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ANALYSIS OF AN ION-SELECTIVE ELECTRODE BASED METHODOLOGY FOR INTEGRATED ON-THE-GO MAPPING OF SOIL pH, POTASSIUM, AND NITRATE CONTENTS

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Analysis of an Ion-Selective Electrode Based Methodology for Integrated On-The-Go Mapping of Soil pH, Potassium, and Nitrate Contents

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ABSTRACT. *Knowledge of the spatial variation of soil attributes is critical for precision agriculture. On-the-go soil sensors have been able to provide relatively high mapping density while assessing this variation. A new ion-selective electrode (ISE) based approach was developed and tested for simultaneous mapping of soil pH, residual nitrate (NO_3^-), and soluble potassium (K^+) contents. In this article, results of laboratory experiments investigating the effects of key measurement factors on ISE performance are presented. In addition to four different soils, these factors included: soil/water ratio (SWR), quality of water used for electrode rinsing (QWR) and for ion extraction (QWE), presence of ionic strength adjuster (ISA), and solution agitation (stirring). After the targeted ion activity presented by different soils, SWR was the second most influential factor causing increased measurement variance, while the influence of QWE was only significant for pH measurements. Based on this study, the following measurement parameters were recommended: agitated purified water extraction without ISA, addition of a fixed amount of water (preferably 1:1 soil/water ratio), and use of regular (tap) water for electrode rinsing.*

Keywords. *Ion-selective electrodes, Nitrate, On-the-go soil sensors, Potassium, Precision agriculture, Soil pH.*

S ensors are currently being developed for on-the-go soil property mapping based on a variety of approaches (Adamchuk et al., 2004). Several researchers have investigated on-the-go measure‐ment of soil chemical properties, including nitrate-nitrogen (NO_3^-–N), potassium (K^+), and pH. These sensing methods have the potential to provide benefits for analyzing soil variability across a field using the increased amount of data obtained at a relatively low cost and within a very short time period (Pierce and Nowak, 1999).

Sensors being developed to map soil chemical properties are based on either spectral reflectance or electrochemical measurements methods. Hyperspectral subsurface reflec‐tance sensors typically provide excellent ability to characterize physical constitution (e.g., organic matter content, texture, water content, etc.) of soils (Viscarra Rossel

et al., 2006). However, if properly processed and calibrated to the local conditions, these data could also be used to assess a number of chemical characteristics (Jahn et al., 2005; Bogrekci and Lee, 2005).

Alternatively, ion-selective electrode (ISE) and ion-selective field-effect transistor (ISFET) technologies have been used to directly measure the activity of selected ions in aqueous solutions. In both cases, the output signal is related to the difference in electrical potential between the ion-selective membrane (e.g., glass, PVC, etc.) and a reference (Artigas et al., 2001; Talibudeen, 1991). Implementation of ISE/ISFET technology to measure soil properties on-the-go requires mechanical collection of soil samples while moving across the field, followed by the real-time measurement cycle performed on a solution phase of each extracted sample.

For example, Adsett et al. (1999) reported the development of an automated on-the-go soil nitrate monitoring system using a soil metering and belt conveying system. They developed a routine for predicting soil nitrate based on a 6 s response. Thottan et al. (1994) undertook a laboratory investigation of the suitability of nitrate ISEs for an automated on-the-go soil nitrate monitoring system. They studied the effects of different soil/extractant ratios and extractant clarity on electrode response. At $\alpha = 0.05$, there was no significant difference among the different soil/extractant ratios (1:15, 1:5, 1:3) as well as among the decanted, filtered, or suspension samples.

Price et al. (2003) developed a real-time soil nitrate extraction system by optimizing system parameters (texture, moisture, core density, nitrate concentration, core diameter, core length, and extraction solution flow rate) using a statistical factorial design. They suggested that *a priori* knowledge of soil type might be necessary for ISFET technology to make accurate real-time measurements of soil nitrate-nitrogen. Birrell and Hummel (2001) investigated the

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effects of flow rate for injection and washout time intervals while developing an ISFET-based soil nitrate sensing system coupled with flow injection. They reported the results of four flow rates (0.06, 0.12, 0.18, and 0.24 mL s^{-1}), three washout times (2, 1, and 0.75 s), and five injection times (2, 1, 0.75, 0.5, and 0.25 s) in a randomized block design. The choice of 0.06 mL s^{-1} with 2 s washout time and 0.5 s injection time was found suitable for accurate measurement of soil solution nitrate levels in real time.

Brouder et al. (2003) as well as McLean and Watson (1985) studied the feasibility of ISE-based measurements of soil potassium content. They concluded that rapid measurement of the solution potassium content in soils was feasible with acceptable accuracy and precision. However, stabilization time, ISE durability, and interfering ions were major concerns. Routine fertilizer recommendations and management guidelines are mostly based on exchangeable soil potassium rather than solution potassium content measured with ISEs.

Viscarra Rossel and McBratney (1997) evaluated different types of pH sensors for continuous on-the-go mapping of soil acidity. They selected ISFETs based on criteria including pH range, fragility, electrode precision, and response time. Furthermore, they evaluated the response time of ISFET electrodes at two different rates of stirring and two different soil/water ratios. The response time increased with increased stirring speed and when a higher soil/water ratio was used. Their findings were used to develop an on-the-go soil sensing system to measure both water and buffer pH using ISFET electrodes (Viscarra Rossel et al., 2005).

