	55.26	61.27
	KNO_3	0.1	113.40			37.07	48.30	49.08	120.34	117.92	118.02	4.74	-1.14	-3.12	2.45	4.69	10.52
Rep 2	KNO_3	0.01	60.88			40.59	52.98	54.57	67.48	64.56	64.75	54.94	50.10	49.59	51.27	56.27	61.98
	KNO_3	0.1	114.41			35.21	48.05	49.99	120.54	118.30	117.58	5.72	0.83	-1.59	1.61	3.98	9.03
	KNO_3	0.01	61.26			41.65	53.18	55.40	67.56	65.95	64.94	55.74	50.94	49.54	52.02	57.03	62.72
	$Mg(NO_3)_2$	0.1	-93.58			-93.29	-105.94	-90.90	-113.99	-112.03	-106.08	-6.18	-9.51	-12.20	-8.86	-6.30	-0.74
	KNO_3	0.01	58.96			38.28	50.39	52.26	63.99	62.00	62.27	52.87	49.42	46.59	49.27	53.76	59.40
	$Ca(NO_3)_2$	0.1	-99.25			-101.14	-112.03	-97.43	-119.02	-117.06	-111.47	-4.73	-8.45	-10.93	-8.07	-5.44	-0.71
	KNO_3	0.01	59.47			39.16	50.95	53.14	64.87	62.61	62.93	53.71	49.22	46.86	49.84	54.33	60.18
	$NaNO_3$	0.1	-91.28			-100.90	-108.26	-97.07	-112.27	-111.23	-105.25	6.66	1.37	-0.86	2.24	4.37	10.54
	KNO_3	0.01	62.88			41.16	55.36	56.65	68.42	66.40	66.81	56.97	51.64	51.29	52.71	57.63	62.94
	$LiNO_3$	0.1	-90.26			-95.89	-97.65	-90.51	-100.13	-100.85	-97.87	6.78	1.79	-0.63	2.23	5.52	11.19
	KNO_3	0.01	62.92			42.21	54.76	56.72	67.93	66.23	65.79	57.02	51.92	50.07	53.13	57.46	63.18
	$Al(NO_3)_3$	0.1	-93.58			-97.59	-106.78	-95.89	-114.84	-111.96	-106.82	-5.98	-10.40	-11.83	-10.70	-8.28	-2.67
	KNO3	0.01	59.11			38.13	51.39	52.76	63.74	61.56	61.64	52.70	48.07	49.19	48.27	53.10	58.28
	NH_4NO_3	0.1	16.79			-8.51	1.11	2.62	14.50	13.21	13.73	5.12	0.93	-0.24	1.63	3.84	9.12
	KNO_3	0.01	61.46			40.63	54.11	55.33	66.47	65.07	65.10	55.16	51.41	50.52	51.83	55.98	61.46
	KNO_3	0.1	116.75			39.12	50.51	52.74	120.00	119.01	118.89	5.64	2.32	0.95	2.89	4.27	9.58
Rep 3	KNO_3	0.01	63.88			43.01	55.21	56.86	66.88	65.60	65.90	57.81	54.03	54.59	52.33	57.93	63.33
	KNO_3	0.1	117.17			39.12	50.96	52.46	120.86	118.44	117.79	6.28	4.14	1.28	2.16	5.10	10.39
	KNO_3	0.01	64.91			44.39	55.86	57.71	68.33	67.68	66.57	58.13	54.59	53.56	53.74	58.67	63.93
	$Mg(NO_3)_2$	0.1	-94.77			-100.49	-105.07	-94.77	-114.56	-108.84	-108.30	-4.54	-7.79	-11.08	-8.76	-6.64	-1.01
	KNO_3	0.01	62.83			41.27	54.95	56.00	65.96	66.32	63.84	57.04	52.52	50.76	51.38	56.87	62.01
	$Ca(NO_3)_2$	0.1	-99.96			-107.56	-110.61	-101.72	-119.61	-115.83	-112.53	-4.21	-6.51	-9.87	-8.49	-5.71	0.87
	KNO_3	0.01	62.86			42.06	54.08	56.39	66.56	66.05	64.22	56.98	54.15	49.80	52.11	57.01	62.65
	$NaNO_3$	0.1	-91.10			-103.20	-103.87	-99.97	-111.97	-108.54	-104.72	8.91	7.25	2.64	4.16	7.69	13.62
	KNO_3	0.01	66.43			46.73	59.52	59.38	70.32	69.69	67.88	61.75	59.77	56.70	55.98	61.37	66.36
	$LiNO_3$	0.1	-89.57			-97.13	-96.15	-91.74	-99.59	-98.54	-97.86	9.09	7.16	3.92	3.59	7.33	12.53
	KNO_3	0.01	66.05			45.76	59.07	58.58	69.35	68.58	66.43	61.47	58.63	58.38	55.22	60.81	65.58
	$Al(NO_3)_3$	0.1	-94.28			-101.33	-104.72	-98.06	-114.71	-111.19	-104.84	-3.90	-7.41	-8.31	-9.71	-7.62	-1.45
	KNO3	0.01	61.46			42.27	54.99	54.16	64.87	64.54	63.74	56.98	55.24	52.76	51.43	56.11	61.48
	NH_4NO_3	0.1	19.31			-5.36	5.16	4.58	15.04	15.15	16.10	7.74	5.77	2.44	2.52	4.56	10.57
	KNO_3	0.01	63.64			43.77	57.60	56.86	66.93	66.29	65.78	59.56	57.58	54.96	54.60	58.55	63.45
	KNO_3	0.1	118.53			42.78	54.08	54.11	121.08	120.93	119.56	8.70	7.03	4.50	3.63	6.07	11.12

Table C.11. EMF data taken from selectivity tests of K electrodes in Kelowna extractant.

