DEVELOPMENT OF ON-THE-GO SOIL SENSING TECHNOLOGY FOR MAPPING
SOIL pH, POTASSIUM AND NITRATE CONTENTS

by

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DEVELOPMENT OF ON-THE-GO SOIL SENSORS FOR MAPPING SOIL pH,
POTASSIUM AND NITRATE CONTENTS

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The main objective of precision agriculture is optimized management of spatial and temporal field variability to reduce waste, increase profits and protect the quality of the environment. Knowledge of spatial variability of soil attributes is critical for precision agriculture. Different approaches to assess this variability on-the-go have been pursued through development of soil sensors. One of the methods, direct soil measurement (DSM), has been applied in a commercial implement for on-the-go mapping of soil pH. In this research, DSM was evaluated in terms of extendibility to other soil chemical properties, including soluble potassium and residual nitrate. Further, superior ISE based approach called agitated soil measurement (ASM) has been developed and analyzed. Electrode calibration, precision and accuracy while performing DSM and ASM under laboratory and field simulation conditions were analyzed. The potential applicability of DSM/ASM for studied chemical soil properties declined in the order: pH > potassium > nitrate. The reason for this decline was attributed to the nature of the methodology itself. While developing ASM technique, the following factors have been evaluated: 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). It was concluded that for on-the-go mapping agitated purified water extraction without ISA,

addition of a fixed amount of water (1:1 SWR), and regular (tap) water for ISE rinsing should be used. To physically implement the ASM methodology, an Integrated Agitation Chamber Module (IACM) was developed and incorporated into the commercial soil pH mapping equipment. Based on the field simulation test, neither precision nor accuracy estimates have been improved as compared to the DSM field simulation test (precision

error ranged between 0.11 for pH to 0.22 for pNO_3). However, in addition to reduced electrode abuse, laboratory evaluation of ASM has revealed significantly lower measurement errors for all three properties and, therefore, retained the potential for improved quality of on-the-go field mapping.

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1. INTRODUCTION

1.1 Precision Farming

Precision agriculture/farming is all about managing the farm based on spatial and temporal field variability with respect to properties associated with all aspects of

agricultural production that optimizes inputs on a site-specific basis to reduce waste, increase profits and maintain quality of the environment. Precision agriculture is based on modern technologies broadly grouped into five major categories: computer hardware, sensors, global positioning system (GPS) receivers, geographical information system (GIS) software, and variable rate application controls. Advances in computer technology, availability of global positioning systems, evolution of geographic information systems, control systems and their subsequent integration has contributed to the growth of precision agriculture.

Precision agriculture encompasses a broad spectrum of areas including soil variability, plant genetics, crop diversity, machinery performance, influence of weather, and other inputs used in production agriculture. Owing to the scope of this research, the forthcoming discussion pertains to precision agriculture as applied to soil properties and site specific crop management based on soil variability. Success in precision agriculture is related to how well it can be applied to assess, manage and evaluate the space-time continuum in crop production, thereby bringing the site-specific management component into picture (Pierce and Nowak, 1999). Agronomic knowledge of the information generated by advances in technology is very critical in gaining benefits from site-specific crop management.

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Precision agriculture has become very promising since its formulation based on sound scientific principles of managing agricultural crop production. Against the high expectations for precision agriculture, practically achievable agronomic and environmental benefits are still limited (Lowenberg-DeBoer and Swinton, 1997, Sawyer, 1994, and Larson et al., 1997).

The first and foremost step in adopting precision agriculture is assessment of information that accurately quantifies the field variability with several data layers, e.g., yield, soil properties, etc. Traditionally, grid soil sampling has been used widely for soil fertility treatments. The cost of grid soil sampling using soil test laboratory techniques hinders higher than 1 ha sampling density. Also, uncertainties associated with interpolation of measured variables from grid soil sampling limits the potential of site specific crop management. There is a need for high-density spatial data that is accurate, inexpensive and easy to obtain. Availability of such data would facilitate to infer critical pieces of information regarding the nature of the soil for effective management in terms of tillage, liming, fertilizer application, etc.