As an alternative to a solution-based method, an automated system for on-the-go mapping of soil pH based on a direct soil measurement (DSM) approach was developed by Adamchuk et al. (1999). Collins et al. (2003) modified the sampling mechanism, and Veris Technologies, Inc. (Salina, Kansas) commercialized the system as the Veris Mobile Sensor Platform (MSP). With this method, a soil core is periodically obtained at a predefined depth and brought into direct contact with a set of ISEs. Adamchuk et al. (2005) studied the applicability of this technique to other ions (K^+, NO_3^-, and Na^+). The root mean squared error (RMSE) varied from 0.11 to 0.26 pX, increasing in the order pH < pK < pNO$_3$ < pNa. They concluded that the practical application of potassium, nitrate, and sodium ion-selective electrodes using the DSM technique may be questionable. Although the DSM method is simple, major drawbacks include: (1) unreliable physical contact between electrodes and soil solution (resulting in increased random errors), and (2) possible mechanical damage to sensitive membranes.

The overall goal of this research was to develop an improved ISE-based methodology, referred to as agitated soil measurement (ASM), for integrated on-the-go mapping of soil chemical properties (activity of H^+, K^+, and NO_3^- ions). The ASM technique must remain simple (limited number of parts engaged with soil sample/solution), and electrode abuse as well as sample heterogeneity must be minimized. Thus, it was proposed that the soil be brought in contact with ISEs by means of an agitated solution. Once implemented, this method was expected to allow both precise and cost-efficient integrated mapping of soil chemical properties.

OBJECTIVE

The objective of this research was to characterize and optimize several critical factors associated with the integrated ASM-based on-the-go mapping of soil pH, potassium, and nitrate contents, including: soil/water ratio (SWR), quality of water for rinsing (QWR), quality of water for extraction (QWE), addition of an ionic strength adjuster (ISA), and presence of agitation (stirring).

MATERIALS AND METHODS

As the first step toward development of an integrated agitated soil measurement procedure, a set of laboratory experiments using a fixed set of soils and a consistent data acquisition technique was performed.

EXPERIMENTAL MATERIALS

Several ion-selective electrodes that measure the activity of specific ions, such as K^+, NO_3^-, and H^+ (in the case of pH), were used. Each electrode was comprised of a glass or polyvinyl chloride (PVC) sensitive membrane and a reference. The difference in potential between the ion-selective and the reference half-cells was related to the ion activity. Three ISEs were used during this test. They included: 1031BN potassium and 1021BN nitrate half-cell electrodes (Nico Scientific, Inc., Huntingdon Valley, Pa.) and an H028-001 pH combination electrode (Analytical Sensors and Instruments, Ltd., Sugar Land, Tex.), which also served as the reference for NO_3 and K electrodes. A data logging system was assembled using three AMPER PH-1 pH/ORP unity-gain amplifiers (Erlich Industrial Development Corp., Charlotte, N.C.) and a DAQ 1200 PCMCIA multifunction I/O card with CB 50LP I/O connector block (National Instruments, Corp., Austin, Tex.). The data logging system allowed sampling of each sensor voltage output at approximately 1000 Hz and averaged the outputs over a specified time interval (200 ms). Therefore, data recording was conducted at 5 Hz. In this study, the outputs of the three electrodes were recorded during a 60 s interval measuring either soil or calibration solutions. The average of the settled measurements between 55 and 60 s was assumed to be the best estimate of electrode steady-state output.

The relationship between ion activity and measured voltage can be defined as:

$$E = E_0 \pm S \cdot pX \qquad (1)$$

where
- E = measured electrostatic potential difference (mV)
- E_0 = initial ISE potential or electrode intercept (mV)
- S = calibration slope or theoretical Nernst coefficient (mV pX^{-1})
- pX = activity of X ions (e.g., pH, pK, and pNO$_3$) represented as:

$$pX = -\log\left(\frac{C_X \cdot \rho_w}{10^3 \cdot M_X}\right) \qquad (2)$$

where
- C_X = activity of X ions (e.g., H^+, K^+, and NO_3^-) (mg kg^{-1})
- ρ_W = water density (1 kg dm^{-3})
- M_X = molar weight (1 g mole^{-1} for H^+, 39.1 g mole^{-1} for K^+, and 62 g mole^{-1} for NO_3^-).
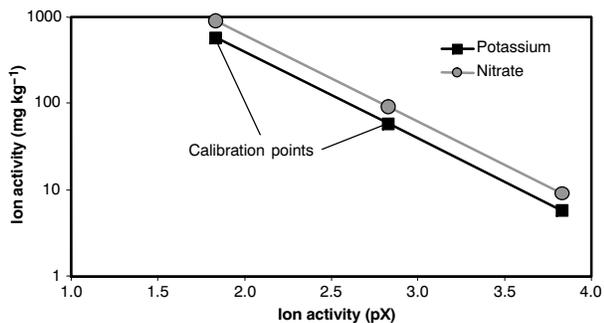
Figure 1. Relationship between ion activities represented according to pX scale and units of concentration (mg kg⁻¹).

Figure 1 illustrates the relationship between pX and corresponding C_X values for potassium and nitrate ions in physical units. Because of the linear relationship between the pX representation of ion activity and electrode voltage output, error analysis should be conducted using the pX scale. If desired, the activity of targeted ions represented in physical units (mg kg⁻¹) can be found using the following equation:

$$C_X = 10^3 \frac{M_X}{\rho_w} 10^{-pX} \qquad (3)$$

Since the response of every ISE changes during its lifetime, especially when engaged with solid soil particles, periodic electrode calibration is necessary. Therefore, a set of standard pH buffer calibration solutions (pHCS) with pH 10, 7, and 4 was used to calibrate the pH electrode. Another set of three integrated calibration solutions (ICS) was used to simultaneously calibrate the potassium and nitrate electrodes (table 1). These solutions were prepared by dissolving KNO_3 in double-deionized water (DDW) to achieve the desired concentrations of targeted ions. In addition, each solution (except when stated otherwise) contained a high concentration of $NaSO_4$ to boost ionic strength for both electrodes. Throughout each experiment described in this article, multiple calibrations of every ISE were performed. Since there was no significant drift in calibration parameters (E_0 and S) during individual experiments, experiment-averaged values were used for these parameters. For every experiment, a different set of electrode-specific calibration parameters was used.