		Kelowna															
		4/29/2004	**V-DOS**			**V-NPOE**			**V-DOA**			**TDDA-NPOE**			**MTDA-NPOE**		
	Ions	Con. (M)	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3
			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV		
Rep 1	KNO_3	0.01	68.64	* drifts	57.49	42.54	50.53	54.63	68.73	69.83	71.56	57.55	54.58	52.74	39.60	49.71	46.09
	KNO_3	0.1	123.53		108.32	30.80	39.26	41.20	122.23	122.87	122.89	1.75	-0.70	-6.93	-8.70	-2.91	-8.85
	KNO_3	0.01	69.13		58.45	42.52	50.74	54.16	71.32	73.20	72.49	57.88	55.93	52.90	40.03	51.39	45.83
	$Mg(NO_3)_2$	0.1	-9.90		-27.77	-46.67	-34.54	-33.98	-19.39	-21.15	-13.00	0.15	-4.46	-7.89	-16.07	-8.87	-15.89
	KNO_3	0.01	70.66		53.36	38.66	46.83	51.20	70.45	67.48	74.68	54.84	51.87	47.60	36.17	47.90	40.80
	$Ca(NO_3)_2$	0.1	-11.92		-30.04	-48.74	-37.32	-36.15	-22.26	-22.21	-18.26	-1.24	-5.43	-9.29	-16.86	-9.95	-17.29
	KNO_3	0.01	68.32		52.87	42.15	48.14	51.15	68.61	73.00	72.22	54.05	52.11	47.36	36.65	48.76	41.41
	$NaNO_3$	0.1	-16.72		-33.51	-47.50	-38.12	-38.18	-23.90	-21.97	-21.17	8.59	4.36	-0.34	-8.46	0.74	-6.90
	KNO_3	0.01	68.14		55.58	46.13	49.51	53.28	76.90	75.68	74.23	57.20	54.22	50.44	38.20	51.30	43.49
	$LiNO_3$	0.1	-16.20		-31.66	-44.57	-37.25	-36.49	-18.16	-20.45	-19.95	9.73	6.79	0.93	-8.15	2.88	-6.16
	KNO_3	0.01	69.69		55.26	47.15	50.87	53.11	75.23	76.12	74.72	57.07	55.19	50.12	38.18	51.78	43.67
	$Al(NO_3)_3$	0.1	-11.50		-26.40	-38.32	-31.82	-32.17	-14.70	-11.31	-13.35	-4.45	-8.53	-14.07	-20.08	-11.52	-20.54
	KNO3	0.01	70.75		53.22	45.41	49.34	52.38	73.88	74.93	73.78	54.55	52.95	47.81	37.03	51.44	42.10
	NH_4NO_3	0.1	34.24		18.28	-2.25	5.32	5.01	25.98	29.50	27.98	8.53	6.52	0.55	-8.49	1.30	-9.51
	KNO_3	0.01	69.32		53.67	39.64	44.14	46.18	69.82	72.01	69.32	36.74	34.88	30.81	19.25	24.88	22.16
	KNO_3	0.1	122.26		106.77	38.21	43.00	45.13	122.25	123.56	122.49	5.17	2.97	-2.42	-7.87	0.39	-7.15
Rep 2	KNO_3	0.01	73.02		57.90	44.85	51.90	54.85	75.35	74.59	77.90	58.23	56.53	52.86	38.61	52.35	44.39
	KNO_3	0.1	127.28		112.52	34.74	43.06	43.74	127.15	127.40	128.65	3.76	0.86	-3.76	-9.91	-1.61	-10.37
	KNO_3	0.01	75.86		60.19	43.36	51.95	55.35	75.85	74.11	77.74	57.53	55.11	51.54	38.44	52.79	43.31
	$Mg(NO_3)_2$	0.1	-5.59		-25.08	-45.47	-32.86	-33.64	-16.18	-19.71	-15.27	-0.04	-2.79	-8.05	-18.09	-7.96	-17.58
	KNO_3	0.01	76.41		57.67	41.18	50.89	52.20	74.59	71.39	76.50	56.31	54.63	48.47	37.60	51.26	41.45
	$Ca(NO_3)_2$	0.1	-7.51		-27.19	-47.09	-35.20	-36.41	-18.71	-18.57	-16.62	-1.21	-3.28	-8.99	-18.11	-8.55	-17.87
	KNO_3	0.01	73.50		60.79	38.70	48.44	50.32	73.96	74.42	76.11	47.42	46.28	40.23	37.68	50.20	40.15
	$NaNO_3$	0.1	-12.22		-26.59	-49.17	-35.55	-36.86	-19.61	-20.93	-18.86	10.09	7.65	1.75	-9.19	1.98	-7.96
	KNO_3	0.01	73.38		61.09	40.61	50.43	51.51	75.80	77.91	77.87	48.74	47.91	40.85	38.77	51.82	41.90
	$LiNO_3$	0.1	-12.68		-27.34	-46.79	-34.10	-35.81	-19.73	-17.59	-17.12	11.23	7.64	2.16	-7.27	3.51	-6.44
	KNO_3	0.01	72.57		58.82	40.88	49.65	50.69	74.94	81.85	76.15	48.01	47.99	40.90	39.07	50.85	40.95
	$Al(NO_3)_3$	0.1	-8.25		-22.53	-43.66	-31.56	-32.31	-15.60	-10.41	-12.39	-4.36	-6.62	-13.95	-18.56	-11.38	-22.00
	KNO3	0.01	71.17		56.04	37.14	47.57	48.32	71.45	75.60	73.73	44.27	44.57	41.57	37.31	48.67	38.48
	NH_4NO_3	0.1	33.03		20.58	-7.70	4.75	3.45	25.81	30.00	28.64	6.89	5.50	-0.28	-7.65	1.43	-10.55
	KNO_3	0.01	77.11		60.69	39.25	51.40	52.05	76.74	79.74	77.47	49.07	48.93	43.32	41.47	53.44	41.43
	KNO_3	0.1	132.09		113.20	33.26	46.45	45.84	128.45	135.31	130.56	4.17	2.28	-3.90	-6.69	0.29	-10.72
Rep 3	KNO_3	0.01	80.37		64.75	37.32	51.78	52.04	77.24	78.97	78.21	50.13	50.95	45.76	41.26	51.55	40.84
	KNO_3	0.1	134.20		116.92	31.47	46.35	45.01	131.58	131.01	131.27	4.34	3.24	-2.56	-7.03	0.55	-10.99
	KNO_3	0.01	78.93		64.64	38.59	51.69	52.08	77.94	77.89	82.81	51.06	51.15	45.90	42.42	52.24	40.93
	$Mg(NO_3)_2$	0.1	-0.62		-20.44	-46.78	-32.03	-32.74	-14.47	-14.48	-9.98	2.10	0.66	-6.12	-12.73	-5.13	-16.73
	KNO_3	0.01	77.72		58.97	33.44	47.38	46.93	71.57	75.57	76.29	44.84	44.60	39.25	37.66	47.63	36.56
	$Ca(NO_3)_2$	0.1	-1.09		-22.97	-49.82	-33.66	-34.34	-17.53	-14.45	-13.13	1.39	-1.10	-6.90	-12.87	-5.66	-17.29
	KNO_3	0.01	75.13		58.44	32.95	46.60	45.95	69.51	75.55	73.68	42.99	42.96	38.13	37.34	46.70	35.68
	$NaNO_3$	0.1	-9.50		-24.78	-49.58	-37.63	-37.47	-20.68	-17.68	-17.82	9.05	9.25	0.02	-6.43	1.78	-8.60
	KNO_3	0.01	76.25		59.76	36.94	48.27	48.45	73.43	76.98	76.35	45.98	46.26	40.12	39.47	48.98	37.68
	$LiNO_3$	0.1	-8.20		-25.42	-47.52	-34.52	-35.22	-19.16	-14.34	-15.91	11.50	10.60	2.68	-4.30	3.71	-7.28
	KNO_3	0.01	73.14		57.95	36.01	48.53	48.67	76.83	78.93	75.87	45.83	46.33	40.07	39.12	48.16	38.20
	$Al(NO_3)_3$	0.1	-2.81		-19.19	-42.61	-28.69	-29.67	-11.73	-7.19	-9.70	-2.27	-2.86	-10.98	-14.97	-9.42	-20.29
	KNO3	0.01	72.44		54.36	31.45	43.25	44.35	71.18	73.04	70.50	40.83	42.36	35.06	36.10	44.47	33.66
	NH_4NO_3	0.1	37.92		21.14	-11.67	3.53	2.28	27.71	29.03	27.75	6.14	5.47	1.50	-7.24	-0.58	-12.46
	KNO_3	0.01	79.99		60.46	36.48	50.12	50.64	75.44	76.63	78.02	46.50	48.47	46.73	41.25	50.19	38.90
	KNO_3	0.1	137.17		113.58	31.55	45.10	44.49	128.26	134.72	131.04	2.85	1.25	-2.42	-6.85	-0.80	-12.28

Table C.12. EMF data taken from selectivity tests of K electrodes in Bray P_1 extractant.