1.2 On-the-go Soil Sensing Technology

The recognition of the fact that plants need adequate and balanced supply of elements or nutrients without toxic concentration of any particular one necessitates quantitative measurement methods to determine nutrient status of soils. Recommendation of optimum nutrient addition requires accurate and precise quantitative estimates of the nutrient status. Application of fertilizer based on soil variability has been followed since ancient times. LeClerg et al. (1962) concluded from their uniformity trials that soil fertility variations are not distributed randomly but are to some degree systematic. However, soil

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fertility is seldom distributed so systematically that it can be described by a mathematical formula. Todayís precision agriculture technology has the potential to generate more sophisticated assessments and responses to within-field heterogeneity and variation of soil fertility (Sonka et al., 1997). This calls for development of new methodologies of measuring soil properties.

There is a need and opportunity for development and implementation of sensing technologies, which would allow semi-automated or completely automated collection of data to characterize spatial variability of influential soil attributes. Sensors used in precision agriculture can be:

- Contact or Non-contact

- Aerial or Ground based

- Direct or Indirect

- Map-based or Real-time

During the measurement process, contact sensors need to be in physical contact (e.g., electrodes, mechanical sensors, etc) while non-contact sensors (e.g., remote sensing) does not require physical contact with the entity measured. Ground based and aerial sensors differ in their physical proximity to the field under investigation. Typically, ground based sensors are either mounted in the implement of a tractor, pickup truck, combine or positioned stationary near the field. Aerial sensors include those mounted on remote sensing satellites or airplanes. Direct sensors measure the property of intent directly (e.g., soil pH, etc), whereas indirect sensors measure a property that acts as a proxy to the property of intent (e.g., optical reflectance to predict soil organic matter). In a map-based approach, a GPS receiver and a data acquisition system are added to the sensing system,

generating a map that could be processed with other layers of spatially variable data. At a later time, variable rate application is performed with respect to the decisions based on the generated map. In real-time systems, sensors are used to adjust variable application rates in response to the sensor output.

On-the-go soil sensors are ground-based, typically mounted on the implement that is

driven through the field. On-the-go measurements of soil properties have the potential to provide benefits from the increased density of measurements at a relatively low cost (Sonka et al., 1997). High resolution maps can significantly decrease overall estimation errors and increase potential profitability of a variable rate soil treatment (Pierce and Nowak, 1999). Sensors for on-the-go soil properties mapping are currently being developed using electrical, electromagnetic, mechanical, electrochemical, pneumatic, acoustic, optical, and radiometric methods. To date, on-the-go systems capable of measuring soil electrical conductivity and pH are available commercially (Adamchuk et al., 2004).

On-the-go mapping of soil chemical properties would provide an assessment of the soil nutrient status based on which site specific management decisions on liming and fertilizer recommendations could be made. Considerable research has been done in the past to measure soil chemical properties both in laboratory and field conditions. Electrochemical measurement of soil based on ion selective electrodes (ISE) and ion selective field effect transistors (ISFET) are the most prominent approaches pursued by several researchers. ISEs could be used for simple, automated measurements, thereby making them ideally applicable for soil measurements on-the-go (Farrell and Scott, 1987). Establishment of ion selective measurement approach for soil pH, soluble

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potassium, and residual nitrate simultaneously on-the-go is the primary goal of this research.

1.3 Objectives

The ultimate objective of this research is to develop an integrated on-the-go sensing technology to quantify spatial variability of several chemical soil properties, including

soil pH, soluble potassium and residual nitrate. The specific goals were to:

- Evaluate the capability of multi-probe usage of a commercialized soil pH sensing technology to map different chemical soil properties on-the-go.

- Investigate alternative methodology for improved soil-sensor interaction applicable for on-the-go implementation.