To optimize the ASM design parameters, this study involved four large samples of soil with different textural and chemical properties obtained from different locations in Nebraska. Prior to storing at 40°C, these soils were air-dried and sieved to <2 mm. Subsamples were analyzed in several commercial analytical soil laboratories, providing a range of measurements typically observed through conventional soil testing (table 2). Based on these results, the soils selected

Table 1. Integrated calibration solutions (ICS).

Concentration	Potassium Ion Concentration		Nitrate Ion Concentration	
	pK	C_K (mg kg⁻¹)	pNO_3	C_{NO_3} (mg kg⁻¹)
Low	3.83	9.11	3.83	5.74
Medium	2.83	91.1	2.83	57.4
High	1.83	911	1.83	574

were deemed to have moderate, naturally occurring ranges of the chemical properties under investigation. Depending on the experiment and treatment, either 10 or 30 g samples of each soil were placed in polyethylene plastic containers and mixed with an appropriate amount of DDW or tap water with or without ISA. Constant-speed magnetic stirrer agitation of soil solutions was performed when assigned by the experimental design. Each ISE was rinsed manually using either DDW or tap water prior to every measurement. Although a randomized sample order was followed during each experiment, electrode calibration was always performed from a "low" to "high" concentration of targeted ions.

EXPERIMENTAL DESIGN
Comprehensive Factorial Experiment
To discriminate among various factors that could have changed electrode output, a one-half replication of a 4×2^5 factorial experiment was performed (Cochran and Cox, 1992). In addition to four soils, each of the three electrodes was subjected to five treatment factors, including SWR, QWE, QWR, ISA, and stirring. Each of these factors had two levels: (1) weight-based SWR of 1:1 vs. 1:5, (2) DDW vs. tap (regular municipal) water for ion extraction, (3) DDW vs. tap water for electrode rinsing, (4) presence vs. absence of ISA, and (5) stirred (agitated) vs. non-stirred measurements. This experiment was performed during a time period of one day, which restricted the testing of every possible combination of influential factors using a complete factorial design. Therefore, only 64 soil samples were prepared for the one-half replication factorial experiment. The main factor effects were aliased with four-factor interactions, which resulted in an inability to distinguish the statistical significance of high-level interactions. Based on prior experience, four- and five-factor interactions could be assumed negligible. The results of the different treatment combinations were analyzed using a set of normal probability plots (Kuehl, 2000). The PROC GLM (general linear model) procedure of SAS (SAS Institute, Inc., Cary, N.C.) was utilized to analyze the sources of variation for each electrode, and the statistical analysis was performed at the $\alpha = 0.05$ rejection level. Electrode calibration was conducted before the beginning of the experiment, between every 16 measurements, and at the end of the experiment.

Table 2. Experimental soil summary.

Soil	Soil pH[a]	Exchangeable K[a] (mg kg⁻¹)	Nitrate–N[b] (mg kg⁻¹)	Sand (%)	Silt (%)	Clay (%)	Soil Texture Class
1	6.3 to 6.6	522 to 606	7 to 10	16	59	25	Silt loam
2	4.8 to 5.3	121 to 184	13 to 16	78	13	9	Loamy sand
3	6.7 to 7.2	513 to 605	21 to 25	25	49	26	Loam
4	4.4 to 4.9	273 to 379	15 to 19	72	20	8	Sandy loam

[a] Range of reports from six different commercial soil laboratories.
[b] Range of reports from three different commercial soil laboratories.

Soil/Water Ratio Experiment

Based on results of the comprehensive factorial experiment to be discussed later, SWR was found to be the second most influential factor after soils with different levels of targeted ion activity. Therefore, another experiment was conducted to study the effects of four different levels of SWR (2:1, 1:1, 1:2.6, and 1:5) with the other factors held constant. This experiment was conducted in a randomized complete block design and was replicated three times, resulting in 48 total measurements per ISE. Electrode calibration (ICS and pHCS) was performed once before the start of the experiment and after every 16 consecutive measurements. The mean squared error (MSE) weighted across all three electrodes was used to select the SWR producing the most repeatable measurements. Root MSE (RMSE) was used to quantify measurement repeatability in pX units. Thus, low RMSE would indicate the electrode's ability to reproduce its own measurements indicating the optimum sample preparation.

Ionic Strength Adjuster Experiment

The effect of ISA, shown to be influential, was studied using four sets of calibration solutions, each with four different ion concentrations (10, 30, 100, and 300 mg kg^{-1} K$^+$, which corresponds to 15.9, 47.6, 158.6, and 475.7 mg kg^{-1} NO$_3^-$). Each set of calibration solutions was prepared using a different ISA. They included a blank (no ISA), integrated ISA (3M Na$_2$SO$_4$), potassium ISA (5M NaCl), and nitrate ISA (1M Al$_2$(SO$_4$)$_3$·18H$_2$O) solutions. The potassium and nitrate ISAs were commonly recommended by electrode manufacturers. Each ISA occupied 2% of the total volume of the calibration solutions. The experiment was randomized in terms of the type of ISA and replicated twice, with a low to high concentration solution order maintained for each set of solutions. Again, RMSE values were used to compare the different ISA treatments.

