Simultaneous Analysis of Soil Macronutrients Using Ion-Selective Electrodes

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Automated sensing of soil macronutrients would be useful in mapping soil nutrient variability for variable-rate nutrient management. Ion-selective electrodes (ISEs) are a promising approach because of their small size, rapid response, and ability to directly measure the analyte. This study reports on the laboratory evaluation of a sensor array including three different ISEs, based on TDDA–NPOE and valinomycin–DOS membranes, and Co rod, for the simultaneous determination of NO$_3$–N, available K, and available P in soil extracts. Thirty-seven Illinois and Missouri soils were extracted using the Kelowna soil extractant (0.25 mol L$^{-1}$ CH$_3$COOH + 0.015 mol L$^{-1}$ NH$_4$F). The response of each electrode type in mixed solutions of NO$_3$–, K, and P ions was modeled based on the Nikolskii–Eisenman equation with all coefficients of determination ($r^2$) ≥0.95 ($P < 0.001$). In soil extracts, the NO$_3$ ISEs provided concentrations similar to those obtained with standard laboratory methods ($r^2 = 0.89$, $P < 0.001$). Concentrations obtained with the K ISEs were about 50% lower than those obtained with standard methods due to lower K extraction by the Kelowna solution ($r^2 = 0.85$, $P < 0.001$). The P ISEs provided concentrations about 64% lower than those obtained with standard methods due to a combination of decreased P estimates in soil extracts and lower P extraction by the Kelowna solution; however, there was a strong linear relationship ($r^2 = 0.81$, $P < 0.001$). Although P and K concentrations were low in comparison to standard laboratory procedures, a calibration factor could address this issue. These results show that ISE technology can be implemented successfully for NO$_3$–N, available K, and available P measurement with the Kelowna extractant.

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Abbreviations: EMF: electromotive force; ICP: inductively coupled argon plasma; ISE: ion-selective electrode.

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doi:10.2136/sssaj2007.0002
Received 2 Jan. 2007.
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Schlemmer, 1998). For example, accurate monitoring of soil NO$_3$ levels has been limited by relatively high temporal and spatial variability of NO$_3$–N in the field (Magdoff et al., 1984; Ruffo et al., 2005), leading to the need for real-time measurements with a high sampling intensity (Birrell and Hummel, 2001).

The need for fast in-field monitoring has led to the investigation of ion-selective electrode (ISE) technology for determining soil chemical properties. Among the advantages of ISE technology over current analytical methods (e.g., spectroscopic techniques) are simplicity of use, direct measurement of analyte, sensitivity across a wide concentration range, low cost, and portability (Carey and Riggan, 1994).

An important component of an ISE is the ion-selective membrane that 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 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 (Nielsen and Hansen, 1976; Tsukada et al., 1989; Knoll et al., 1994; Levitchev et al., 1998). Furthermore, due to the importance of P in biological systems and living organisms, many researchers have tried to develop phosphate 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 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 (0.2 mol L$^{-1}$ CH$_3$COOH +
0.015 mol L\(^{-1}\) NH\(_4\)F + 0.25 mol L\(^{-1}\) NH\(_4\)NO\(_3\) + 0.013 mol L\(^{-1}\) HNO\(_3\) + 0.001 mol L\(^{-1}\) ethylenediaminetetraacetic acid (EDTA) is used to extract P, K, and other cations from soil (Mehlich, 1984). A number of studies have reported strong linear relationships (\(r^2 > 0.9\)) between Mehlich III results and those with other widely used extractants, including Bray P\(_1\) for P (Beegle and Oravec, 1990; Mallarino, 1997; Nathan et al., 2006) and NH\(_4\)OAc for K (Beegle and Oravec, 1990; Mallarino and Blackmer, 1994; Nathan et al., 2006). Additionally, research has documented the relationships between Mehlich III P and K data and plant response (Beegle and Oravec, 1990; Mallarino and Blackmer, 1994; Mallarino, 1997, 2003). Recently, the use of the Mehlich III solution has expanded because of increased adoption of the inductively coupled Ar plasma (ICP) spectrometer that simultaneously measures P, K, and other cations. The Mehlich III solution is not useful for NO\(_3\) extraction, however, because the extracting solution itself contains a high concentration of NO\(_3\).

The Kelowna extractant (0.25 mol L\(^{-1}\) CH\(_2\)COOH + 0.015 mol L\(^{-1}\) NH\(_4\)F), which is used as a multiple ion extractant in British Columbia, Canada, can simultaneously extract P, K, and NO\(_3\) from soils. Strong linear relationships (\(r^2 \geq 0.96\)) have been reported between Kelowna and other extractants, including KCl for NO\(_3\) (Van Lierop, 1986), Bray P\(_1\) (Van Lierop, 1988) for P, and NH\(_4\)OAc for K (Van Lierop and Gough, 1989).