- Develop and evaluate a system attachment prototype for simultaneous measurement of soil pH, soluble potassium, and residual nitrate contents.

2. LITERATURE REVIEW

2.1 Definition and Importance

2.1.1 Soil pH

Sorenson (1909) defined pH as the negative logarithm of H^+ ion activity, where activity relates to the concentration adjusted for non-ideality caused by charge-charge interactions with other ions in the solution. The presence and activity of H^+ ion in soils is of significant interest in natural science and agriculture. Soil pH is a variable that influences a spectrum of soil properties as well as the growth and survival of soil microorganisms (McBride, 1994), and it plays an indirect role in the development of several diseases and effectiveness of certain herbicides (Wolf, 1999).

In general, soil pH is the single most critical chemical characteristic of a soil, whose knowledge is needed to understand chemical processes such as ion mobility, precipitation and dissolution equilibria, precipitation and dissolution kinetics, and oxidation-reduction equilibria (Bloom, 1999). It influences the mobility and availability of plant available nutrients and toxins. Hence, measurement of soil pH enables estimation of the availability

of other essential nutrients and toxins based on their interrelationship with soil pH.

Lime requirement is the amount of basic material (e.g., limestone) required to increase the soil pH from an acidic condition toward an optimum value. As the soil pH reflects the amount of acidity present in the soil solution and serves as an index of the acid-base status of the soil, pH needs to be measured and adjusted to ensure optimum soil management practices (Sims, 1996).

2.1.2 Soil Nitrogen

Although nitrogen is abundantly available in the atmosphere, the sources of soil nitrogen are mineralization, rainfall, nitrogen fixation by symbiotic microorganisms, plant or animal decay, applied manure and fertilizer. Soil nitrogen is lost due to consumption by plants, volatilization, denitrification, immobilization, leaching or erosion. The process of nitrogenís entry into soil and subsequent loss is governed by the nitrogen cycle.

Soil nitrogen exists in three forms - organic form (accounts for 95 - 99%), ammonium ions, and nitrate ions. The plant available forms of nitrogen are both ammonium and nitrate ions. Due to a process called nitrification, soil microorganisms convert ammonium to nitrate and hence, most of the plant available nitrogen is in the form of nitrate (Schmidt, 1982). This nitrogen is needed to form chlorophyll, proteins, and many other molecules essential for plant growth, as plant tissues contain more nitrogen than any other nutrient normally applied as a fertilizer. Although, some plants, such as soybeans, acquire nitrogen by fixation, most crops, such as corn and sorghum, rely on nitrogen acquisition through roots from soil (Norton, 2000).

Deficiencies or excesses of nitrogen probably influence the world's ecosystems more than any other essential element. A nitrogen deficient plant is generally small and develops slowly because it lacks the nitrogen necessary to manufacture adequate structural and genetic materials. The leaves of nitrogen deficient plant are pale green or yellowish, because they lack adequate chlorophyll (Blackmer, 2000). Nitrogen deficiency is a common nutrient fertility problem for grain crops resulting in low yield. On the other

hand, excess nitrogen could adversely affect biological, animal and human health, denigrating the quality of the environment. For example, high nitrate levels in soils could lead to sufficiently high nitrates in drinking water as to endanger the health of human infants and ruminant animals (Brady and Weil, 2004).

Advances in commercial nitrogen fertilizer manufacturing has not diminished the importance of nitrogen management but has markedly increased the need for more efficient management of nitrogen in agricultural production systems. One negative impact of availability of cheap nitrogen fertilizer is over application of nitrogen fertilizer from fear of financial risk of lost yield from under applying nitrogen. Therefore, nitrogen management in production agriculture is of great concern.