Soil Buffering Experiment

A final experiment was conducted to explore the ability of the soil media to serve as a buffer supplementing the need for ISA. Based on a factorial design with two SWR levels, each soil solution was prepared using potassium nitrate solutions with four different concentrations of K$^+$ (0, 30, 100, and 300 mg kg^{-1}) and NO$_3^-$ (0, 47.6, 159, and 476 mg kg^{-1}) ions instead of purified water as in the previous experiments. The electrode responses were analyzed in terms of relationships between artificial change of ion concentration and observed change of ion activity (similar to quantity/intensity plots). The experiment was replicated two times, with a total of 64 measurements per electrode. Electrode calibrations were performed once before the start of the experiment and after each group of 32 measurements. Slopes of quantity/intensity plots were evaluated in terms of their proximity to 1:1 linear relationships.

RESULTS AND DISCUSSION

COMPREHENSIVE FACTORIAL EXPERIMENT

The normal probability plots for the main effects (including individual soils) and all two-factor interactions are shown in figure 2. These results indicated that different soils had the greatest effect on ISE output due to the different levels of targeted ion activities. A similar conclusion was drawn based on the GLM statistical analysis of the sources of variation (table 3). In addition to soils, major factors affecting ISE measurements were SWR and the addition of ISA, which were consistently significant among all three properties. QWE was critical only for the pH electrode, since the use of tap water (high pH) as the extraction medium produced higher pH measurements when compared to neutral DDW. The QWE factor was marginally significant for the nitrate ISE (p-value = 0.047), but no two-factor interactions containing QWE appeared significant. Therefore, it was concluded that the effect of QWE on pK and pNO$_3$ measurements was relatively minor, and that either DDW or tap water would be acceptable for these analyses. On the contrary, stirring the solutions being measured affected the responses of the half-cell (potassium and nitrate) electrodes. Therefore, maintaining a stable solution agitation mode is important. This conclusion pertains only to half-cell electrodes and not to the combination electrodes, which also can be used to measure pK and pNO$_3$. QWR did not significantly influence any of the three ISEs. Therefore, as long as each electrode was rinsed well, municipal tap water could be used for the rinsing.

In addition, several two-factor interactions were found to be significant and needed further investigation. For the pH electrode, the Soil × QWE interaction was significant (fig. 3a). As mentioned above, the use of tap water as the extraction solution resulted in increased pH. Perhaps this was due to the relatively high alkalinity and hardness of the Lincoln, Nebraska, municipal water. However, due to differences in pH buffering characteristics, soils 1 and 3 (medium texture) had lower levels of water-induced pH increase than soils 2 and 4 (coarse texture). In many instances, the quality of tap water can be poorer than what was used in this study. Therefore, when measuring pH, DDW (or at least distilled water) should be used to prepare the soil solutions.

Another important interaction (Soil × SWR) was found to be insignificant. The change in electrode output due to two different levels of SWR was similar for each ISE except when the pNO$_3$ electrode was used to measure soil 4 (fig. 3b). Therefore, the major influencing factor, SWR, did not affect the comparison between soils as long as it was kept constant. In fact, a similar ranking of soils according to measured ion activities was observed when using measurements involving either 1:1 or 1:5 SWR. The results of a follow-up study of the SWR influence are discussed below.

Similar to the QWE main effect, the SWR × QWE interaction was significant for the pH electrode only (fig. 3c). The effect of QWE was significantly stronger for 1:5 SWR compared to 1:1 SWR. Because of the lower potential interference of the non-purified water used for extraction, SWR 1:1 seemed to be more desirable.

The SWR × Stir interaction was significant for all three ISEs. Stirring affected the SWR 1:1 treatment more than the SWR 1:5 treatment (fig. 3d). Student's t-test for probability of differences between stirred and non-stirred conditions was insignificant for SWR 1:5, while it was significant for SWR 1:1. Hence, stable solution agitation (stirring) was essential when the amount of extraction solution was smaller.