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 simultaneously analyze mixtures of NO\(_3\), orthophosphate P, and K ions in soil extracts can be limited by interference from other ions present in soil extracting solutions and in soil itself. To overcome these limitations, various data processing methods and mathematical models have been used in analytical chemistry. For example, multivariate calibration models have been proposed to decouple cross responses arising from primary and interfering ions, thus allowing accurate determination of individual ion concentrations within mixtures (Forster et al., 1991). Methods used to determine calibration parameters for each electrode and the form of the non-linear model have included multiple linear regression based on the Nikolskii–Eisenman equation (Otto and Thomas, 1985) and nonparametric projection pursuit regression (Beebe and Kowalski, 1988). Recently, an artificial neural network (ANN) was used with multiple electrodes to determine NH\(_4\), K, and Na in wastewater and fertilizer samples (Gallardo et al., 2005). The ANN was able to predict ionic concentrations accurately in wastewater without the need to remove interfering effects, but showed biased results for Na and K ions in fertilizer samples.

Stability and repeatability of response can be a concern when using multiple ion-selective electrodes to measure concentrations in a series of samples because accuracy might be limited by drifts in electrode potential during the measurements (Dyblo, 2001). A computer-based automatic measurement system would improve accuracy and precision because consistent control of sample preparation, sensor calibration, and data collection can reduce variability among multiple electrodes and during replicate measurements.

The overall objective of this research was to evaluate the ability of a sensor array composed of previously identified (Kim et al., 2006, 2007) ion-selective electrodes to simultaneously determine NO\(_3\), K, and P ion concentrations in soil extracts. Specific objectives were to: (i) develop calibration models for the sensors by relating sensor responses to analyte concentrations using known mixtures of NO\(_3\), H\(_2\)PO\(_4\), and K ions; and (ii) evaluate the ability of the ion-selective electrodes, when used in conjunction with the Kelowna extractant, to estimate NO\(_3\), P, and K concentrations in a range of agricultural soils from Illinois and Missouri.

### MATERIALS AND METHODS

#### Preparation of Ion-Selective Electrodes

Our previously reported research (Kim et al., 2006, 2007) screened a number of candidate ion-selective electrodes for NO\(_3\)-N, available P, and available K measurement, and selected a best electrode for each ion. Electrodes of these types were then fabricated for this study. For efficiency in describing the electrodes and experiments, we will use the abbreviations N, P, and K to represent NO\(_3\)-N, plant-available P, and plant-available K, respectively.

The polyvinyl chloride (PVC)-based N membranes (Kim et al., 2006) were prepared with a mixture of 30 mg (15% w/w) of ligand (tetradecylammonium nitrate [TDDA]), 80 mg (40% w/w) of plasticizer (nitrophenyl octyl ether [NPOE]), and 90 mg (45% w/w) of high-molecular-weight PVC dissolved in 2 mL of tetrahydrofuran (THF). Potassium ion-selective membranes (Kim et al., 2006) were prepared with 4 mg (2% wt) of ionophore (valinomycin), 1 mg (0.5% w/w) of lipophilic additive (KTpCIPB), 129.4 mg (64.7% w/w) of plasticizer [bis(2-ethylhexyl) sebacate (DOS)], and 65.6 mg (32.8% w/w) of PVC in 2 mL of THF. The N and K membrane disks were attached to the ends of Hitachi ISE electrode bodies (Hitachi, Ltd., Tokyo) using THF solvent. Each N ISE electrode was filled with an internal solution of 0.01 mol L\(^{-1}\) NaNO\(_3\) and 0.01 mol L\(^{-1}\) NaCl. Potassium chloride (0.01 mol L\(^{-1}\)) was used as the internal reference solution of the K electrodes. A Ag/AgCl electrode was used as the inner reference electrode within each ISE body. For sensing P, Co electrodes with a purity of 99.95% were prepared as reported by Kim et al. (2007). A commercial double-junction Ag/AgCl electrode (Model PHE 3211, Omega Engineering, Stamford, CT) was used as the system reference electrode. The test array consisted of 16 sensors: five each for NO\(_3\), K, and phosphate, and one system reference electrode.

#### Test Equipment and Procedures

Tests of the N, P, and K sensors were conducted with an automated test stand (Fig. 1) that included a sample solution holder into which the electrodes were inserted, containers to hold solutions, and a computer-based data acquisition and control system that allowed simultaneous
collection of electromotive force (EMF) data from the 15 test electrodes measured relative to the reference electrode. Additional details of the test stand are given in Kim et al. (2006).