2.1.3 Soil Potassium

Soil potassium exists in four forms: soluble, exchangeable, fixed (non-exchangeable), and structural or mineral form. Plants can only use the exchangeable potassium on the surface of the soil particles and potassium dissolved in the soil solution. Exchangeable potassium is electro-statically bound to the surfaces of clay minerals and humic substances. The availability of soluble potassium is generally very low as compared to

the exchangeable form and is governed by the equilibrium and kinetic reactions that occur between the various forms of soil potassium. Soil moisture content and concentration of the exchangeable and solution bivalent cations are also reported to have an effect on the levels of soluble potassium (Sparks and Huang, 1985). Potassium deficiency in corn and soybean results in yellowing to necrosis of the leaf margins and in several cases browning of leaf edges may occur (Mallarino, 2005).

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To describe the potassium status in soils, current potential of potassium in the labile pool is not sufficient as the quantity/intensity (Q/I) relationship determines potassium availability. Beckett (1964) investigated the immediate Q/I relations on changes in activity ratio of potassium after it was added or removed. He plotted the activity ratio $(K)/[(Ca) + (Mg)]^{1/2}$ against ΔK (addition of potassium by fertilization or removal by plant roots) and observed a typical buffering relationship with a linear upper part and curved lower part. The slope of the linear portion is the buffer capacity of potassium in that soil.

2.1.4 Other Soil Chemical Properties

As the name of the most common fertilizer ìNPKî suggests, phosphorus stands next to nitrogen on the widespread influence of an element in agriculture and natural science. Unlike nitrogen, phosphorus does not commonly cause leaching into ground water, as it is non-specifically retained in the soil (highly insoluble). However, there have been several instances of phosphorus runoff to streams, lakes, and reservoirs causing eutrophication, mostly due to over application of phosphorus fertilizer/manure over time in agriculture. Basically, phosphorous is an essential element needed by plants in order to grow as it is involved in energy transfer and biochemical processes within plant.

Phosphorus deficiency usually results in delayed maturity, poor seed quality and sparse flowering in plants (Brady and Weil, 2004).

Soil phosphorus exists in three forms: soluble, labile in solid phase and non-labile. Thse forms in dynamic equilibrium with each other in response to plant uptake, addition of fertilizer, and leaching, which is seldom predictable. The equilibrium existing between

these pools are complex, have differential reaction rates, are dependent on strengths of bonding and ion supply in each pool and these collectively account for the phosphate buffering action in the soil (Kuo, 1996).

The applicability of polyvinyl chloride (PVC) based phosphate membrane was evaluated in buffer solutions (Kim et al., 2005). They reported a very low shelf life (14 days) for the phosphate membrane and interference from high fluoride contents in Kelowna, Bray P1 and Mehlich III solutions. Although, laboratory evaluation of phosphate membranes has been reported recently, there is no commercially available phosphate ion sensor that could be used with soils.

Sodium is not considered to be an essential element for plant nutrition. Many plants do respond favorably to additions of sodium. However, excessive sodium in soils could cause adverse effects and is of considerable interest, especially soils infested with salinity/sodicity issues. When the exchangeable sodium content in soils as measured using the sodium adsorption ratio exceeds 15 meq per 100 g soil, it could be classified as a sodic soil. Sodic soils cause dispersion resulting in poor water infiltration and aeration, and cause erosion. Soil sodium also increases the soil pH resulting in affecting soil physical properties indirectly. Symptoms of excessive sodium in soils are similar to those

caused by drought or root injury. Leaves tend to turn yellow, have damaged margins, and may show early autumn coloration (Wolf, 1999).

Cation exchange capacity (CEC) is also a critical soil chemical property that is used for classifying soils in soil taxonomy as well as for assessing soil fertility and environmental behavior (Brady and Weil, 2004). Usually, the cation exchange capacity is

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expressed in milliequivalents per 100 g of soil and is a measure of the quantity of readily exchangeable cations neutralizing negative charge. It provides an index to the amounts of cations held strongly enough to slow leaching or volatilization, but yet readily available. Soils with high CEC have the ability to hold large quantities of cations, which can act as a nutrients reservoir. Cultivation of soils and crop harvest tend to remove large quantities of cations, which also can leave soils too infertile to support adequate crop growth. Sufficient liming and fertilization are necessary to replace those lost cations (Wolf, 1999).