It was expected that the SWR × ISA interaction could be significant for potassium and nitrate measurements, since ions present in the soil might not provide adequate ionic strength when a large amount of extraction water was used
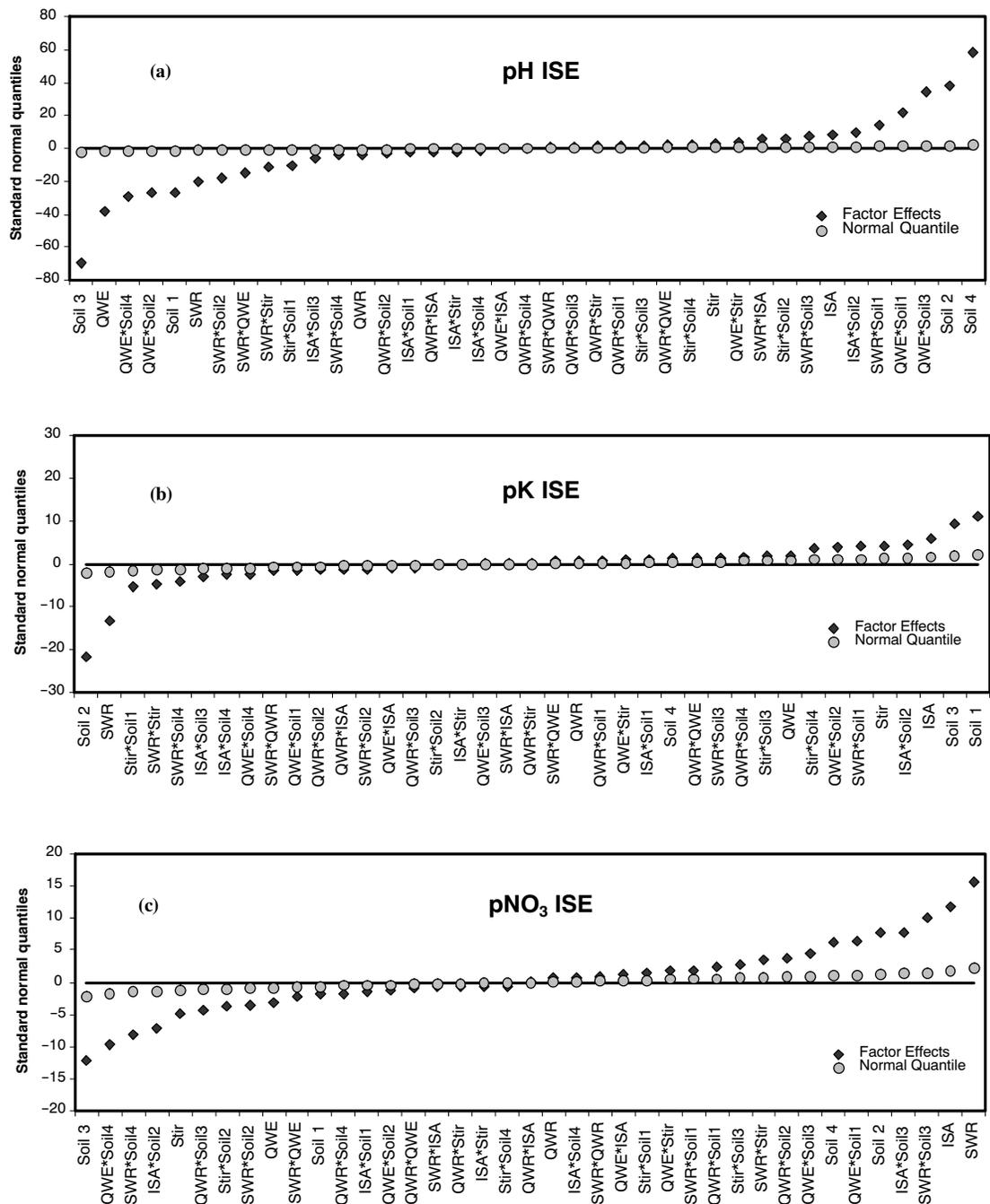
Figure 2. Normal probability plots of treatment factors and two-factor interactions from the comprehensive factorial experiment for (a) pH, (b) pK, and (c) pNO₃ ion-selective electrodes (SWR = soil/water ratio, QWR = quality of water for rinsing, QWE = quality of water for extraction, ISA = presence of ionic strength adjustor, and Stir = presence of solution agitation).

Table 3. Results of the comprehensive factorial experiment.

Selected Treatment Factors and Interactions[a]	pK Electrode		pNO₃ Electrode		pH Electrode	
	F statistic[b]	p-value	F statistic[b]	p-value	F statistic[b]	p-value
Soil	89.62*	<0.0001	19.01*	<0.0001	185.46*	<0.0001
SWR	125.14*	<0.0001	97.52*	<0.0001	38.32*	<0.0001
QWR	0.33	0.5678	0.19	0.6645	1.21	0.2804
QWE	2.82	0.1032	4.29*	0.0471	138.37*	<0.0001
ISA	23.86*	<0.0001	57.85*	<0.0001	6.09*	0.0195
Stir	12.38*	0.0014	10.15*	0.0034	0.75	0.3924
Soil × SWR	1.25	0.3099	3.54	0.0262	2.66	0.0663
Soil × QWR	0.24	0.8703	0.71	0.5544	0.07	0.973

(continued)

Table 3 (cont'd). Results of the comprehensive factorial experiment.

Selected Treatment Factors and Interactions[a]	pK Electrode		pNO$_3$ Electrode		pH Electrode	
	F statistic[b]	p-value	F statistic[b]	p-value	F statistic[b]	p-value
SWR × QWR	1.86	0.1822	0.41	0.5289	0.07	0.789
Soil × QWE	0.73	0.5422	3.08	0.0423	14.57*	<0.0001
SWR × QWE	0.33	0.5678	1.94	0.1736	20.54*	<0.0001
QWR × QWE	1.46	0.2365	0.41	0.5289	0.40	0.5294
Soil × ISA	1.27	0.3025	2.26	0.1022	0.63	0.6014
SWR × ISA	0.10	0.7549	0.23	0.6362	3.36	0.0769
QWR × ISA	1.59	0.2172	0.00	0.9685	0.57	0.4579
QWE × ISA	1.00	0.3263	0.51	0.4791	0.00	0.9695
Soil × Stir	1.38	0.2668	0.51	0.6752	0.69	0.5642
SWR × Stir	14.30*	0.0007	5.15*	0.0306	11.52*	0.002
QWR × Stir	0.04	0.8350	0.23	0.6362	0.12	0.7309
QWE × Stir	0.62	0.4370	1.33	0.2573	1.29	0.2642
ISA × Stir	0.01	0.9170	0.16	0.6933	0.46	0.5049
SWR × ISA × Stir	0.75	0.3906	1.98	0.1667	0.02	0.8951
SWR × QWE × ISA	0.10	0.7592	0.03	0.8635	0.01	0.9879

[a] SWR = soil/water ratio, QWR = quality of water for rinsing, QWE = quality of water for extraction, ISA = presence of ionic strength adjustor, and Stir = presence of solution agitation.

