이온선택성 전극을 이용한 토양추출물의 질산 및 칼륨이온 측정

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Sensing Nitrate and Potassium Ions in Soil Extracts Using Ion-Selective Electrodes

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Abstract

Automated sensing of soil macronutrients would allow more efficient mapping of soil nutrient spatial variability for variable-rate nutrient management. 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 multiple 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 concentrations in 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 ($r^2 = 0.96$). 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.

Keywords : Soil nutrient sensing, Nitrate, Potassium, Kelowna extractant, Ion-selective electrodes

1. INTRODUCTION

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 investigation of ion-selective electrode (ISE) technology for 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 (Oien and Selmer-Olsen, 1969; Dahnke, 1971; Hansen et al., 1977; Li and Smith, 1984). Similarly, several researchers have used K-selective electrodes to estimate soil potassium concentration (Farrell and Scott, 1987; Adamchuk, 2002; Brouder et al., 2003).

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 P1 (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 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 and 1988) and Van Lierop and Gough (1989) reported that the Kelowna multiple ion ex-

tractant (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^- (Nielson and Hansen, 1976; Tsukada et al., 1989; Morf et al., 1990; Knoll et al., 1994; 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 and 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 for fast, real-time, and simultaneous measurement of soil macronutrients.

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 were to 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 and to investigate the applicability of previously selected nitrate and potassium ion-selective electrodes (Kim et al., 2006) to the simultaneous determination of NO_3-N and K concentrations in Kelowna-based soil extracts.

2. MATERIALS AND METHODS

A. 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 1). The Kelowna solution, which was proposed as a multiple element extractant in British

Table 1 Characteristics of the 4 Missouri and 4 Illinois soils used in the study

Sample Origin	Soil Name	Textural Class	ID	Textural properties (%) 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.

Columbia, Canada (Van Lierop, 1986 and 1988; Haby et al., 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 P_1, and Mehlich III). These extracting agents were prepared according to the 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 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 (Gee and Or, 2002).

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 solu-

tion 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.

B. Sensing NO_3-N and K in Soil Extracts

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; Kim et al., 2006). 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 (Kim et al., 2006), 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 used in this test included the seven soils used in the soil extraction tests and a Leonard silt loam soil from Missouri (Table 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. 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 the critical nitrate-N levels.

Figure 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 (Kim

et al., 2006) 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/L NO_3-N and 4, 8, 16, 20, 24, 32, and 40 mg/L K, respectively). Calibration curves relating EMF (mV) to concentration (mg/L) for each type of electrode were constructed based on non-linear logarithmic regression.

Immediately after each complete calibration sequence, the electrodes were immersed in 40-ml soil extract samples in randomized order (Fig. 2). The duration 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. 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.

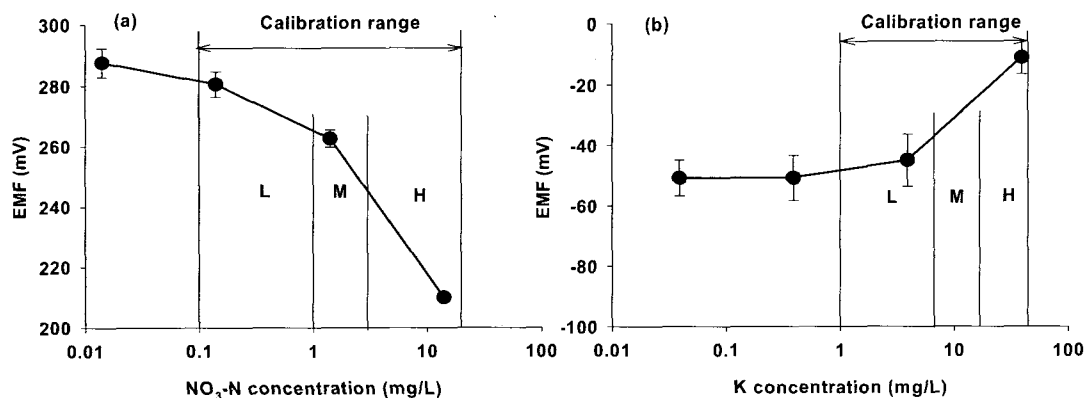Because nitrate levels of soils in the first extract test did

Fig. 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.