It is to be noted that the scope of this dissertation deals with the measurement of soil pH, potassium and nitrate contents only. However, the developed methodologies could be extended to the other soil chemical properties, like sodium and phosphate contents. The major difficulties in implementation of the developed methodologies to the other soil chemical properties are: 1) lack of availability of reliable sensors, and 2) agronomic value of such measurements.

2.2 Conventional Laboratory Practices, Measurement and Prescription Methods
2.2.1 Soil pH and Lime Requirement

Measurement of soil pH is usually conducted either by colorimetric or electrometric methods. The former involves suitable dyes or acid-base indicators, the colors of which

change with H^+ ion activity and the latter involves a glass, H^+ sensitive ISE paired with a reference electrode attached to a suitable meter for measuring electro motive force, which is proportional to pH. Colorimetric methods are less suitable as they tend to be slower, less precise and subjective.

In a modern ISE, passive membranes separate the internal standard and test solutions of the ions. Electrons, simple ions as well as charged or neutral complexes of the test ion are transported across the membrane interfaces to extents that are proportional to the compositions of solutions on either side of the membrane. The electrostatic potential difference (E), in mV, developed across the membrane can be measured by coupling the membrane half-cell with a standard reference electrode half-cell and is theoretically given by the Nernst equation (Talibudeen, 1991):

$$_iF\, a_i\, E = E_0 + (RT\,/\,z\,)\log \quad (1)$$

where E_0 = initial electrode potential or intercept (mV)

R = universal gas constant (8.3144 J mol^{-1} K^{-1})

T = absolute temperature (K)

F = faradayís constant (96,485.3 C mol^{-1})

z_i = valence of the ion

$a_i = y_i\, c_i$, ion activity (pX)

y = ionic activity coefficient

c = ion concentration (pX)

The theoretical slope RT/F at 25° C (298 K) is 59.12 mV pX^{-1} for ions with $z = 1$, being positive for cations (including H^+) and negative for anions.

In most laboratories, a glass electrode paired with a reference Ag-AgCl or calomel ($Hg-Hg_2Cl_2$) electrode is used. Upon proper calibration with standard buffer calibration solutions of known pH, the voltage indicator/meter indicates the pH of the soil suspension when the two electrodes are placed in it. Soil test laboratories differ on the

details of pH measurement, including: choice of soil water ratio (SWR), method of mixing, time to equilibration, stirring of soil suspension, use of 0.01M $CaCl_2$ for background ionic strength, etc. The pH of a solution in equilibrium with soil varies with the composition and concentration of the salts in the solution as cations in solution displace H^+ and Al^{3+} ions from soil surfaces. Most soil testing laboratories measure the pH in a suspension of soil in distilled water (water pH or soil pH), while other laboratories use a neutral salt solution like 0.01M $CaCl_2$ or 1M KCl (McClean, 1982).

According to the method prescribed by Thomas (1996), a common procedure for soil pH measurement in the laboratory is as follows:

1. Weigh or measure with a scoop, 10 g of air-dry soil into a 50 ml beaker. 2. With a pipette, add 10 ml of distilled water into the same beaker. 1 drop of 0.05 ml 1M $CaCl_2$ may be added to determine soil pH in 0.01M $CaCl_2$.

3. Mix thoroughly for 5 s, preferably with portable mechanical stirrer or glass rod and let stand for 10 ñ 30 min.

4. Insert the electrode pair into the container, and stir the soil suspension by swirling the electrodes slightly.

5. Read the pH measurement value from the standardized pH meter as the reading stabilizes.

Liming recommendations are usually based on the buffering capacity of soils. Buffering capacity is the ability to resist to changes in pH and is largely due to reserved acidity (buffer pH). Although a relationship between active and reserve acidities exists, it is not constant across different soil types. Clay content, organic matter and free lime

influence the soil buffering capacity of the soil. Therefore, application of lime over the same amount of sandy and clay soil would have different effect on each other (Wortman et al., 2003). University of Nebraska lime recommendations for corn are based on raising soil pH to 6.5. When soil pH is less than 6.3, buffer pH measurements are needed to estimate lime requirement (Mamo et al., 2003).