	Bray P1															
	5/6/2004	**V-DOS**			**V-NPOE**			**V-DOA**			**TDDA-NPOE**			**MTDA-NPOE**		
Ions	Con. (M)	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3
		Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV		
KNO_3	0.01	63.81	56.42	59.09	38.32	49.04	46.52	65.59	66.05	74.20	35.90	60.19	48.96	19.18	25.21	35.46
KNO_3	0.1	118.07	109.97	112.89	38.03	48.60	44.59	118.64	120.86	125.86	1.82	7.48	-0.01	-14.43	-14.65	-7.08
KNO_3	0.01	67.19	55.23	60.52	37.30	50.13	45.47	70.56	68.09	73.87	34.91	58.27	47.99	23.13	29.68	36.77
$Mg(NO_3)_2$	0.1	1.74	-6.52	0.14	-24.53	-10.19	-18.13	-0.70	-4.00	1.61	4.30	4.33	-1.67	-14.91	-14.89	-9.18
KNO_3	0.01	63.07	55.33	61.67	34.22	48.81	43.64	69.45	66.48	73.79	33.43	55.91	47.28	21.79	27.32	39.38
$Ca(NO_3)_2$	0.1	-1.78	-11.41	-3.15	-29.11	-13.55	-24.28	-4.45	-9.28	-3.48	0.79	2.57	-6.48	-15.50	-17.54	-10.50
KNO_3	0.01	62.38	55.14	62.32	50.58	47.88	42.08	71.64	68.71	71.64	32.21	53.85	44.32	23.09	27.72	36.92
$NaNO_3$	0.1	-5.00	-12.93	-5.84	-7.95	-14.37	-22.27	-4.82	-7.98	-3.85	11.20	16.57	6.78	-8.96	-5.59	0.12
KNO_3	0.01	64.47	55.90	64.39	64.56	49.47	44.78	71.66	70.06	72.43	32.71	54.99	47.57	21.79	28.42	37.86
$LiNO_3$	0.1	-1.49	-10.21	-0.55	9.55	-9.38	-21.93	-1.74	-3.32	0.75	13.28	23.99	9.65	-7.77	-1.76	2.78
KNO_3	0.01	61.34	55.56	64.89	74.43	48.54	43.15	70.58	70.92	73.57	33.01	60.55	44.90	20.27	28.46	35.72
$Al(NO_3)_3$	0.1	-1.61	-8.70	4.31	7.96	-11.17	-21.51	-1.98	-2.28	2.74	-3.13	2.33	-10.95	-19.64	-22.13	-15.75
KNO3	0.01	63.66	57.92	67.12	65.94	50.00	44.70	71.46	74.25	74.38	32.35	56.01	46.86	23.42	29.98	40.18
NH_4NO_3	0.1	20.76	16.04	32.12	20.22	11.51	3.09	26.81	25.08	29.45	34.65	12.65	3.23	-11.31	-10.00	-4.38
KNO_3	0.01	63.14	56.76	69.74	58.12	53.33	45.62	91.69	71.99	77.42	49.59	55.35	45.28	24.50	32.58	42.28
KNO_3	0.1	116.21	111.15	119.83	54.38	54.04	45.61	136.92	125.36	130.65	31.33	11.34	3.54	-10.58	-11.01	-3.42
KNO_3	0.01	72.15	58.76	72.34	53.77	55.74	48.38	82.93	73.57	93.99	54.72	54.27	50.46	22.59	32.90	40.65
KNO_3	0.1	124.50	114.11	122.25	50.09	54.09	47.54	133.55	125.14	140.96	32.65	10.49	4.21	-10.60	-9.19	-3.60
KNO_3	0.01	77.86	59.62	70.33	50.89	53.64	46.50	84.34	72.79	90.06	55.03	53.69	51.21	25.65	32.78	39.92
$Mg(NO_3)_2$	0.1	12.16	-3.56	2.82	-14.75	-5.43	-17.40	11.17	3.63	14.50	31.81	9.11	-0.83	-13.12	-12.57	-6.32
KNO_3	0.01	70.72	62.64	65.31	46.37	52.76	45.78	81.69	76.50	85.05	49.93	48.79	50.72	24.51	31.15	39.98
$Ca(NO_3)_2$	0.1	4.44	-8.15	3.77	-20.99	-11.68	-21.89	5.12	-0.69	10.20	42.02	6.00	-2.94	-14.80	-14.17	-9.52
KNO_3	0.01	69.14	59.08	72.85	51.61	53.07	46.20	82.13	74.58	84.71	55.76	48.65	45.69	24.55	32.02	38.88
$NaNO_3$	0.1	2.26	-8.72	5.67	-15.96	-9.31	-21.54	4.47	0.21	7.55	43.46	18.31	9.77	-7.31	-3.30	1.70
KNO_3	0.01	68.57	60.81	78.78	52.69	56.67	47.43	80.27	75.77	86.22	57.18	50.45	49.61	25.89	33.49	42.10
$LiNO_3$	0.1	4.16	-4.99	12.56	-14.71	-7.13	-16.45	6.98	9.18	11.74	44.56	24.95	12.27	-5.17	-1.20	4.90
KNO_3	0.01	69.58	59.85	84.17	51.71	56.18	46.97	81.96	86.45	86.46	58.25	54.28	47.74	25.48	33.13	40.97
$Al(NO_3)_3$	0.1	3.77	-4.09	22.27	-15.63	-7.79	-16.33	6.89	10.57	11.69	39.93	3.22	-6.09	-17.70	-18.01	-15.04
KNO3	0.01	74.36	64.02	84.33	50.04	56.45	49.52	81.10	81.21	86.54	57.46	50.25	49.36	26.68	34.38	41.01
NH_4NO_3	0.1	33.62	23.06	42.55	7.02	15.81	6.49	36.16	36.15	41.57	49.56	15.36	6.35	-8.62	-5.60	-1.24
KNO_3	0.01	75.18	61.77	81.33	48.58	57.57	50.39	82.85	79.96	96.95	63.04	51.57	51.58	28.59	35.79	39.83
KNO_3	0.1	126.76	116.21	133.48	46.83	59.65	50.64	134.37	133.05	141.35	48.32	12.36	4.85	-9.53	-8.52	-2.82
KNO_3	0.01	86.23	61.49	85.31	45.52	57.70	48.46	81.36	80.14	91.15	68.95	52.03	52.26	22.53	32.71	38.39
KNO_3	0.1	137.33	118.31	135.01	46.79	63.73	52.99	134.67	131.77	143.83	56.62	13.41	7.44	-8.53	-6.36	-2.69
KNO_3	0.01	85.13	63.94	80.05	43.84	57.97	51.46	83.28	79.94	90.92	69.92	54.28	54.07	26.79	33.00	40.05
$Mg(NO_3)_2$	0.1	22.86	-2.00	13.99	-19.26	-1.61	-15.87	5.71	10.78	17.69	49.41	12.22	5.70	-11.02	-11.01	-5.22
KNO_3	0.01	80.82	60.58	77.32	38.86	55.35	48.35	80.60	77.96	87.03	64.98	47.74	51.00	25.40	31.28	37.48
$Ca(NO_3)_2$	0.1	13.22	-8.46	7.83	-27.39	-5.99	-19.83	5.11	8.80	12.12	50.74	9.54	1.42	-13.57	-12.78	-9.15
KNO_3	0.01	76.93	60.55	80.28	46.23	55.64	47.85	80.17	82.97	87.32	62.09	48.01	51.37	25.68	32.28	38.66
$NaNO_3$	0.1	9.13	-6.70	15.94	-13.47	-5.74	-17.59	3.74	6.12	9.56	51.02	21.45	13.70	-5.82	-1.59	0.96
KNO_3	0.01	77.80	62.66	89.18	53.52	59.46	51.02	81.38	84.42	88.89	62.53	48.47	52.94	26.99	33.28	38.96
$LiNO_3$	0.1	10.18	-5.23	29.40	-12.19	-3.47	-15.62	6.81	10.17	14.33	52.17	23.94	15.98	-4.27	0.32	3.67
KNO_3	0.01	76.34	63.99	94.05	52.05	58.00	50.42	80.28	85.10	88.10	63.75	48.37	52.81	25.09	34.21	39.70
$Al(NO_3)_3$	0.1	12.02	-0.51	33.93	-12.25	-4.50	-14.71	8.89	13.92	16.88	52.56	5.14	-3.02	-16.82	-17.54	-14.82
KNO3	0.01	74.40	63.29	91.89	46.39	57.32	49.99	82.44	82.65	92.14	63.00	45.97	48.67	26.08	31.89	38.26
NH_4NO_3	0.1	36.05	23.17	50.08	4.86	18.40	10.18	39.04	40.45	47.02	57.22	16.86	8.90	-8.22	-5.79	-2.89
KNO_3	0.01	74.19	63.17	87.79	41.00	57.30	50.82	86.84	83.66	93.79	69.32	44.44	50.35	27.77	33.70	39.02
KNO_3	0.1	133.73	120.02	139.86	43.78	62.01	54.36	139.99	137.43	147.81	57.06	12.19	8.91	-7.13	-6.17	-1.94

Table C.13. EMF data taken from selectivity tests of K electrodes in Mehlich III extractant.