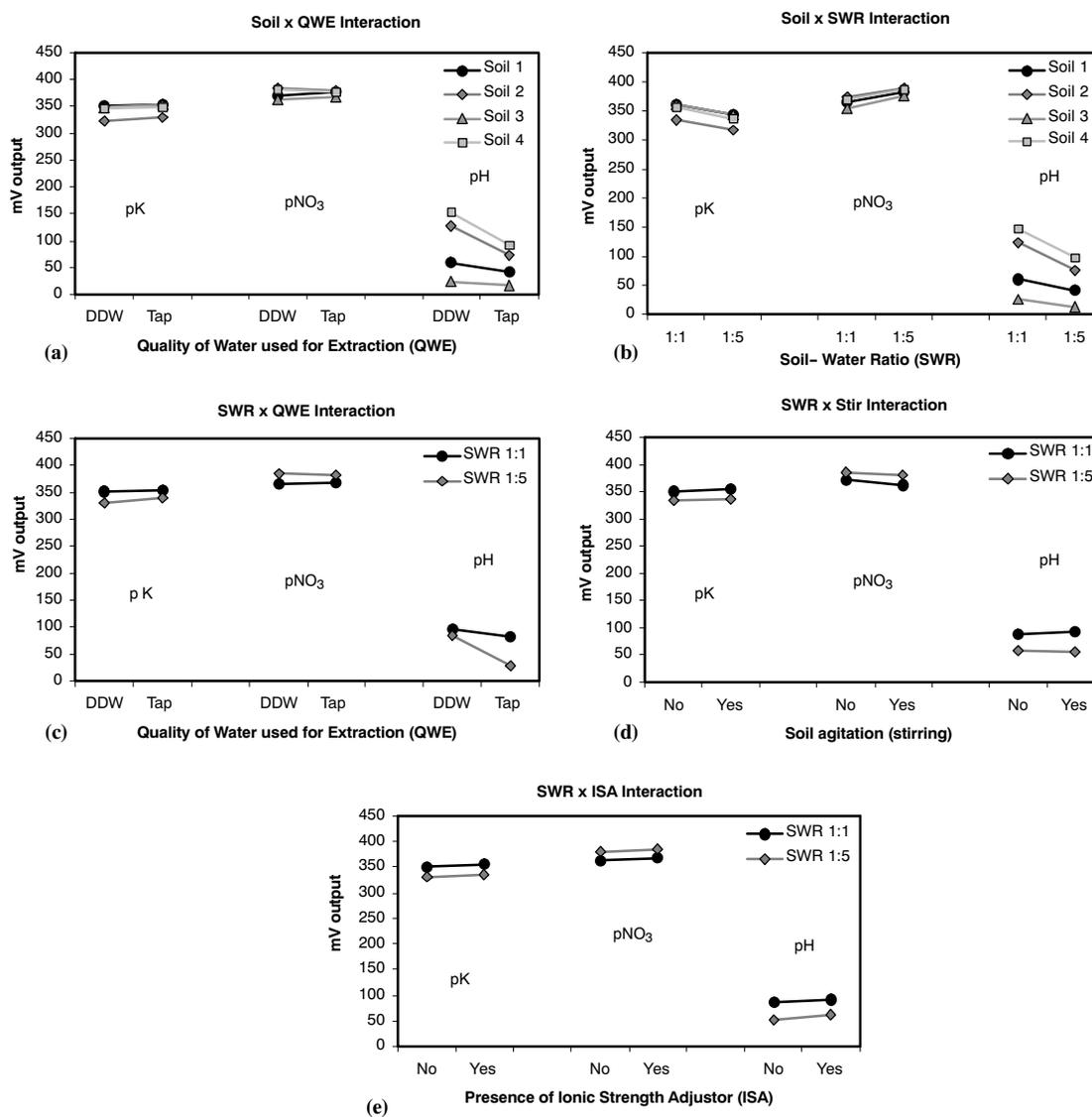[b] Asterisk (*) indicates statistical significance at α = 0.05.

Figure 3. Plots for: (a) Soil × QWE, (b) Soil × SWR, (c) SWR × QWE, (d) SWR × Stir, and (e) SWR × ISA two-factor interactions (SWR = soil/water ratio, QWE = quality of water for extraction, ISA = presence of ionic strength adjustor, and Stir = presence of solution agitation).

**Table 4. Root mean square error (RMSE – pX)
as affected by four levels of soil/water ratio (SWR).**

ISE	Soil/Water Ratio (SWR)			
	2:1	1:1	1:2.6	1:5
pH	0.071	**0.038**[a]	0.072	0.095
pK	0.055	**0.031**	0.041	0.095
pNO$_3$	0.232	0.187	**0.147**	0.221

[a] Values in **bold** indicate RMSEs that correspond to SWR with the highest ISE repeatability.
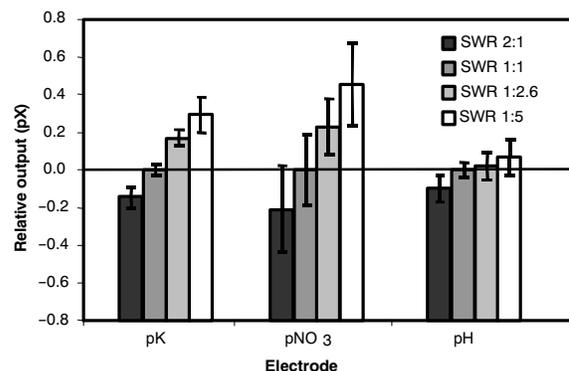

Figure 4. Relative electrode output for four different levels of soil/water ratios (SWR). Error bars indicate corresponding standard deviations, and 0 pX represents the average output at 1:1 SWR.