Several correlation studies are reported in literature between soil pH buffering capacity and other properties. Aitken et al. (1990) reported the relationship of soil pH buffering capacity to organic carbon and clay concentrations. Using multivariate linear regression analysis, they showed that organic carbon accounted for 78% of the variance in pH buffering capacity, and clay for the remaining 32%.

Weaver et al. (2004) developed a procedure to map soil pH buffering capacity to define sampling zones for lime requirement assessment. These maps originated from organic carbon and clay contents measured from field soil samples. Regression between the measured and mapped pH buffering capacities resulted in R^2 of 0.88 with a slope of 1.04 for a group of soils that varied approximately unit buffer pH. They also concluded that knowledge of spatial variation in biological reactions of nitrogen and soil pH buffering capacity would be essential to completely understand the distribution of soil pH.

Viscara Rossel and Walter (2004) demonstrated the validity of the high-density on the-go soil pH data as compared to the sparse sampled laboratory soil pH estimations using a co-kriging approach. They concluded that the rapid on-the-go field measurement of soil pH has an economical value for precision agriculture. Therefore, on-the-go field

measurement of soil pH with other secondary data layers obtained from soil electrical conductivity, remote sensing and other sources would be a promising solution to effectively manage soil acidity in production agriculture.

2.2.2 Soil Nitrate Management

Nitrate is an ion highly soluble in water and non-specifically retained in the soil. This makes extraction of nitrate from soil easy and simple, compared to other anions like phosphorus. There are many methods of nitrate determination available in the literature, although each method has its own limitations and advantages. The most common procedures used for the measurement of nitrate are the ISEs and calorimetric cadmium reduction (CR) method. CR method involves preparing 1:2.5 to 1:10 SWR solution with possible addition of CaO to facilitate dispersion of clay particles, followed by a flow injection analysis. Although ISEs are simple to use and widely reported in standard laboratory practices, commercial laboratories rarely use them. The reasons could be attributed to the sensitivity and fragility of the electrodes, their limited operational lifetime, and the adverse effect of interfering ions.

A nitrate ISE is very similar to a conventional pH electrode in principle and construction. Most commonly available nitrate ISEs are constructed with PVC membranes involving charged sites or neutral complexing carriers dissolved in a water

immiscible solvent, or impregnated in solid solution with an inert carrier. According to the procedure outlined by Bremner et al. (1968) and Orion Research Inc. (1990), the following steps for a laboratory ISE measurements, should be taken:

1. Pipette 20 ml of an aqueous soil extract into a 30 or 50 ml beaker containing a Teflon^{Æ} coated stirring bar.

2. Place the beaker on a magnetic stirrer and add 2 ml of 2M $(NH_4)_2SO_4$. Immerse both the nitrate and reference electrodes in solution, connected to a meter. 3. Stir the solution for 1 min, and record the meter reading

4. To calibrate the meter, carry out the same procedure measuring 20 ml aliquots of at least three standard nitrate calibration solutions.

Numerous nitrogen availability indices are available and their basic use is to identify appropriate rates of nitrogen fertilization for plant growth. Choice of nitrogen application rates should also complement quantities of available nitrogen already in soils for optimum fertilization. Pre-plant testing of soil nitrate is recommended and is used in many states of the Great Plains region to predict crop available nitrogen. In these low rainfall areas, nitrate carryover from the previous growing season is frequent due to relatively low potential for nitrate loss through leaching and denitrification (Dahnke et al., 1990 and Hegert et al., 1987).