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 1) were coupled with varying levels of NO_3-N addition or extract dilution, similar to methods reported previously (Oien and Selmer-Olsen, 1969). 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/L NO_3-N) 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 2).

In the test sequence, immediately after the electrodes were calibrated with seven different nitrate solutions ranging from 0.014 to 50 mg/L NO_3-N, three iterations of each sequence were conducted using the three replicates of the sixteen soil
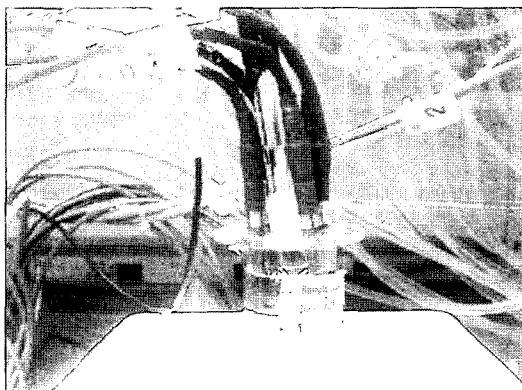

Fig. 2 Electrodes inserted in soil extract sample.

Table 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

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 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.

3. Results and Discussion

A. 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 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
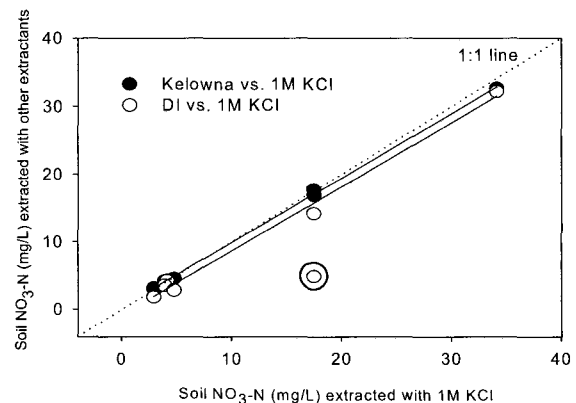

Fig. 3 Comparison of nitrate-N amounts extracted with different solutions (encircled point was excluded from regression).

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 could not 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 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 3). These results are comparable to those reported by Van Lierop (1986).

A highly significant linear 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. 4 and Table 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 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 P1 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). On average, potassium concentrations obtained with the Kelowna and Bray P1 solutions were 42 to 43% less than those extracted with Mehlich III (Table 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 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,

Table 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 P_1	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.

as illustrated by a strong linear relationship between the results with two solutions (r^2 = 0.96, p < 0.01).

B. Analysis of NO₃-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 6.

Non-linear logarithmic regression analysis based on the Nikolskii-Eisenman equation (Ammann, 1986) was utilized to develop the calibration equations relating membrane response to 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 7 shows the response profiles of the TDDA-NPOE nitrate electrode, and the valinomycin-DOS potassium electrodes. For each measurement, the electrodes were sequentially

inserted into three rinse solutions contained in 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. 7a), whereas the changes in potential of the potassium membranes occurred rapidly and approached an equilibrium level within 1 to 2 s (Fig. 7b). Such a difference in response shape is due to different time constants of the nitrate and potassium electrodes. In the dip-type measurement using three 15-s rinses, as illustrated in Figure 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.
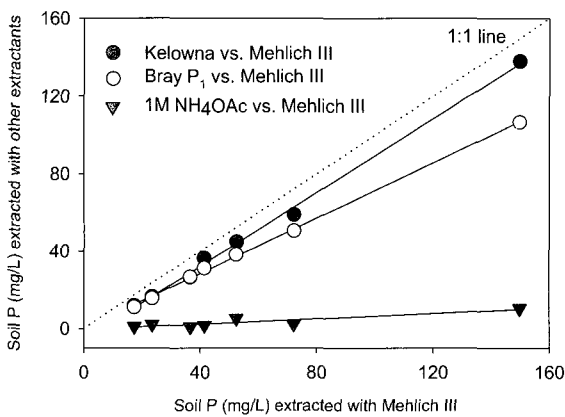
Figure 8 shows the regression results between Kelowna