(as had been observed in preliminary trials). However, as shown in figure 3e, the influence of ISA was similar for dilute (SWR 1:5) and more concentrated (SWR 1:1) solutions. Yet, complete removal of the ISA option could not be recommended when mapping soils with very low buffering capacity (not present in our experiment) using a relatively large amount of water for extraction.

Several three-way interactions, such as SWR × ISA × Stir and SWR × QWE × ISA, that could be theoretically significant were also studied, but they were not found to be influential. Based on the results of this factorial experiment, it appeared that a fixed-volume purified water extraction with stable agitation was essential, but non-purified water could be used to clean the electrodes. Additional experiments were performed to determine proper SWR and to make a recommendation in terms of use of ISA.

SOIL/WATER RATIO EXPERIMENT

Analysis of electrode repeatability revealed that RMSE values (indicators of measurement repeatability) corresponding to different levels of SWR did not vary significantly for a specific ISE. The pH and pK electrodes were both more repeatable than the pNO$_3$ electrode. In addition, generally lower RMSEs were found for 1:1 SWR (table 4). The difference caused by changing the SWR was quantified by subtracting the per soil average ISE output (SWR 1:1) from each measurement (fig. 4). Based on this comparison, the output of each ISE changed significantly when a different SWR was used. This reaffirmed our previous conclusion that maintaining a constant SWR is important. On the other hand, the maximum change (corresponding to 1:5 SWR) was only 0.08 pH, 0.28 pK, and 0.43 pNO$_3$. Assuming that in practice the amount of water added to a given soil sample would not deviate by more than 100%, smaller measurement errors could be anticipated. Since QWE was shown to be less influential with less water added to a soil sample (when measuring soil pH), SWR 1:1 was chosen for the ASM methodology. This selection also made pH measurements compatible with the standard laboratory routine and lowered the volume of the extracting solution

needed for testing while providing sufficient dilution. This selection did not significantly affect pK and pNO$_3$ measurements.

IONIC STRENGTH ADJUSTER EXPERIMENT

The absence of proper ISA was expected to significantly reduce electrode repeatability within the same calibration standard as well as affect both calibration parameters. On the contrary, such a conclusion could not be made based on the experimental results (table 5). In terms of repeatability, the use of the manufacturer-recommended ISAs (NaCl for pK and Al$_2$(SO$_4$)$_3$·18H$_2$O for pNO$_3$) as well as the integrated ISA (Na$_2$SO$_4$) did not produce significantly lower RMSE when compared to the blank (no ISA) solutions. In addition, with changes in slopes and intercepts, standard errors for calibration parameters did not change significantly. Therefore, to maintain consistency within the values of the calibration parameters, ISA should be used for calibration solutions. However, its use for soil solutions was deemed unnecessary, at least for the range of soils used in this study.

SOIL BUFFERING EXPERIMENT

To confirm the hypothesis of sufficient ionic strength existing within soil solutions (making unnecessary the use of ISA), a series of quantity/intensity relationships was evaluated (fig. 5). Most slopes of regression lines between the known change of ion concentration and an observed increase in ion activity were not significantly different from 1 (fig. 6), indicating an adequate rate of response. Therefore, it was concluded that every soil in this study had sufficient ionic strength to facilitate an accurate measurement when monitoring the increase in concentration of targeted ions. On the other hand, an option to add ISA to the purified water used

**Table 5. Summary of regression parameters for potassium and nitrate electrodes when
calibrating in standard solution with different types of ionic-strength adjuster (ISA).**

KNO$_3$ Calibration Solutions with:	Potassium ISE			Nitrate ISE		
	RMSE (pX)	Slope[a] (mV pX^{-1})	Intercept[a] (mV)	RMSE (pX)	Slope[a] (mV pX^{-1})	Intercept[a] (mV)
Blank (No ISA)	0.028	–56.1 (0.02)	502 (0.05)	0.046	52.9 (0.03)	229 (0.08)
3M Na$_2$SO$_4$ ISA	0.094[b]	–57.3 (0.06)	491 (0.17)	0.008[b]	56.1 (0.01)	225 (0.02)
5M NaCl ISA	0.012[b]	–57.2 (0.01)	494 (0.02)	0.088	31.3 (0.06)	279 (0.16)
1M Al$_2$(SO$_4$)$_3$·18H$_2$O ISA	0.040	–56.6 (0.03)	491 (0.07)	0.029[b]	61.0 (0.02)	210 (0.05)