Each test sequence began with triple rinsing of the electrodes using a solution of 10⁻⁶ mol L⁻¹ KNO₃ before 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 to provide a stirring action while 110 mL of sample solution was manually loaded. The operator pressed a key after sample loading 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.

For each test, EMF data were collected for the final rinse solution and the test solution at both 15 and 60 s after injection of each solution into the test stand. At each of the two data collection times, three measurements were obtained 3 s apart and then averaged. Each of these three measurements consisted of the mean of a 0.1-s burst of 600 Hz data. 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 immediately before introducing each test solution were used to compensate for potential drift and the resulting bias that might occur during continuous measurement. Baseline-corrected EMF measurements were calculated by subtracting the baseline (rinse) EMF from each sensor reading.

Standard potentials and sensitivity slopes typically vary among electrodes because of differences in internal resistance or physical conditions of the electrodes. Therefore, a procedure to standardize responses of multiple electrodes for each ion was developed. These standardized responses allowed a single calibration equation to be used across all electrodes of a given type. This two-point normalization procedure also compensated for any long-term change in electrode response and allowed the same calibration to be applied across multiple test dates.

The two-point normalization consisted of a sensitivity adjustment followed by an offset adjustment. These adjustments were performed with known standard solutions of high and low concentrations (Fig. 2), which is similar to how pH meters are calibrated. First, standardized EMF values for the high- and low-concentration reference points were determined by averaging readings of the five electrodes and three replications for each sensor type. The difference in standardized EMF between the high- and low-concentration reference points is shown as B in Fig. 2. Then, individual sensitivity slopes for each electrode in each replication were normalized by multiplying baseline-corrected EMF data by the ratio of $B/A$, where $A$ is the EMF difference between high- and low-concentration solutions for each replication–electrode combination (Fig. 2). Finally, an offset adjustment was applied by shifting the modified sensitivity line such that the EMF value for the high-concentration level matched the standardized value. The high-concentration point was used because it provided better resolution than did the low-concentration point. The same sensitivity adjustment and offset were applied to all data points within each replication–electrode combination.

**Development of Calibration Equations Using Mixtures of Nitrate, Phosphorus, and Potassium Ions**

Mixed solutions containing N, P, and K ions 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 chosen to encompass the typical concentration ranges of soil samples based on a dilution ratio of 10:1 (solution/soil) (Buchholz et al., 1992), i.e., 0.1, 1, 5, and 20 mg L⁻¹ of NO₃⁻–N using NaNO₃; 0.1, 1, 5, and 20 mg L⁻¹ of PO₄³⁻–P using NaH₂PO₄; and 1, 3, 10, and 50 mg L⁻¹ of K⁺ using CH₃COOK. The concentrations for each ion were categorized as very low, low, medium, and high concentration levels, respectively.

Using a three-factor (i.e., N, P, and K) four-level, randomized complete block design, each replication, consisting of 64 mixtures of N, P, and K ions, was tested on a separate day. The mixed calibration solutions were prepared by adding three highly concentrated N, P, and K solutions (i.e., 400 mg L⁻¹ NO₃⁻–N, 400 mg L⁻¹ PO₄³⁻–P, and 1000 mg L⁻¹ K⁺) respectively to the Kelowna solution and were titrated to pH 4.0 using 1 mol L⁻¹ NaOH to remove the effect of pH on the equilibrium between P ionic forms (Lindsay, 1979). The concentrations of the test solutions were verified by analysis in an independent soil testing laboratory (A&L Great Lakes Laboratories, Fort Wayne, IN).

The EMF data measured with all five sensors for each ion were normalized by first applying the baseline correction to each reading and then by applying the two-point normalization approach separately to each replication. As reference points for normalization, a solution containing a mixture of N, P, and K ions at concentration levels of 0.1, 0.1, and 1 mg L⁻¹, respectively, was chosen as the low-concentration normalization point for all the sensors and three other solutions containing a mixture of N, P, and K ions at concentration levels of 20, 0.1, and 1 mg L⁻¹; 0.1, 20, and 1 mg L⁻¹; and 0.1, 0.1, and 50 mg L⁻¹ were used to provide high concentration levels for the N, P, and K sensors, respectively. Analysis of variance using the SAS GLM procedure (SAS Institute, 2004) was performed to test if the primary ions (i.e., NO₃⁻, phosphate, and K) had significant effects on the responses of each sensor.