In Nebraska, for example, nitrogen fertilizer recommendation is based on the residual nitrate, yield goal, organic matter and other nitrogen credits like legumes, manure, irrigation, etc. The nitrogen fertilizer recommendation algorithm for corn is given by the following equation (Shapiro et al., 2001):

$$[35 (1.2) (0.14) (8)] \; Nrate = + \cdot YG - \cdot YG \cdot OM - \cdot SoilNO_3 - N - N_{cr} \; (2)$$

where *Nrate* = Recommended nitrogen fertilizer application (lb acre^{-1})

YG = Yield goal (bu acre^{-1})

OM = Soil organic matter at 0 - 8 in. depth (%)

$SoilNO_3$ -N = Root zone soil residual nitrate-nitrogen at 5 - 10 in. depth (mg kg^{-1})

N_{cr} = Other nitrogen credits like legumes, manure, irrigation, etc

The newly revised (unpublished) University of Nebraska-Lincoln nitrogen recommendation also includes multiplication of the above *Nrate* by the factor f_R x f_A to account for better economic returns at high nitrogen fertilizer costs.

where f_R = Price ratio adjustment factor

f_A = Application timing adjustment factor

In Kansas, nitrogen recommendations for corn are based on a model representing a state average of several soils, localized growing conditions, and historical data. The recommended nitrogen application depends on yield goal, soil texture, previous crop, previous manure applications, and residual soil nitrate. The recommendation algorithm is given by the following equation (Schmidt et al., 2002)

$$Nrate = YG \cdot \cdot STA - PCA - PCM - P_{NST} (\ (3)\ 1.35)$$

where *STA* = Soil texture adjustment

PCA = Previous crop adjustment (lb acre^{-1})

PYM = Previous year manure (lb acre^{-1})

P_{NST} = Profile nitrogen soil test (lb acre^{-1})

In Minnesota, nitrogen recommendations for corn are different for various parts of the

state. The recommendation algorithm for western Minnesota is given by the equation (Schmitt et al., 1998):

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$$N_{cr} Nrate = (\ (4) \ 1.2 {\cdot} YG) - STN(0 - 24 in.) -$$

where *STN (0 - 24 in.)* = Amount of nitrate-nitrogen measured by using the soil nitrate test (lb acre^{-1})

However, optimized nitrogen fertilizer application is difficult as the variability of residual nitrate is very high between fields, and even within the same field. Applying the exact nitrogen fertilizer based on crop requirement has the potential to increase yield in areas that were previously under-fertilized, reduce application of nitrogen in areas that were previously over-fertilized, and therefore reduce unused soil nitrogen at harvest and minimize movement of nitrate to water bodies (Scharf et al., 2001).

2.2.3 Soil Potassium Management

Soil test laboratories measure exchangeable potassium using several extractants. In general, extracts of soils can be analyzed for potassium ion using atomic absorption spectroscopy (AAS), inductively coupled plasma-mass spectroscopy, flame emission spectroscopy, ion chromatography, or ISEs. These techniques require liquid samples. Solid soil samples can be analyzed by neutron activation analysis or x-ray fluorescence (Helmke and Sparks, 1996). The laboratory soil test procedure recommended for the North central USA involves 1M NH_4OAc at pH 7 extraction (Warncke and Brown, 1998), and is as follows:

1. Measure 1 g of soil into an extraction flask and add 10 ml of 1M NH_4OAc

   extraction solutions.

2. Shake for 5 min and filter the suspension through Whatman No. 2 or equivalent filter paper.

3. Set up the atomic absorption/emission spectrometer or another analytical device for potassium by emission. Determine the standard curve using the standards and obtain the concentration of potassium in soil extracts.

4. To convert potassium concentration (mg kg^{-1}) in the soil extract solution to mg kg^{-1} in soil, multiply by 10.

In Nebraska soils, minerals containing potassium are present in large quantities, and when weathering occurs, relatively large amounts of potassium are released for use by plants. Mostly, Nebraska soils are well supplied with potassium throughout the root zone. Therefore, use of potassium fertilizers is not recommended unless deficiency is found (Rehm, 1982).