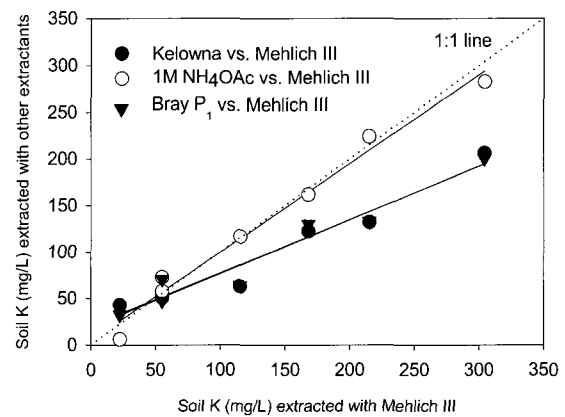Fig. 4 Comparison of phosphorus amounts extracted with different solutions.

Fig. 5 Comparison of potassium amounts extracted with diffrent solutions.
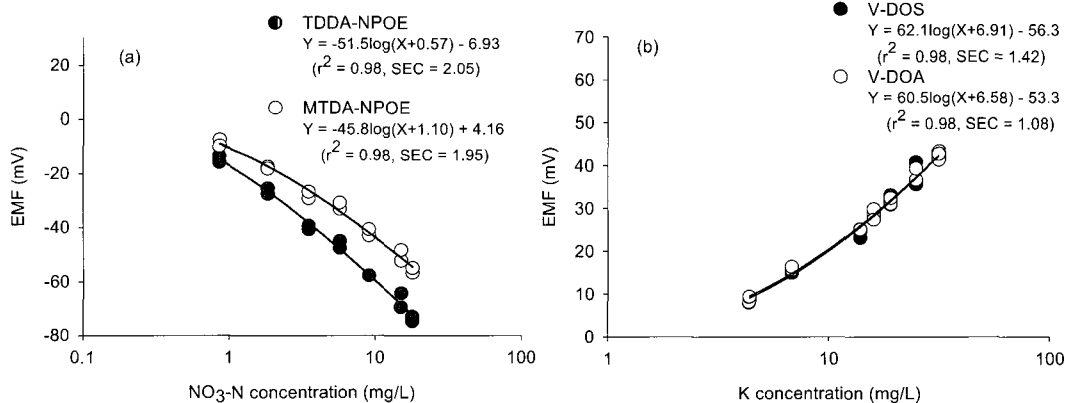

Fig. 6 Calibration curves for nitrate (a) and potassium (b) ISEs relating concentration (X) and electric potential (Y).

extractable N and K values determined by 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 solution and 1.96 to 19.1 mg/L, 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 8 and a histogram (Fig. 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 solution whereas the remainder had concentrations lower than 5 mg/L solution. This distri-
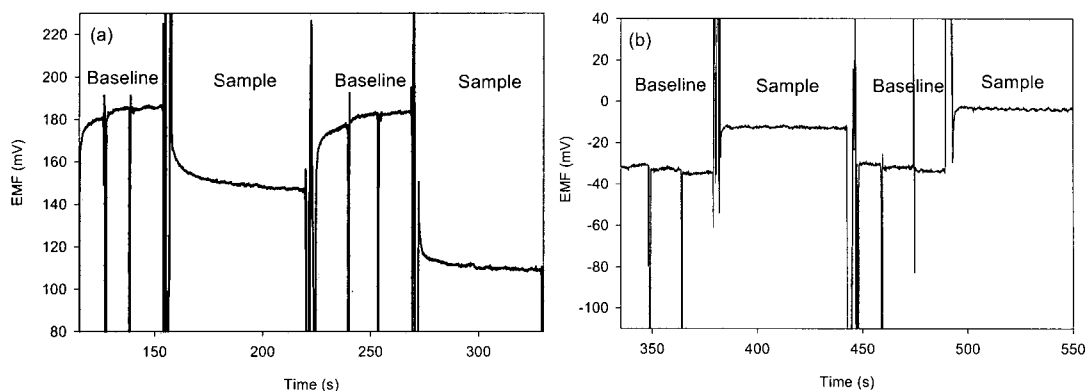