The method used to build calibration equations from the mixed solution tests was based on the transformation of the Nikolskii–Eisenman equation (Eq. [1]; Ammann, 1986). 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:

$$\text{EMF} = E_0 + E_j + S \log \left[ a_i + \sum K_j (a_j)^{1/2} \right]$$
where EMF is the potential measured with each electrode, $E_0$ and $E_f$ are the standard and liquid-junction potentials, respectively, $S$ is the slope of the electrode, $a_i$ and $a_j$ are the activities of the primary and interference ions, respectively, $Z_i$ and $Z_j$ are the charges of the primary and interference ions, and $K_q$ is the selectivity coefficient of the electrode.

The Nikolski–Eisenman equation (Eq. [1]) was transformed for nonlinear regression analysis into Eq. [2], consisting of ionic activity as a response variable and electric potential as an independent variable. Nonlinear regression analysis into Eq. [2], consisting of ionic activity as a response variable and electric potential as an independent variable, was performed using the nonlinear calibration models where the slopes, $S$, as well as the sums of standard and liquid junction potentials, $E_0$ and $E_f$, respectively, and the selectivity terms, $\sum K_q(a_i/Z_i)$, were determined iteratively:

$$a_j = 10^{(EMF-E_0-E_f)} S \sum K_q Z_i a_i / Z_j$$

### Soil Extract Tests

#### Soil Selection

A total of 37 soils, 17 from Illinois and 20 from Missouri (Table 1), were selected to represent the diverse soil characteristics of important agricultural areas of Illinois and Missouri, and to provide a range of N, P, and K concentration levels. The Illinois samples were subsamples 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 four soils collected from a long-term cropping system research site (Kitchen et al., 2005). The soil samples were ground and screened using a 2-mm sieve and then oven dried at 105°C before extraction. Soil pH, organic matter, and cation exchange capacity were determined in the University of Missouri Soil and Plant Testing Laboratory following documented procedures (Brown and Rodriguez, 1983). Soil textural properties were obtained from previous studies.

#### Soil Nutrient Extraction

Soil extracts were obtained with the Kelowna multiple element extractant (Van Lierop, 1986, 1988; Van Lierop and Gough, 1989). Because the goal of this research was to develop an automated sensor system providing nutrient information similar to that currently obtained from soil testing laboratories, procedures for soil extraction were adapted from published procedures in use by such laboratories (Brown, 1998). A nominal 30-g soil sample was obtained by 15 fillings of an NCR-13 standard 2-g soil scoop (Peck, 1998). Use of calibrated scoops is a common practice in soil testing to improve the efficiency of the process, and has been shown to usually add only a small amount of error to the analysis (Peck, 1998). The measured soil was then transferred into a 500-mL glass bottle. Soil extractant (300 mL) was added to obtain a nominal 10:1 solution/solid ratio. The mixture of soil and solution was shaken on a reciprocating shaker at about 140 cycles min$^{-1}$ for 5 min and then filtered through Whatman no. 42 filter paper. All soil extracts were titrated to pH 4.0 with 1 mol L$^{-1}$ NaOH.

#### Measurement of Ion Concentrations in Soil Extracts Using the 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 37 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 concentration level combinations were tested in a random order. Five other mixed solution samples (0.1, 5, and 50; 1, 20, and 10; 5, 0.1, 50; 20, 1, and 3; and 20, 20, and 1 mg L$^{-1}$ of N, P, and K ions, respectively) were inserted into

### Table 1. Chemical and physical characteristics of the 17 Illinois and 20 Missouri soils used in the study.

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<th>ID no.</th>
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<th>Soil name</th>
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<th>Organic matter</th>
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<tr>
<td>36</td>
<td>113</td>
<td>Leonard</td>
<td>silt loam</td>
<td>6.1</td>
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</tr>
<tr>
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<td>silt loam</td>
<td>6.1</td>
<td>29</td>
<td>19.9</td>
</tr>
</tbody>
</table>

† Major Land Resource Areas as defined by Soil Conservation Service (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.

§ Soil pH in a dilute salt solution as described in Buchholz et al. (1992).