		Mehlich III															
		5/10/2004	**V-DOS**			**V-NPOE**			**V-DOA**			**TDDA-NPOE**			**MTDA-NPOE**		
	Ions	Con. (M)	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3	3-1	3-2	3-3
			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV			Measured voltage, mV		
Rep 1	KNO_3	0.01	61.98	57.42	62.65	20.03	14.16	9.44	64.68	70.45	84.58	54.67	4.21	-19.37	-17.68	-36.89	-22.65
	KNO_3	0.1	109.55	106.13	105.78	22.99	16.56	10.78	110.65	114.60	133.27	52.69	0.67	-22.37	-20.48	-41.77	-26.06
	KNO_3	0.01	64.35	57.47	61.57	24.39	16.95	8.06	67.54	72.48	97.48	55.56	4.30	-18.45	-16.29	-36.91	-19.10
	$Mg(NO_3)_2$	0.1	37.72	32.30	38.18	9.81	1.83	-3.85	37.81	44.80	67.92	50.32	-1.13	-23.70	-19.96	-42.53	-26.06
	KNO_3	0.01	63.58	59.03	62.85	25.11	15.23	10.06	67.07	79.25	100.44	54.91	5.04	-19.04	-16.42	-35.97	-18.11
	$Ca(NO_3)_2$	0.1	37.93	32.12	39.27	14.64	1.01	-3.17	37.18	47.26	72.69	53.26	3.86	-22.37	-19.50	-41.28	-21.01
	KNO_3	0.01	64.59	59.87	61.28	28.41	16.53	10.98	67.98	76.82	111.63	57.26	9.39	-15.19	-15.52	-35.83	-15.86
	$NaNO_3$	0.1	35.51	32.81	37.06	15.60	5.18	-1.24	37.20	47.74	79.78	54.87	4.03	-19.89	-19.14	-40.26	-20.52
	KNO_3	0.01	65.36	62.36	61.74	30.74	17.41	10.44	68.51	85.63	113.59	58.14	9.16	-17.21	-15.59	-34.90	-16.30
	$LiNO_3$	0.1	37.01	35.94	37.91	22.11	3.99	-1.36	38.10	52.80	90.28	55.64	4.53	-19.15	-19.01	-41.00	-20.34
	KNO_3	0.01	63.99	66.55	63.15	39.24	17.22	11.76	69.83	82.69	133.48	60.15	8.02	-15.44	-15.23	-33.78	-16.02
	$Al(NO_3)_3$	0.1	38.36	40.15	37.76	20.73	1.87	-3.16	38.77	51.85	99.85	61.30	-0.48	-25.10	-19.81	-45.44	-25.70
	KNO3	0.01	63.95	64.56	61.76	35.80	18.46	12.82	67.44	81.06	130.06	60.62	10.96	-16.10	-14.42	-35.44	-15.20
	NH_4NO_3	0.1	36.43	34.61	38.11	28.64	-1.67	-4.89	42.45	48.73	113.58	45.67	-3.17	-32.20	-24.04	-45.55	-37.78
	KNO_3	0.01	64.34	64.83	60.15	40.26	16.57	10.25	69.13	78.18	144.61	58.45	10.34	-16.58	-16.28	-34.95	-15.56
	KNO_3	0.1	110.46	111.24	105.25	55.48	19.02	13.50	113.12	123.80	170.54	54.19	0.82	-24.89	-20.44	-42.83	-22.80
Rep 2	KNO_3	0.01	65.82	64.21	62.15	52.05	19.76	10.53	71.51	83.06	178.38	59.18	11.37	-15.98	-15.62	-33.20	-14.49
	KNO_3	0.1	113.32	111.95	109.30	51.03	21.63	15.56	119.19	127.24	189.06	58.50	5.55	-20.36	-19.06	-40.33	-20.86
	KNO_3	0.01	65.42	61.98	62.76	49.63	20.34	12.72	71.12	82.15	150.28	60.48	13.48	-17.78	-15.82	-34.51	-15.01
	$Mg(NO_3)_2$	0.1	39.09	34.48	39.39	32.88	5.33	-2.58	43.04	52.24	111.72	54.58	3.35	-24.15	-21.94	-40.85	-22.72
	KNO_3	0.01	63.22	62.40	64.54	45.08	17.01	11.51	71.19	81.37	150.23	61.54	9.93	-16.28	-15.70	-34.76	-13.21
	$Ca(NO_3)_2$	0.1	40.22	35.02	39.40	33.97	5.95	-1.68	41.32	50.77	138.37	55.35	6.04	-20.77	-20.82	-40.91	-20.81
	KNO_3	0.01	64.19	61.87	62.88	47.07	17.99	11.30	70.11	80.63	311.76	59.93	12.03	-17.19	-15.81	-34.51	-17.58
	$NaNO_3$	0.1	36.50	33.07	37.16	33.34	5.67	0.27	39.01	48.23	149.77	56.16	5.57	-20.41	-20.65	-39.33	-21.30
	KNO_3	0.01	66.51	61.29	61.88	45.09	19.61	10.48	70.39	80.31	330.56	59.11	11.44	-15.65	-17.07	-34.64	-16.45
	$LiNO_3$	0.1	37.63	33.72	38.01	33.21	5.43	-1.15	39.67	49.98	353.98	54.18	7.21	-21.28	-20.57	-40.66	-21.05
	KNO_3	0.01	65.70	61.34	62.74	46.14	19.50	11.26	69.30	78.99	374.50	56.79	10.87	-17.54	-16.60	-33.75	-15.67
	$Al(NO_3)_3$	0.1	39.29	35.03	38.26	28.15	3.26	-3.44	40.20	49.16	228.37	58.20	1.50	-28.27	-23.62	-45.81	-27.66
	KNO3	0.01	64.42	59.99	60.48	45.56	17.61	12.30	68.66	77.17	363.06	56.59	10.80	-18.94	-17.68	-35.62	-17.79
	NH_4NO_3	0.1	42.69	39.05	42.96	36.81	8.40	0.42	45.90	55.22	346.62	53.64	4.02	-26.24	-21.78	-41.68	-24.20
	KNO_3	0.01	64.72	61.25	61.06	44.61	18.89	10.91	70.71	78.09	348.78	56.68	12.56	-19.91	-17.12	-35.13	-16.72
	KNO_3	0.1	111.63	108.89	108.51	51.55	21.83	11.91	117.00	124.67	232.80	53.36	4.79	-23.43	-19.41	-40.83	-22.57
Rep 3	KNO_3	0.01	64.04	59.96	61.13	37.00	17.04	10.09	76.16	75.76	138.86	56.07	6.73	-17.84	-17.13	-35.40	-17.72
	KNO_3	0.1	111.12	109.47	108.06	39.55	22.11	13.62	117.21	122.64	181.07	53.35	2.86	-24.19	-21.51	-40.90	-23.05
	KNO_3	0.01	65.23	59.59	62.48	37.68	17.05	9.82	71.56	76.51	135.46	56.88	8.23	-20.00	-16.61	-34.75	-17.34
	$Mg(NO_3)_2$	0.1	39.50	33.98	40.40	24.93	5.22	-0.99	43.30	48.00	111.86	49.62	-0.61	-26.93	-24.60	-43.35	-26.24
	KNO_3	0.01	64.15	59.13	61.30	38.09	17.22	10.74	70.51	76.46	138.96	55.01	6.05	-20.50	-17.07	-35.08	-18.62
	$Ca(NO_3)_2$	0.1	38.68	34.43	39.87	30.21	6.07	-1.18	42.06	48.62	157.60	51.54	2.14	-24.38	-22.39	-42.16	-23.83
	KNO_3	0.01	63.76	61.01	60.69	42.10	19.12	9.56	70.21	77.48	171.01	56.42	10.08	-17.82	-17.13	-35.28	-17.67
	$NaNO_3$	0.1	38.27	32.64	38.70	30.01	8.18	-1.09	40.00	47.21	248.30	51.05	2.48	-24.17	-21.25	-39.70	-22.86
	KNO_3	0.01	64.89	59.97	61.95	39.31	19.08	10.04	69.87	77.63	165.10	56.06	10.00	-19.26	-16.17	-34.89	-16.65
	$LiNO_3$	0.1	36.16	31.06	36.32	28.04	5.08	-0.68	39.55	46.63	133.64	50.32	0.72	-24.12	-23.30	-40.74	-24.19
	KNO_3	0.01	68.65	64.25	65.63	42.43	24.07	18.28	74.55	80.62	142.66	62.13	9.84	-12.82	-11.40	-29.29	-14.31
	$Al(NO_3)_3$	0.1	47.80	42.87	47.95	29.05	11.56	6.75	51.52	57.58	110.36	62.23	-0.84	-21.96	-17.96	-39.55	-25.24
	KNO3	0.01	66.91	62.44	64.27	36.28	21.65	16.45	72.49	78.35	125.16	65.59	3.90	-16.51	-12.07	-32.97	-18.54
	NH_4NO_3	0.1	51.79	46.12	52.09	29.64	15.28	10.53	55.30	60.79	103.62	57.28	-0.07	-19.54	-15.53	-36.22	-22.30
	KNO_3	0.01	67.34	62.04	64.71	35.38	22.62	18.24	72.41	78.40	117.31	59.42	3.75	-15.22	-12.09	-31.77	-17.79
	KNO_3	0.1	114.28	110.49	110.07	38.95	28.01	23.00	118.42	124.37	160.22	56.39	-0.49	-18.79	-15.33	-35.52	-22.05

Table C.14. EMF data taken from for sensitivity tests of bis(p-chlorobenzly)tin dichloride-based P electrodes in pH 7 Tris (upper) and pH 8.5 Kelowna (lower) solutions.