Fig. 7 Response behavior of (a) TDDA-NPOE nitrate ISE and (b) V-DOS potassium ISE in rinse solution and soil extract samples.
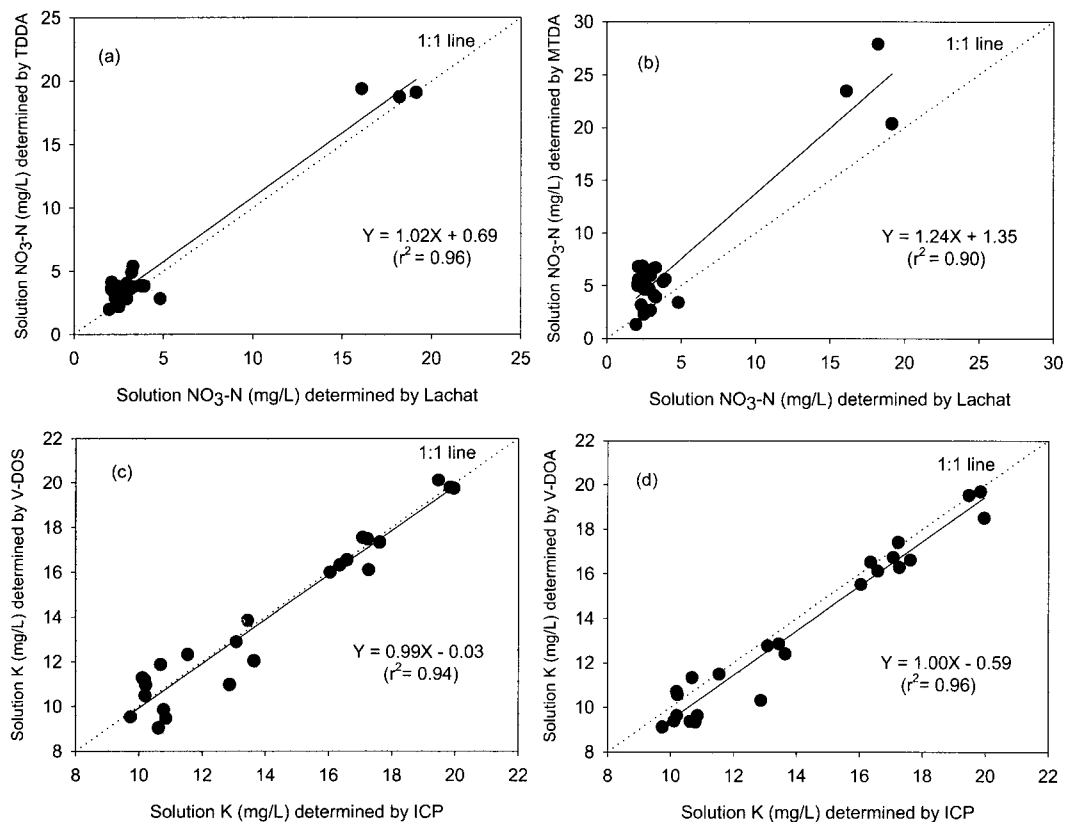

Fig. 8 Relationships between soil extract nitrate-N and potassium determined by electrodes and standard instruments: (a) TDDA-based N ISE vs. Lachat, (b) MTDA-based N ISE vs. Lachat, (c) V-DOS based K ISE vs. ICP, and (d) V-DOA based K ISE vs. ICP.

bution 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 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/L K solution (Fig. 9b). The DOS and DOA-based potassium ISEs predicted similar levels of potassium in the tested soil extract samples.