¶ Not determined.
each group of randomized soil extracts as validation samples. The validation samples, a subset of the solutions used in the calibration procedure, were selected to span the range of expected concentrations of each ion and to allow evaluation of the interaction effect between N and P ions. Immediately after collecting the normalization data, each expanded group (which now included a total of either 17 or 18 samples) was analyzed. After testing the expanded groups, the four normalization solutions were retested 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 6 h 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 NO3−, P, and K ions in soil extracts and validation samples. Subsamples of the extracted solutions were analyzed in an independent soil testing laboratory (A&L Great Lakes Laboratories, Fort Wayne, IN) to determine the actual concentrations present. There, an automated ion analyzer (Lachat QuickChem Analyzer, Lachat Instruments, Loveland, CO) was used to determine NO3−−N following methods reported by Lachat Instruments (2003). An ICP spectrometer (Fixons ARL Accuris, Ecublens, Switzerland) was used to measure P and K. The commercial laboratory calibrated the instruments with Kelowna extract solution to compensate for any differences in the absorbance between the background solution and the sample matrix. The N, P, and K concentrations measured in the soil extract samples with the sensor array were compared with those determined by the commercial laboratory using linear regression analysis.

To compare the ISE sensor array method with standard soil testing methods, subsamples of the 37 soils were provided to the same soil testing laboratory for extraction and analysis. The soil testing laboratory extracted soil NO3−−N by adding 25 mL of 1 mol L−1 KCl to a nominal 5-g soil sample obtained with an NCR-13 standard 5-g scoop (Peck, 1998). After a 30-min extraction time and filtration through Whatman no. 2 filter paper, the extract was analyzed with the automated ion analyzer. Soil P and K were extracted by adding 20 mL of Mehlich III solution to a nominal 2-g soil sample obtained with an NCR-13 standard 2-g scoop. After a 5-min extraction time and filtering through Whatman no. 2 filter paper, the extract samples were measured with the ICP spectrometer. To investigate the efficiency of extraction with the Kelowna extractant, and then analyzed using the same instrumentation described above for the standard methods.

RESULTS AND DISCUSSION
Development of Mixed Solution Calibration Equations
Investigation of Interactive Effects between Ions
An investigation of interactive effects of N, P, and K ions on electrode response was conducted with the 64 solutions containing four different concentrations of each ion. Figures 3 and 4 show how the presence of three ions in solution affected the EMF responses of each sensor type. The three-dimensional response surfaces (Fig. 3) of the three different electrode types to mixtures of four different concentrations of ions were obtained based on a least squares method using SigmaPlot 9.0 (SPSS, 2005) to find the best surface for each sensor type.

All three sensors were highly responsive to their target ions. Being sensitive to cations, the K electrode had a positive response curve. Because the N and P electrodes were sensitive to anions, their response curves were negative (Fig. 3). The N and K ISEs were not particularly sensitive to P concentrations (Fig. 3a and 4a for N; Fig. 3c and 4c for K). In addition, the N and K ISEs were not sensitive to concentrations of K and N ions, respectively (data not shown). As shown in Fig. 4b, however, the responses of the P electrodes were influenced by the presence of high concentrations of N (≥5 mg L−1) in mixtures, yielding an EMF change of about 5 to 10 mV. Thus, there was reduced P sensitivity at high N concentrations. These results were statistically confirmed by SAS GLM analysis, where both N and P ions had significant (P < 0.0001) effects on the P electrode response. The N and K electrodes, however, were significantly affected by only their corresponding ions (i.e., N and K, respectively; P < 0.0001). Therefore, it was expected that a model of the EMF response function of the P electrodes should include terms consisting of both the P and N concentrations, whereas the N and K electrode responses could be modeled considering only the effects of the N and K ions, respectively.

Mixed Calibration Equations
For the N and K electrodes, the ionic activity terms in Eq. [2] were replaced by concentrations of the corresponding ions (i.e., N
and K) because high concentrations of other ions in the Kelowna solution (0.25 mol L\(^{-1}\) CH\(_3\)COOH + 0.015 mol L\(^{-1}\) NH\(_4\)F) kept the activity coefficients of analyte ions constant in the range of concentrations tested. The selectivity terms were simplified into constant interference terms, i.e., \(S_N\) and \(S_K\) for N and K:

\[
C_N = 10^{(\text{EMF}_N - E_{0N})/S_N} - K_{SN}
\]

where \(C_N\) and \(C_K\) are N and K concentrations, \(\text{EMF}_N\) and \(\text{EMF}_K\) are electric potentials measured with the N and K electrodes, respectively, \(S_N\) and \(S_K\) are sensitivity slopes, \(E_{0N}\) and \(E_{0K}\) are sums of standard potential and liquid junction potential for the N and K electrodes, respectively, and \(K_{SN}\) and \(K_{SK}\) are interference terms for the N and K electrodes, respectively.