	4/20/2005			Bis(p-chlorobenzyl)tin dichloride-based P membrane								TDDA-NPOE		V-DOS	
	K2HPO4			Age = 4 days											
	Con. (M)	P-01	P-02	P-03	P-04	P-05	P-06	14days	33days	20days-1	20days-2	N-01	N-02	K-01	K-02
pH=7.0	Tris			Measured voltage, mV					Meaured voltage, mV			Meaured voltage, mV		Meaured voltage, mV	
Rep 1	0.000001	88.85	122.17	163.96	46.90	67.67	59.79	180.10	-105.66	-65.55	-73.62	185.37	174.60	-209.30	-198.31
	0.00001	87.15	121.21	158.43	45.66	62.42	55.85	177.88	-105.77	-67.59	-73.56	183.29	172.48	-147.93	-135.08
	0.0001	80.59	110.32	168.13	46.28	48.61	44.55	172.38	-122.92	-67.93	-73.46	184.23	172.45	-111.57	-97.59
	0.001	49.30	82.47	160.39	39.88	16.80	10.98	163.15	-127.45	-69.09	-73.83	183.00	169.95	-56.68	-40.70
	0.01	19.35	55.02	129.85	23.59	-11.72	-19.82	156.49	-128.57	-73.12	-76.04	175.89	159.69	-8.68	10.54
	0.1	-6.89	27.09	90.06	-5.84	-38.16	-50.96	151.06	-134.54	-80.96	-88.14	162.51	141.36	22.48	48.76
Rep 2	0.000001	80.61	104.76	143.66	51.91	58.45	45.39	169.44	-137.71	-55.16	-70.37	193.18	180.61	-203.20	-192.46
	0.00001	86.55	110.71	151.84	58.95	62.51	51.27	165.79	-139.57	-57.69	-70.85	189.33	176.68	-159.27	-145.48
	0.0001	76.61	101.25	155.43	61.17	45.90	36.98	160.68	-136.73	-60.39	-71.25	188.52	175.59	-110.28	-95.65
	0.001	45.29	74.78	138.13	48.48	14.56	5.68	149.87	-137.66	-62.46	-71.69	187.64	173.12	-53.55	-38.38
	0.01	14.93	46.15	116.60	25.30	-12.77	-25.09	142.07	-137.47	-68.48	-75.21	179.56	162.44	-6.75	12.83
	0.1	-11.04	18.02	75.51	-4.22	-40.24	-56.71	133.28	-145.16	-77.64	-86.88	165.47	142.76	23.65	49.35
Rep 3	0.000001	76.70	97.88	132.24	56.38	55.37	41.19	164.45	-143.96	-50.61	-68.16	196.39	182.84	-202.44	-191.30
	0.00001	83.71	104.24	146.57	55.69	62.15	47.78	160.96	-139.00	-52.98	-68.43	192.40	178.76	-159.32	-145.26
	0.0001	73.22	94.57	142.75	62.23	45.30	34.88	155.13	-139.50	-55.32	-68.48	193.01	178.64	-108.83	-93.96
	0.001	40.63	67.02	118.77	58.10	12.22	-0.21	143.24	-139.79	-59.12	-69.92	189.69	174.45	-53.76	-38.41
	0.01	11.99	37.55	86.01	34.30	-16.55	-30.33	131.36	-141.77	-66.33	-73.68	181.49	163.71	-6.61	12.81
	0.1	-15.37	8.95	51.32	1.14	-41.00	-58.70	122.47	-143.89	-76.10	-85.70	167.01	145.19	25.59	51.28

	4/22/2005			Bis(p-chlorobenzyl)tin dichloride-based P membrane								TDDA-NPOE		V-DOS	
	K2HPO4			Age = 6 days											
	Con. (M)	P-01	P-02	P-03	P-04	P-05	P-06	16days	35days	22days-1	22days-2	N-01	N-02	K-01	K-02
pH=8.5	Kelowna			Measured voltage, mV					Meaured voltage, mV			Meaured voltage, mV		Meaured voltage, mV	
Rep 1	0.000001	-107.13	-85.05	-66.28	-82.77	-29.25	32.89	188.24	-261.88	-112.21	-141.67	144.22	140.60	-49.02	-31.58
	0.00001	-108.17	-85.68	-66.78	-82.08	-29.24	35.48	189.27	-261.63	-111.54	-142.24	143.11	139.23	-47.84	-31.13
	0.0001	-107.29	-85.23	-68.06	-82.99	-29.32	48.32	189.28	-262.23	-110.19	-140.08	143.93	140.89	-46.39	-30.49
	0.001	-105.48	-81.68	-72.67	-84.05	-28.85	37.10	167.90	-261.85	-109.57	-137.16	143.00	140.42	-38.64	-21.23
	0.01	-103.89	-81.82	-78.94	-89.39	-25.66	-19.41	147.63	-260.44	-108.23	-131.28	143.67	139.51	-9.43	13.53
	0.1	-109.81	-88.05	-89.36	-98.12	-35.21	-31.38	128.41	-258.24	-105.69	-128.22	139.49	133.64	33.26	63.25
Rep 2	0.000001	-103.30	-82.82	-78.64	-87.86	-20.12	-18.65	161.85	-256.37	-104.79	-128.77	144.01	141.42	-42.22	-31.36
	0.00001	-104.28	-84.01	-77.84	-87.88	-19.08	-16.71	164.83	-256.82	-104.25	-130.25	142.78	140.00	-41.81	-30.96
	0.0001	-104.42	-84.74	-78.77	-88.39	-22.37	-17.94	157.14	-259.83	-104.33	-130.75	142.77	141.14	-41.72	-31.07
	0.001	-103.06	-80.10	-81.51	-84.60	-32.66	-18.74	141.88	-258.63	-103.59	-129.29	142.48	141.48	-33.55	-21.11
	0.01	-102.25	-81.29	-86.52	-91.47	-39.12	-23.63	126.33	-256.71	-102.75	-125.07	142.44	140.32	-4.08	13.38
	0.1	-108.95	-87.76	-96.93	-100.20	-47.48	-33.93	110.63	-255.34	-100.30	-123.65	138.88	134.46	39.07	63.54
Rep 3	0.000001	-101.78	-80.83	-85.96	-90.19	-30.33	-22.77	143.54	-255.26	-99.63	-124.80	143.33	141.96	-39.77	-31.96
	0.00001	-102.47	-83.02	-84.92	-90.15	-35.74	-20.23	146.45	-254.00	-99.32	-126.74	142.25	140.89	-39.01	-31.29
	0.0001	-102.71	-83.78	-84.78	-90.44	-34.23	-20.04	139.16	-255.03	-98.52	-126.75	142.93	142.58	-38.20	-30.83
	0.001	-101.20	-78.89	-88.19	-92.37	-34.75	-22.10	124.89	-255.93	-99.03	-126.03	141.13	141.43	-31.26	-22.29
	0.01	-101.00	-80.67	-92.74	-96.37	-40.18	-25.75	112.73	-252.78	-97.69	-122.11	141.72	140.49	-0.86	13.04
	0.1	-108.28	-87.04	-102.44	-104.02	-47.61	-36.01	97.98	-250.63	-95.92	-121.12	138.29	134.94	42.30	63.28

Table C.15. EMF data taken from sensitivity tests of cobalt-based P electrodes in pH 4 KHP (upper) and Kelowna (lower) solutions.