[a] Standard errors for calibration parameters are given in parentheses.
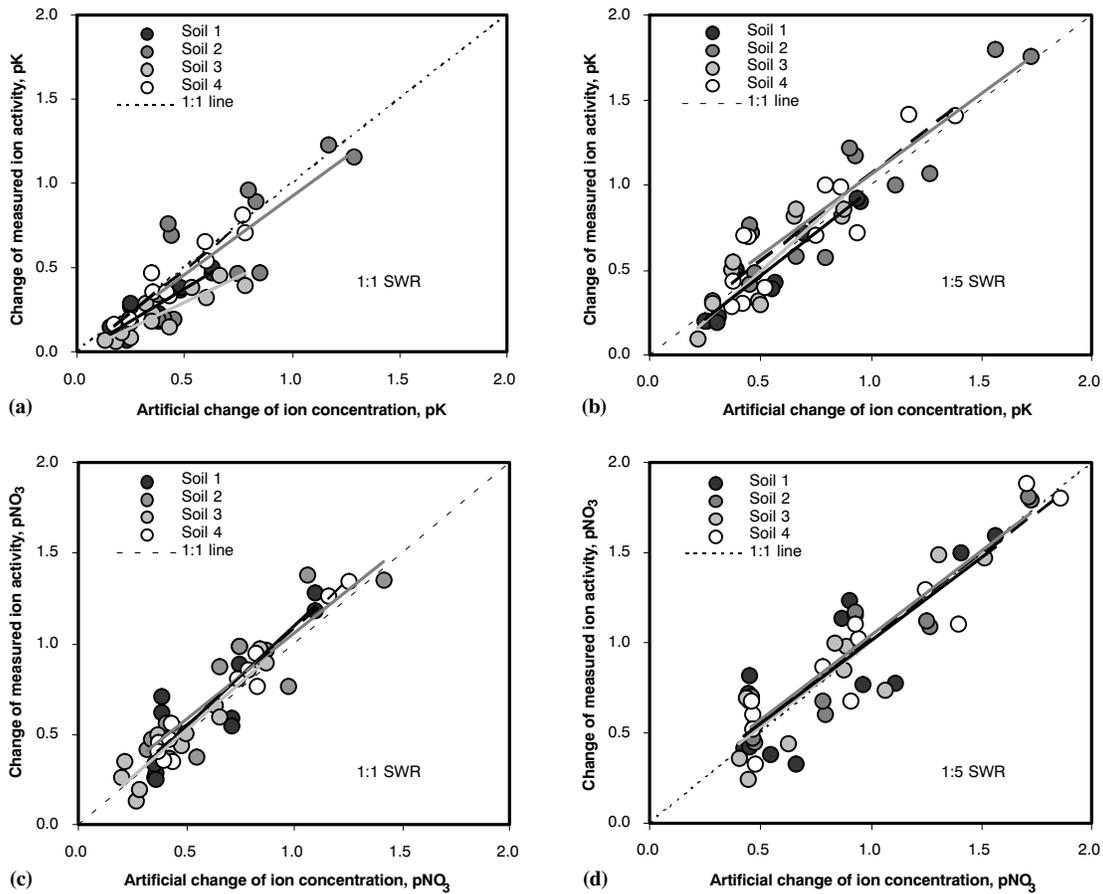[b] Proper ISA was used.

Figure 5. Electrode response to the artificial change in ion concentration (quantity/intensity plots) for (a) pK ISE with 1:1 SWR, (b) pK ISE with 1:5 SWR, (c) pNO$_3$ ISE with 1:1 SWR, and (d) pNO$_3$ ISE with 1:5 SWR (a change of one pX unit corresponds to a 10-fold change in ion concentration/activity).
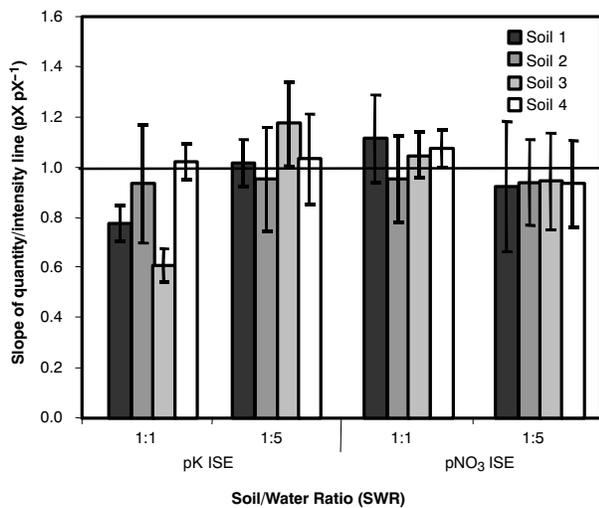

Figure 6. Slopes of quantity/intensity lines (error bars represent standard errors).

as the extractor should be reserved for future research. Such an option could be useful when mapping soils with extremely low buffering characteristics (e.g., sands) and when pursuing direct measurements of buffer pH and/or exchangeable potassium.

Based on the results of these experiments, the ASM methodology was recommended to be based on: 1:1 SWR,

DDW QWE, tap water QWR, no ISA, and stable agitation (stirring). Our continued research has evaluated both the precision and the accuracy of this method, as implemented though an agitation soil measurement chamber module. Results of that research will be reported in a separate article.

CONCLUSIONS

With the long-term goal of developing an integrated on-the-go soil sensing technology to increase the adoptability of precision agriculture, previous research resulted in a commercially available device for on-the-go mapping of soil pH with a relatively weak capability to integrate potassium and nitrate ISEs. The new agitated soil measurement method presented in this article did not complicate the measurement process significantly, and it provided an opportunity to engage fragile PVC membranes with aqueous soil solutions more gently when compared to naturally moist soils. Based on a one-half replication of a 4×2^5 comprehensive factorial experiment, it was found that, besides soils, soil/water ratio was the major factor causing electrode output to vary. The quality of water used for extraction did not affect potassium and nitrate measurement, but it was essential for soil pH. The presence of ISA and soil agitation were influential factors as well. However, no effect of the rinsing water quality was detected. With additional experiments involving four different levels of SWR, different types of ISA, and a soil

buffering study, a set of factors was chosen to provide an optimized measurement process, including: use of constant SWR (1:1), tap water for rinsing electrodes between measurements, purified (deionized or distilled) water without ISA for ion extraction, and fixed-rate solution agitation (stirring).

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