Since significant effects of both P and N ions on responses of the P electrodes were found from the SAS GLM analysis, \(\text{NO}_3^-\) effects were added to the concentration and sensitivity terms in the following equation using Eq. [2]:

\[
C_{P} = 10^{(\text{EMF}_P - E_{0P})/S_P} - K_{SN}C_N - K_{SP}
\]

where \(C_P\) is the P concentration, \(\text{EMF}_P\) is the electric potential measured with the P electrode, \(K_{SN}\) and \(K_{SP}\) are interference terms for the \(\text{NO}_3^-\) ion, \(S_P\) is the sensitivity slope, \(E_{0P}\) is the sum of standard potential and liquid junction potential, and \(K_{SP}\) is the interference term due to other ions.

Regression-estimated calibration equations and corresponding fit statistics are shown in Table 2. All three calibration equations fit the data very well.

### Soil Extract Tests

#### Validation Tests with Known Samples

Initial comparison of ISE validation sample data with standard analyses showed that one P ISE was giving inconsistent and often erroneous readings, possibly due to a failure of the sealing material around the Co rod or a problem with electrical continuity. Therefore, the data from this ISE was eliminated from all soil extract test analyses. This resulted in a total of 12 P observations for each soil (4 ISEs × 3 replications), but 15 N and K observations.

Using this reduced data set, validation sample results are shown in Fig. 5. Overall, concentrations determined by the N and K electrodes were in good agreement with the actual values, yielding almost 1:1 relationships between the ISE-measured (y) and actual (x) values. The P ISEs also showed a slope near unity; however, variable ISE measurements (maximum standard deviation of 5.1 mg L\(^{-1}\)) were seen for the validation samples with P concentrations within the range of soil extract P concentrations (Fig. 5b). The validation test provided us with (i) the means to identify the one malfunctioning P ISE and (ii) assurance that the remaining N, P, and K ISEs were providing generally consistent responses to soil extract samples across the multiple days required for sample analysis.

## Comparison of Solution Ion Determinations by Ion-Selective Electrodes and Standard Instruments

Figure 6 shows the regression relationships between N, P, and K concentrations in soil extracts determined by the ISEs and by standard instruments, i.e., the automated analyzer for N and the ICP spectrometer for P and K. When comparing the N concentrations determined by the N ISEs to the automated ion analyzer values (Fig. 6a), strong linear relationships (\(\rho^2 = 0.92\), \(P < 0.001\))

\[
C_K = 10^{(\text{EMF}_K - E_{0K})/S_K} - K_{SK}
\]

were obtained at the highest P concentration of 20 mg L\(^{-1}\). Strong linear relationships were seen for the validation samples with P concentrations within the range of soil extract P concentrations (Fig. 5b). The validation test analyses showed that one P ISE was giving inconsistent and often erroneous readings, possibly due to a failure of the sealing material around the Co rod or a problem with electrical continuity. Therefore, the data from this ISE was eliminated from all soil extract test analyses. This resulted in a total of 12 P observations for each soil (4 ISEs × 3 replications), but 15 N and K observations.

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were observed with a slope near 1. On average, however, a relatively high offset of 2 mg L\(^{-1}\) was obtained. Highly significant relationships (\(r^2 = 0.97, P < 0.001\)) were found between K concentrations measured with the K ISEs and the ICP spectrometer (Fig. 6c). Since the regression slopes were close to 1 and there were only relatively small y intercepts of <1 mg L\(^{-1}\), little difference in K concentration was estimated by the two methods.

In contrast, the regression slope of the P relationship was only 0.46 (\(r^2 = 0.82, P < 0.001\)), indicating that, across the range of measurement, the average ISE P concentration was 54% lower than the ICP P concentration (Fig. 6b). In addition, the Co electrodes showed variable responses (standard deviation of 2.54 mg L\(^{-1}\)) to one soil extract sample (Drummer no. 13, Table 1) in the first replication. The reason for the high variability of this soil extract sample could not be explained.

A literature review revealed that, because the ICP can measure other P forms in addition to orthophosphate P, the P measured with an ICP spectrometer has been up to 50% higher than P measured with colorimetric methods (Mallarino, 2003; Pittman et al., 2005). Engblom (1999) reported that the ICP method yielded about 19% higher P concentrations than did the colorimeter, whereas the measurements with Co electrodes predicted the lowest concentrations among three methods tested (ICP, colorimetric, and Co ISE). Validation sample results (Fig. 5) showed a near 1:1 relationship between ISE P and ICP P, reinforcing the theory that the difference in soil extract results was probably due to the ICP measuring other P forms in addition to the orthophosphate P measured by the Co electrodes.

### Efficiency of Nitrate, Phosphorus, and Potassium 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 Fig. 7a, 7b, and 7c, respectively.