9/14/2005

	KH2PO4	**Cobalt-based P electrodes**						**Tributyltin-based P membrane**			**V-DOS**			**TDDA-NPOE**		
KHP	Con. (M)	Co-low-1	Co-low-2	Co-low-3	Co-high-1	Co-high-2	Co-high-3	Tri-01	Tri-02	Tri-03	K-01	K-02	K-03	N-01	N-02	N-03
pH=4	KHP	Measured voltage, mV						Measured voltage, mV			Measured voltage, mV			Measured voltage, mV		
Rep 1	0.000001	-532.51	-527.32	-533.25	-516.03	-525.65	-543.43	-173.12	-92.61	-62.77	-44.77	-29.87	-97.23	-101.41	-86.18	-101.84
	0.00001	-548.35	-539.07	-544.03	-533.01	-537.05	-548.52	-175.50	-91.23	-60.96	-44.49	-31.25	-99.22	-103.92	-85.25	-104.34
	0.0001	-558.72	-548.27	-552.77	-544.69	-547.78	-554.75	-176.05	-87.73	-55.51	-43.34	-31.42	-99.71	-105.37	-84.98	-105.75
	0.001	-589.97	-580.11	-584.43	-579.91	-586.11	-584.46	-175.73	-59.96	-14.52	-41.61	-30.31	-99.76	-106.12	-83.80	-106.16
	0.01	-631.30	-625.12	-628.78	-624.35	-623.88	-628.66	-172.68	-27.83	-2.60	-40.54	-26.64	-99.93	-107.93	-85.56	-108.13
	0.1	-695.08	-682.31	-687.06	-681.48	-672.57	-680.94	-166.02	-19.84	-2.95	-39.18	-14.41	-91.79	-114.94	-92.25	-115.43
Rep 2	0.000001	-544.15	-533.47	-541.33	-519.28	-546.80	-547.51	-174.17	-95.57	-61.40	-38.14	-28.52	-98.60	-105.77	-84.83	-105.84
	0.00001	-544.20	-534.68	-541.55	-522.96	-543.54	-543.47	-175.03	-97.13	-62.51	-38.57	-29.00	-99.24	-106.86	-85.25	-106.77
	0.0001	-563.76	-553.22	-558.62	-550.01	-556.66	-556.10	-175.22	-87.44	-50.10	-39.13	-27.85	-99.43	-107.41	-84.46	-107.29
	0.001	-592.93	-583.35	-588.19	-583.03	-585.73	-586.22	-174.57	-60.47	-8.91	-37.88	-27.39	-99.89	-107.90	-85.42	-107.65
	0.01	-632.06	-625.12	-628.94	-624.04	-623.74	-628.03	-171.75	-31.68	-3.36	-37.35	-23.92	-99.45	-109.89	-86.98	-109.26
	0.1	-695.72	-682.30	-689.09	-681.11	-675.81	-682.54	-165.26	-19.25	-2.93	-36.47	-12.16	-93.35	-117.25	-94.24	-116.44
Rep 3	0.000001	-542.07	-533.21	-540.30	-519.87	-545.01	-540.12	-173.44	-102.79	-61.62	-34.86	-26.46	-97.70	-107.91	-86.68	-107.63
	0.00001	-544.91	-534.76	-540.33	-523.20	-538.94	-539.80	-174.11	-105.12	-62.50	-35.89	-26.53	-98.39	-108.58	-87.13	-108.17
	0.0001	-558.04	-548.59	-553.85	-544.35	-549.05	-551.33	-172.92	-99.67	-53.84	-36.26	-26.01	-98.61	-109.02	-86.74	-108.43
	0.001	-589.94	-579.69	-585.12	-579.82	-582.43	-581.92	-173.89	-72.74	-14.20	-36.12	-25.62	-98.87	-109.99	-87.29	-109.19
	0.01	-631.62	-624.53	-628.66	-623.81	-624.48	-627.60	-171.06	-40.75	-2.54	-35.49	-21.87	-98.81	-111.79	-87.70	-110.94
	0.1	-694.16	-681.77	-689.52	-681.38	-679.51	-684.48	-164.87	-23.05	-2.72	-34.80	-11.03	-94.29	-119.08	-96.01	-118.30

9/22/2005

	KH2PO4	**Cobalt-based P electrodes**						**Tributyltin-based P membrane**			**V-DOS**			**TDDA-NPOE**		
	Con. (M)	Co-low-1	Co-low-2	Co-low-3	Co-high-1	Co-high-2	Co-high-3	Tri-01	Tri-02	Tri-03	K-01	K-02	K-03	N-01	N-02	N-03
pH=4	Kelowna	Measured voltage, mV						Measured voltage, mV			Measured voltage, mV			Measured voltage, mV		
Rep 1	0.000001	-535.56	-536.68	-534.89	-546.32	-530.68	-535.05	-77.69	-148.15	-80.33	-123.34	-121.37	-126.83	-14.11	-15.46	-15.63
	0.00001	-545.28	-545.30	-545.28	-547.04	-541.57	-544.76	-77.12	-146.69	-80.65	-125.30	-123.32	-128.77	-14.44	-15.56	-15.53
	0.0001	-573.29	-571.83	-573.67	-570.83	-569.86	-572.26	-78.79	-144.89	-81.12	-119.88	-117.34	-123.76	-14.22	-15.67	-15.49
	0.001	-596.68	-594.64	-597.91	-593.56	-592.80	-595.66	-77.33	-137.62	-79.43	-103.43	-99.94	-108.71	-14.18	-15.63	-15.74
	0.01	-627.02	-624.59	-628.69	-621.98	-622.32	-626.25	-70.67	-130.28	-68.22	-58.58	-54.70	-64.40	-14.11	-15.69	-15.39
	0.1	-671.27	-668.65	-676.60	-666.28	-667.11	-671.76	-26.63	-124.95	-19.40	-17.90	-7.47	-17.12	-14.17	-15.69	-15.29
Rep 2	0.000001	-538.46	-538.06	-536.54	-549.38	-531.50	-538.15	-68.44	-134.99	-73.75	-122.70	-121.66	-125.56	-14.57	-15.83	-15.43
	0.00001	-545.26	-545.29	-545.32	-549.44	-541.10	-545.38	-68.17	-134.76	-73.88	-125.10	-123.83	-127.91	-14.22	-15.63	-15.52
	0.0001	-573.11	-571.55	-573.71	-570.93	-569.11	-572.72	-70.86	-135.37	-77.03	-119.26	-117.56	-122.84	-14.20	-15.55	-15.43
	0.001	-596.98	-594.44	-598.67	-595.08	-592.28	-596.40	-69.35	-129.65	-74.45	-102.94	-99.65	-107.94	-14.37	-15.56	-15.67
	0.01	-627.29	-624.45	-629.55	-623.11	-622.08	-626.68	-62.62	-123.17	-62.91	-58.75	-54.79	-63.58	-14.15	-15.82	-15.49
	0.1	-672.16	-667.84	-676.55	-668.36	-665.85	-672.42	-22.73	-119.44	-17.05	-18.01	-7.75	-16.63	-14.18	-15.61	-15.56
Rep 3	0.000001	-540.33	-538.64	-537.56	-548.89	-531.91	-538.47	-63.91	-132.90	-71.64	-122.42	-121.53	-124.93	-14.18	-15.73	-15.42
	0.00001	-545.70	-545.33	-545.81	-551.91	-540.78	-545.67	-63.49	-134.76	-71.90	-124.76	-123.47	-127.13	-14.39	-15.84	-15.25
	0.0001	-573.43	-571.57	-574.35	-572.44	-569.08	-573.06	-67.15	-134.30	-74.25	-119.08	-117.31	-122.62	-14.27	-15.47	-15.42
	0.001	-597.09	-594.59	-598.88	-595.01	-592.60	-596.83	-65.67	-129.29	-72.54	-102.72	-99.86	-107.46	-14.36	-15.80	-15.48
	0.01	-627.93	-624.32	-629.86	-624.20	-621.84	-626.26	-58.17	-124.33	-59.80	-58.30	-54.83	-63.18	-14.15	-15.68	-15.58
	0.1	-672.06	-667.73	-677.65	-669.23	-665.19	-672.33	-19.25	-121.07	-14.08	-18.09	-7.58	-16.54	-14.25	-15.70	-15.69

Table C.16. EMF data taken from selectivity tests of cobalt-based P electrodes in pH 4 KHP solution.