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. 10a) and the MTDA membrane (Fig. 10b) 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 provided 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
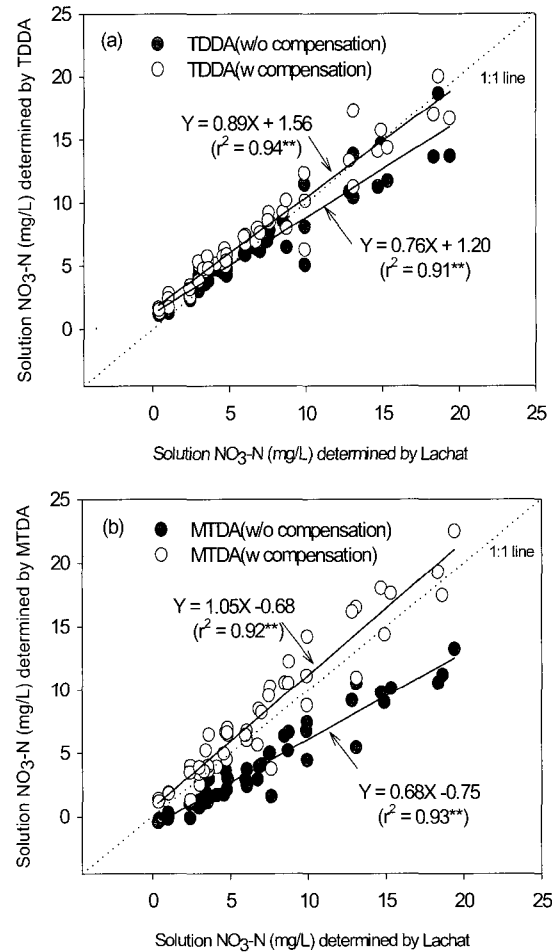

Fig. 10 Relationships between soil extract NO_3-N determined by membranes ((a) TDDA and (b) MTDA)) and Lachat analyzer with and without compensation.
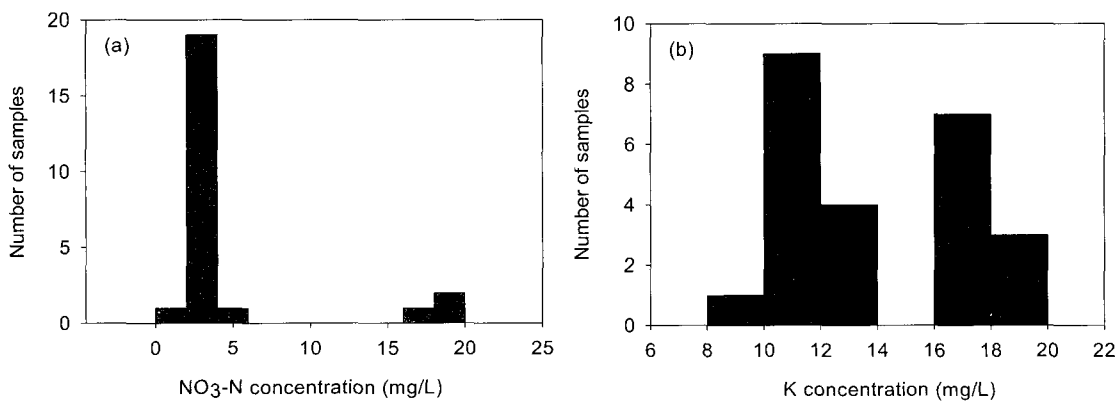

Fig. 9 Histograms of sample distributions for (a) NO_3-N and (b) K concentrations.

problem might be related to a graphical observation (Fig. 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.

4. Conclusions

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 be applied to the determination of nitrate and potassium contents of the 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 ($r^2 = 0.96**$).

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 those with 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.

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