The NO\(_3\)-N amounts extracted from the test soils with the Kelowna solution were comparable to those obtained with 1 mol L\(^{-1}\) KCl, yielding an almost 1:1 relationship, a small y intercept of 0.72, and a high coefficient of determination of 0.99 (Fig. 7a).

There was a strong relationship between P concentrations with Kelowna and Mehlich III extractants (\(r^2 = 0.98, P < 0.001\)) when using the 37 soils having a pH range of 4.1 to 7.1 (Table 1); however, the Kelowna solution extracted 26% less P than did the Mehlich III extractant (Fig. 7b). These results are reasonably consistent with previous research. Van Lierop (1988) reported that P extracted with Kelowna from 40 soils with pH <7.0 averaged approximately 3% greater than that obtained with Bray P\(_1\) solution. Other researchers (Beegle and Oravec, 1990; Mallarino, 1997; Nathan et al., 2006) compared extraction by Mehlich III and Bray P\(_1\), generally reporting efficiencies 10 to 20% greater with Mehlich III. In combination, these efficiency results would indicate a somewhat smaller difference between Kelowna and Mehlich III than the 26% we found, but some uncertainty would be expected when combining these results from studies conducted with different soils.

The Kelowna solution extracted 51% less K from the soils than the Mehlich III extractant (\(r^2 = 0.94, P < 0.001\)). Van Lierop and Gough (1989) reported that Kelowna extracted about 15% less K than did 1 mol L\(^{-1}\) NH\(_4\)OAc using 100 soils from various regions of Canada. Beegle and Oravec (1990) and Nathan et al. (2006) reported that Mehlich III-extracted K was about 10 to 16% lower than NH\(_4\)OAc-extracted K. Therefore, we expected Kelowna and Mehlich III-extracted K values to be similar. The reason for the 51% difference is unknown.

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

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**Fig. 5.** Relationships between validation sample (a) NO\(_3\)-N, (b) P, and (c) K determined by ion-selective electrode (ISE) and by standard instruments, i.e., automated ion analyzer (Lachat) for N and inductively coupled Ar plasma (ICP) spectrometer for P and K. Data are presented as mean and standard deviation; however, regression equations and statistics were calculated using individual data points.
useful, however, to investigate the apparent discrepancies between our extraction efficiencies and those reported in the literature.

**Comparison of Soil Ion Determinations by Ion-Selective Electrodes and Standard Methods**

Figure 8 compares N, P, and K concentrations in soil determined by ISE and Kelowna extractant with those obtained by standard laboratory analysis. In comparing soil N concentrations by standard and ISE methods (Fig. 8a), the regression slope was close to 1 with $r^2 = 0.89$ ($P < 0.001$). The $y$ intercept, however, was relatively high (22.1 mg L$^{-1}$) and standard deviations of estimated NO$_3$–N values for the 37 soil extracts ranged from 8.04 to 19.7 mg L$^{-1}$.

Soil P concentrations by ISE and Kelowna extractant (Fig. 8b) averaged 64% lower than those obtained with the ICP spectrometer and Mehlich III extraction, with standard deviations of estimated P concentrations ranging from 1.48 to 26.1 mg L$^{-1}$; however, a strong relationship ($r^2 = 0.81$, $P < 0.001$) was observed between the two methods. These low P estimates might be due to the fact that, as noted above, solution P concentrations determined by the P electrodes were 54% less than those obtained with
the ICP spectrometer, and the Kelowna solution extracted about 26% less P than did the Mehlich III solution. Thus, the regression slope of 0.36 may be explained by multiplying a slope of 0.74 for extraction efficiency by another slope of 0.46 for measurement.

In the comparison of soil K concentrations determined by ISE and Kelowna extractant to those by standard methods (Fig. 8c), a significant relationship ($r^2 = 0.85, P < 0.001$) 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 ICP spectrometer and Mehlich III solution, with standard deviations of K estimates ranging from 2.94 to 23.5 mg L$^{-1}$.

In summary, the Kelowna solution did not influence the ISE-based measurement of NO$_3$ in soils due to similar extraction efficiencies between Kelowna and 1 mol L$^{-1}$ KCl; however, the ISE K concentrations for the tested soils were lower than the ICP K concentrations due to lower K extraction efficiencies with Kelowna solution. The combination of lower P concentration estimates in soil extracts and reduced P extraction efficiencies when using Kelowna solution made the results with Co electrodes considerably lower than those with standard methods. Strong relationships between ISE and standard methods for K and P concentrations ($r^2 \geq 0.81$), however, made the use of a calibration factor to address this issue feasible.