	pH=4	KHP											
		10/20/2005	**Cobalt-based P electrodes**						**V-DOS**			**TDDA-NPOE**	
	Ions	Con.(M)	Co-low-1	Co-low-2	Co-low-3	Co-high-1	Co-high-2	Co-high-3	K-01	K-02	K-03	N-01	N-02	N-03
			Measured voltage, mV						Measured voltage, mV			Measured voltage, mV		
Rep 1	KH_2PO_4	0.01	-603.17	-597.97	-603.83	-599.64	-596.62	-599.37	-47.05	-5.86	-18.49	-79.06	-77.38	-86.29
	KH_2PO_4	0.1	-663.00	-647.09	-664.06	-655.99	-653.80	-653.06	-44.71	-6.16	-17.04	-83.91	-82.29	-90.71
	KH_2PO_4	0.01	-601.87	-596.43	-602.18	-597.43	-594.61	-596.68	-43.60	-6.43	-16.80	-77.51	-75.81	-83.28
	$KHCO_3$	0.1	-558.83	-568.70	-554.81	-556.94	-533.32	-558.08	-48.53	-6.41	-17.20	-76.57	-74.85	-81.83
	KH_2PO_4	0.01	-601.94	-597.00	-602.25	-597.94	-595.64	-597.66	-51.67	-6.25	-16.89	-77.72	-76.22	-82.99
	KCl	0.1	-543.56	-552.51	-547.30	-543.51	-534.63	-543.90	-39.88	-6.18	-17.01	-74.43	-73.22	-79.44
	KH_2PO_4	0.01	-602.66	-597.45	-602.28	-599.41	-596.79	-598.47	-48.74	-5.93	-16.82	-79.60	-78.76	-85.28
	KBr	0.1	-526.41	-548.11	-529.05	-532.47	-520.78	-528.64	-37.44	-6.61	-17.19	-74.83	-74.71	-81.54
	KH_2PO_4	0.01	-602.76	-598.21	-602.41	-600.36	-597.10	-598.57	-47.00	-6.17	-16.74	-80.26	-80.24	-86.56
	KNO3	0.1	-532.61	-530.78	-527.77	-529.98	-511.44	-520.57	-40.83	-6.35	-17.19	-82.95	-80.67	-86.48
	KH_2PO_4	0.01	-605.16	-600.20	-603.45	-600.79	-598.25	-600.42	-45.63	-6.38	-16.84	-79.28	-80.66	-86.64
	KAc	0.1	-538.86	-554.67	-533.53	-556.37	-522.00	-531.52	-40.11	-6.51	-17.13	-80.41	-82.22	-87.93
	KH_2PO_4	0.01	-603.62	-598.88	-602.13	-598.87	-596.90	-599.25	-43.08	-6.23	-16.85	-77.97	-79.98	-85.73
	KF	0.1	-511.89	-531.74	-501.84	-529.44	-494.35	-502.52	-32.96	-6.60	-17.24	-76.26	-78.16	-82.10
	KH_2PO_4	0.01	-601.87	-597.01	-600.04	-597.74	-595.88	-597.39	-42.36	-6.38	-17.12	-78.39	-80.25	-85.60
	KH_2PO_4	0.1	-663.75	-654.81	-660.89	-656.50	-655.52	-655.85	-40.83	-6.57	-17.09	-83.87	-86.12	-90.94
Rep 2	KH_2PO_4	0.01	-604.83	-599.48	-602.39	-599.91	-596.90	-599.53	-41.52	-6.16	-17.09	-78.91	-81.12	-84.96
	KH_2PO_4	0.1	-666.14	-658.20	-662.91	-658.64	-654.53	-656.32	-40.12	-6.48	-17.28	-85.12	-86.69	-90.57
	KH_2PO_4	0.01	-603.26	-597.79	-601.03	-598.53	-594.60	-596.61	-39.60	-5.95	-17.11	-78.75	-79.97	-84.87
	$KHCO_3$	0.1	-551.16	-547.46	-546.19	-540.97	-529.42	-534.91	-36.07	-6.45	-17.23	-78.33	-79.85	-83.42
	KH_2PO_4	0.01	-602.41	-598.86	-601.29	-598.29	-595.94	-598.18	-40.63	-6.34	-17.26	-79.25	-80.84	-84.92
	KCl	0.1	-544.25	-544.27	-545.10	-540.42	-534.57	-535.51	-30.95	-6.76	-17.38	-76.83	-77.88	-80.96
	KH_2PO_4	0.01	-602.20	-599.60	-601.47	-599.04	-596.38	-598.13	-41.26	-6.15	-17.06	-81.89	-83.15	-87.28
	KBr	0.1	-527.17	-535.79	-529.24	-528.33	-521.37	-520.19	-30.30	-6.57	-17.21	-77.87	-79.53	-82.93
	KH_2PO_4	0.01	-603.96	-600.08	-602.38	-599.73	-596.53	-599.54	-40.79	-6.32	-17.14	-84.00	-84.56	-88.17
	KNO3	0.1	-530.62	-523.74	-530.84	-527.34	-514.54	-516.16	-34.92	-6.30	-17.32	-84.00	-85.29	-88.44
	KH_2PO_4	0.01	-605.63	-602.04	-603.84	-601.09	-598.00	-601.18	-40.40	-5.99	-17.13	-83.67	-85.08	-88.69
	KAc	0.1	-533.50	-543.16	-531.40	-550.45	-519.95	-519.31	-35.20	-6.35	-17.35	-85.63	-86.88	-90.16
	KH_2PO_4	0.01	-603.10	-600.45	-602.47	-599.55	-596.66	-599.49	-38.69	-6.08	-17.28	-83.13	-84.35	-87.93
	KF	0.1	-506.99	-521.04	-499.92	-531.34	-495.02	-496.12	-28.81	-6.41	-17.30	-81.11	-82.55	-85.16
	KH_2PO_4	0.01	-603.80	-600.04	-602.28	-599.37	-597.01	-600.26	-38.83	-6.12	-17.28	-84.08	-84.69	-88.38
	KH_2PO_4	0.1	-665.63	-661.12	-663.00	-657.60	-656.40	-658.09	-37.27	-6.56	-17.47	-89.61	-90.58	-93.82
Rep 3	KH_2PO_4	0.01	-605.80	-601.92	-603.90	-601.45	-597.28	-601.78	-38.18	-6.09	-17.21	-83.23	-84.70	-87.36
	KH_2PO_4	0.1	-668.39	-663.37	-665.99	-659.90	-656.26	-660.44	-37.48	-6.45	-17.45	-90.20	-91.97	-95.17
	KH_2PO_4	0.01	-605.71	-601.12	-603.90	-599.57	-596.35	-600.36	-36.43	-6.40	-17.19	-82.70	-84.09	-87.48
	$KHCO_3$	0.1	-549.93	-544.61	-549.48	-535.86	-531.18	-532.21	-32.22	-6.47	-17.37	-83.39	-85.20	-87.59
	KH_2PO_4	0.01	-603.90	-601.07	-602.60	-600.48	-597.66	-600.28	-36.49	-6.16	-17.24	-82.96	-84.89	-87.34
	KCl	0.1	-547.10	-544.73	-549.36	-541.17	-537.85	-539.46	-27.52	-6.39	-17.52	-80.62	-82.85	-84.46
	KH_2PO_4	0.01	-604.33	-601.23	-603.06	-600.13	-597.85	-600.42	-37.68	-6.15	-17.13	-85.17	-87.23	-89.62
	KBr	0.1	-531.26	-534.56	-532.05	-529.16	-522.70	-523.88	-26.98	-6.50	-17.29	-82.12	-84.48	-85.73
	KH_2PO_4	0.01	-605.53	-601.14	-603.62	-600.93	-598.14	-600.68	-37.90	-5.98	-17.21	-86.22	-88.59	-90.09
	KNO3	0.1	-535.73	-526.20	-533.20	-528.35	-517.81	-520.81	-31.96	-6.22	-17.39	-87.60	-89.93	-90.82
	KH_2PO_4	0.01	-607.63	-603.30	-605.31	-602.15	-599.31	-602.57	-37.44	-5.99	-17.00	-86.42	-88.92	-90.04
	KAc	0.1	-532.94	-539.64	-530.07	-548.14	-520.63	-517.79	-32.79	-6.53	-17.32	-89.14	-91.65	-92.20
	KH_2PO_4	0.01	-605.86	-602.70	-603.87	-601.08	-598.59	-601.86	-35.67	-6.01	-17.28	-85.37	-87.91	-89.18
	KF	0.1	-504.38	-520.55	-500.17	-534.43	-497.53	-495.46	-26.57	-6.37	-17.35	-84.32	-86.95	-87.52
	KH_2PO_4	0.01	-606.40	-601.73	-603.79	-600.51	-598.53	-601.47	-36.26	-6.24	-17.41	-86.13	-89.18	-89.80
	KH_2PO_4	0.1	-667.64	-661.88	-664.36	-658.54	-657.24	-660.41	-35.47	-6.52	-17.22	-92.83	-95.65	-96.93

Table C.17. EMF data taken from selectivity tests of cobalt-based P electrodes in pH 4 Kelowna solution.

	pH=4	Kelowna												
		10/6/2005	Cobalt-based P electrodes						V-DOS			TDDA-NPOE		
	Ions	Con.(M)	Co-low-1	Co-low-2	Co-low-3	Co-high-1	Co-high-2	Co-high-3	K-01	K-02	K-03	N-01	N-02	N-03
			Measured voltage, mV						Measured voltage, mV			Measured voltage, mV		
Rep 1	KH_2PO_4	0.01	-630.57	-622.05	-626.47	-621.14	-623.29	-622.97	-40.06	-55.14	-69.14	-14.91	-16.15	-16.16
	KH_2PO_4	0.1	-680.70	-669.40	-677.52	-669.09	-671.68	-669.90	-19.29	-8.26	-22.49	-14.68	-16.03	-15.77
	KH_2PO_4	0.01	-630.75	-622.83	-626.30	-621.87	-624.68	-622.71	-38.74	-49.01	-68.43	-14.94	-16.09	-15.88
	$KHCO_3$	0.1	-573.67	-560.37	-562.20	-560.06	-559.75	-559.43	-19.20	-5.95	-19.25	-14.78	-16.02	-15.78
	KH_2PO_4	0.01	-632.24	-623.60	-628.06	-621.82	-624.63	-624.24	-38.82	-52.54	-68.61	-14.87	-15.95	-15.85
	KCl	0.1	-545.11	-540.56	-539.74	-544.85	-537.96	-536.83	-19.46	-6.26	-16.53	-14.65	-15.77	-15.69
	KH_2PO_4	0.01	-625.34	-616.55	-619.26	-617.76	-618.44	-617.95	-36.09	-54.36	-69.50	-14.66	-16.19	-15.74
	KBr	0.1	-523.74	-523.61	-520.21	-530.11	-516.54	-517.99	-19.73	-6.15	-17.65	-44.91	-39.75	-46.76
	KH_2PO_4	0.01	-622.10	-616.63	-619.29	-618.96	-618.84	-619.41	-32.96	-54.64	-69.86	-14.43	-16.08	-15.79
	KNO3	0.1	-520.54	-510.99	-513.33	-514.93	-517.44	-512.54	-19.26	-6.94	-23.22	-97.77	-92.85	-97.86
	KH_2PO_4	0.01	-630.32	-620.73	-624.20	-619.66	-621.22	-621.78	-32.60	-51.59	-69.88	-14.63	-15.92	-15.99
	KAc	0.1	-573.79	-566.35	-566.39	-567.12	-565.75	-565.72	-19.39	-6.35	-18.41	-14.76	-15.96	-15.57
	KH_2PO_4	0.01	-633.43	-622.50	-625.64	-621.33	-623.57	-623.30	-37.44	-52.09	-68.68	-15.09	-16.20	-16.23
	KF	0.1	-535.96	-531.08	-526.23	-537.10	-528.48	-527.15	-19.30	-5.92	-18.37	-14.34	-15.92	-15.40
	KH_2PO_4	0.01	-628.82	-621.64	-623.37	-619.16	-620.87	-621.83	-35.83	-52.47	-69.10	-14.40	-15.99	-15.72
	KH_2PO_4	0.1	-682.11	-671.15	-677.19	-668.51	-672.49	-672.38	-19.32	-6.18	-22.55	-14.61	-15.99	-15.94
Rep 2	KH_2PO_4	0.01	-633.17	-623.66	-626.99	-621.57	-624.49	-624.03	-34.16	-50.73	-60.11	-14.75	-16.22	-16.00
	KH_2PO_4	0.1	-684.23	-671.62	-677.32	-669.02	-675.34	-672.54	-19.65	-6.36	-17.18	-15.04	-16.15	-16.11
	KH_2PO_4	0.01	-632.31	-622.61	-627.50	-620.20	-623.98	-623.10	-28.76	-48.43	-55.40	-15.03	-16.20	-15.92
	$KHCO_3$	0.1	-573.12	-560.83	-561.82	-560.49	-561.75	-559.66	-19.50	-6.92	-17.48	-15.11	-16.23	-16.23
	KH_2PO_4	0.01	-633.90	-624.42	-628.65	-621.73	-625.51	-624.86	-28.69	-45.89	-52.21	-14.84	-16.40	-15.83
	KCl	0.1	-547.92	-539.79	-539.10	-543.73	-539.00	-536.94	-19.66	-6.91	-17.51	-15.12	-15.98	-16.20
	KH_2PO_4	0.01	-627.65	-617.74	-621.74	-617.31	-620.95	-619.93	-28.57	-44.24	-49.13	-15.14	-16.26	-15.85
	KBr	0.1	-525.65	-522.30	-519.35	-529.51	-518.28	-517.66	-19.69	-6.89	-17.39	-46.64	-39.07	-40.98
	KH_2PO_4	0.01	-624.29	-616.37	-619.86	-617.77	-620.47	-618.67	-29.62	-43.05	-48.06	-15.02	-16.05	-15.89
	KNO3	0.1	-522.52	-512.20	-515.27	-519.35	-520.32	-514.66	-19.78	-6.83	-17.71	-98.36	-91.57	-92.44
	KH_2PO_4	0.01	-629.33	-620.94	-623.56	-619.62	-621.76	-621.93	-28.05	-40.93	-45.39	-14.93	-16.11	-15.75
	KAc	0.1	-573.54	-566.97	-567.13	-567.71	-565.78	-565.75	-19.79	-6.78	-17.55	-14.76	-16.28	-15.93
	KH_2PO_4	0.01	-631.56	-623.32	-628.07	-621.01	-623.17	-623.42	-29.14	-40.38	-45.72	-14.88	-16.33	-16.09
	KF	0.1	-535.04	-533.38	-527.12	-541.28	-529.92	-527.20	-19.75	-7.03	-17.40	-14.99	-16.27	-15.82
	KH_2PO_4	0.01	-632.42	-623.12	-626.43	-620.25	-623.99	-624.34	-27.55	-39.13	-45.02	-14.99	-16.45	-16.06
	KH_2PO_4	0.1	-678.94	-666.95	-673.82	-664.41	-669.33	-668.37	-19.57	-6.89	-17.50	-14.89	-16.46	-15.90
Rep 3	KH_2PO_4	0.01	-633.86	-623.91	-627.15	-621.37	-625.39	-625.02	-28.38	-38.41	-44.99	-14.93	-16.38	-15.92
	KH_2PO_4	0.1	-680.24	-667.79	-672.67	-664.44	-670.36	-668.15	-19.52	-6.99	-17.34	-15.10	-16.54	-16.00
	KH_2PO_4	0.01	-634.38	-623.92	-627.74	-621.21	-625.50	-623.95	-29.08	-38.13	-44.52	-14.93	-16.34	-15.87
	$KHCO_3$	0.1	-573.86	-564.14	-566.40	-564.93	-565.61	-562.69	-19.65	-6.74	-17.77	-15.07	-16.40	-15.83
	KH_2PO_4	0.01	-632.71	-625.30	-628.39	-621.55	-626.62	-625.61	-29.56	-36.54	-44.64	-14.87	-16.23	-15.98
	KCl	0.1	-546.40	-540.04	-539.10	-544.35	-539.62	-537.83	-19.73	-6.85	-17.72	-14.77	-16.25	-15.88
	KH_2PO_4	0.01	-629.18	-618.71	-622.22	-618.76	-623.61	-621.15	-29.67	-35.24	-45.27	-15.11	-16.37	-16.05
	KBr	0.1	-526.43	-522.78	-519.87	-529.36	-520.05	-518.59	-19.77	-7.33	-17.66	-47.43	-39.55	-42.01
	KH_2PO_4	0.01	-624.55	-617.46	-621.15	-618.06	-622.44	-621.15	-27.59	-36.27	-45.80	-14.97	-16.22	-16.33
	KNO3	0.1	-524.07	-514.32	-516.08	-522.10	-522.77	-517.38	-19.73	-6.85	-17.50	-96.04	-91.58	-94.55
	KH_2PO_4	0.01	-632.65	-623.80	-625.68	-621.21	-623.64	-624.27	-29.92	-37.22	-46.91	-15.11	-16.34	-16.06
	KAc	0.1	-573.41	-567.71	-566.65	-568.06	-567.18	-566.15	-19.74	-6.81	-17.62	-14.88	-16.14	-16.09
	KH_2PO_4	0.01	-632.61	-624.12	-627.32	-622.34	-625.12	-624.95	-30.28	-36.59	-47.58	-14.92	-16.31	-16.11
	KF	0.1	-533.82	-535.48	-528.25	-543.58	-531.10	-528.63	-19.63	-6.73	-17.52	-14.80	-16.20	-15.86
	KH_2PO_4	0.01	-632.52	-624.13	-628.47	-620.74	-624.98	-625.36	-27.91	-35.68	-47.73	-15.27	-16.33	-15.96
	KH_2PO_4	0.1	-672.99	-662.99	-668.20	-659.51	-665.72	-664.02	-19.58	-6.97	-17.52	-15.08	-16.50	-15.78

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