The results of this study showed that the tested electrodes could estimate N, P, and K in soil extracts. Additional research will be required to integrate these electrodes into a real-time, on-the-go soil nutrient measurement system and to evaluate their performance in that application. The electrodes might also be useful in other applications, e.g., as part of a more rapid and low-maintenance laboratory-based analytical system, or for in situ monitoring of soil NO$_3$ and phosphate levels with time.

One drawback to these ISE sensors is the relatively large amount of variation present among multiple measurements of the same sample, particularly for NO$_3$. One must keep in mind, however, that the overall goal of this research is to develop a relatively rapid, cost-effective method of quantifying N, P, and K in an on-the-go system. In such a system, we envision collecting simultaneous channels of data for each ion of interest from multiple sensors. Additionally, it will be possible to obtain measurements at a closer spatial resolution than is feasible with sample collection and laboratory analysis. Thus, we believe this approach will be able to map soil fertility with greater accuracy than current methods. As part of the on-the-go system development, additional research will be needed to determine the best way to integrate multiple measurement channels, detect and deal with outliers, and provide the most accurate estimates of N, P, and K.

An additional issue to address in future research is correlation of ISE-determined, Kelowna-extracted N, P, and K concentrations to plant uptake or crop yield in the U.S. Midwest. In this research, we related ion concentrations with the ISE–Kelowna system to results from the Mehlich III extractant rather than the more widely used Bray P$_1$ and NH$_4$OAc methods. Although calibrations of Mehlich III results to plant response have been reported in the literature, much more data exists for the other methods. Relating ISE–Kelowna results to Bray P$_1$ and NH$_4$OAc results, as well as directly to plant response, will be important soil fertility research topics to support development and implementation of the on-the-go ISE sensing system.

**CONCLUSIONS**

In this study, a sensor array of three different ISEs, based on TDDA–NPOE and valinomycin–DOS membranes and Co rod, was evaluated for the simultaneous determination of NO$_3$, phosphate, and K ions in soil. Soil extract samples were obtained from 37 different Missouri and Illinois soils with the Kelowna soil extractant. The relationships between the concentrations obtained with the electrodes and Kelowna solution and with...
standard soil tests were investigated. The following conclusions can be drawn from these tests:

1. The NO₃ and K ISEs measured NO₃⁻–N and K ions in Kelowna-based soil extracts with approximately 1:1 relationships between the concentrations determined by the ISEs and by standard laboratory instruments. Furthermore, the NO₃ ISE method used in conjunction with the Kelowna extractant provided results in close agreement with the standard method using the Lachat analyzer and 1 mol L⁻¹ KCl extractant. The Kelowna K amounts obtained with the K ISEs, however, were about 50% lower than the Mehlich III K concentrations measured with the ICP spectrometer due to decreased K extraction by the Kelowna solution.

2. Soil P concentrations obtained with the Kelowna extractant and Co P ISEs were about 64% lower than those obtained for samples 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 Co P ISEs. Further studies on the decreased sensitivity of the Co P electrodes in soil extracts are needed to improve the predictive ability of the soil P sensor.

3. The Kelowna multiple-ion extractant (0.25 mol L⁻¹ CH₃COOH + 0.015 mol L⁻¹ NH₄F) was usable for simultaneous extraction of soil N, P, and K ions, showing strong linear relationships between the quantities of ions extracted with the Kelowna solution and with standard soil extracting solutions (i.e., 1 mol L⁻¹ KCl for NO₃⁻–N and Mehlich III for P and K) from 37 Missouri and Illinois acid soils. Since the Kelowna solution is not currently used in the U.S. Midwest, however, further investigations of the correlation between Kelowna-extractable ions and plant uptake would increase the potential for adoption.

The ion-selective membrane technology for N and K nutrient measurement, and the Co rod technology for P nutrient measurement, can be implemented simultaneously when using the Kelowna extractant, at least for the 37 Illinois and Missouri soils included in these tests. Additional tests with a broader range of soils from these two states and from a broader geographical region are needed to further validate the applicability of these results. The reduced P and K detection with these technologies, compared with standard laboratory procedures, could be problematic when levels of these nutrients are low. For the target use in on-the-go real-time measurement, however, this deficiency may not be critical since the objective is to identify areas where existing nutrient levels are sufficiently high to support crop production with reduced application rates.

ACKNOWLEDGMENTS
This research was supported in part by the International Cooperative Research Program, Rural Development Administration, Republic of Korea. We appreciate the assistance of the following USDA-ARS Cropping Systems & Water Quality Research Unit employees: Scott Drummond, Bob Mahurin, Kurt Holiman, Bettina Coggeshall, Jen Nelson, and Joe Asheer.

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