The Kansas State University recommendation for potassium fertilizer (K$_2$O) application rate is:

$$Krate = -STK \cdot Years + K_{RM}[((5)\,130)\,9)/\,]$$

Where *Krate* = recommended potassium application rate (lb acre^{-1})

    Years = time to rebuild (years)

    STK = current soil K test in 0 ñ 8 in. (mg kg^{-1})

    K_{RM} = annual K removal with harvested crop (lb acre^{-1})

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The University of Minnesota (Rehm et al., 2001) recommendation for K application is:

$$Krate = (1.66 - 0.0073 \cdot STK) \cdot YG) \text{ for } STK > 160 \; ppm \; (6) \;\; Krate = 0 \text{ for } STK \leq$$

$$160 \; ppm$$

The potassium recommendation for corn, based on the buildup ñ maintenance concept for Indiana, Michigan and Ohio is as follows:

$$Krate = (CL - STK) \cdot ((1 + (CEC))] + (YG \cdot CR) + 20 \text{ for } STK < CL_1$$

$$Krate = (YG \cdot CR) + 20 \text{ for } CL_1 \leq STK < CL_2$$

$$Krate = (YG \cdot CR) + 20 - [((YG \cdot CR) + 20) \cdot (STK - (CL + 30))/ 20] \text{ for } STK \geq CL_1$$

$$(7)$$

where $CL_{1,2}$ = critical soil K test levels (mg kg^{-1}), CL_1 = 75 + 2.5 CEC

CEC = cation exchange capacity (cmol kg^{-1})

CR = nutrient removed per unit yield (corn: 0.27 lb bu^{-1})

Recommendation of potassium fertilizer application rates requires exchangeable potassium, as suggested by the soil test procedure. ISE based non-extractable measurement could only estimate the soluble portion of soil potassium, which is inadequate for fertilizer recommendation. However, exchangeable potassium is related to other soil properties, including soil texture, clay content, exchangeable and non exchangeable soil potassium, and CEC. Integration of the on-the-go sensing of soluble potassium with other data layers collected at a higher spatial density would be a reliable solution to predict potassium requirements of plants (Sudduth et al., 1997).

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2.3 Sensing Soil Chemical Properties

Mapping soil properties is an integral part of precision agriculture. With advances in site-specific management, there is a need for dense sampling to produce a representative

soil map of chemical properties. The economically feasible density of soil sampling and the uncertainties associated with interpolation methods limit the potential of conventional grid soil sampling. Higher resolution maps can significantly decrease overall estimation errors and result in higher potential profitability of variable rate soil treatment (Pierce and Nowak, 1999). There is a range of techniques that are currently pursued to measure soil properties on-the-go (Adamchuk et al., 2004).

As discussed earlier, the sensing technology could be broadly classified as direct and indirect methods based on how the targeted property is measured. The indirect methods include electrical, electromagnetic, optical and radiometric methods. The data layers measured using the indirect methods may be utilized to complement existing soil information for site-specific management. The practical use of such data layers may require field specific calibrations to infer a property of interest and is not straight forward. However, they prevent a valuable piece of information that could aid with site specific management decisions.

2.3.1 Electrical and Electromagnetic Methods

In many areas, presence of electrolytes (acids, bases and salts) in solutions can be detected by electrical conductivity measurement methods. Determination of electrical conductivity in soil solution (laboratory) or bulk soil (field) gives an indirect

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measurement of the salt content, soil texture and other properties. On-the-go mapping of electrical conductivity has become a widely popular method.

Electrical conductivity measurements are based on the resistivity property of the soil. Some of the sensors that are commercially available for mapping electrical conductivity

use either galvanic contact (e.g., Veris[Æ] 3100 EC Surveyor, Veris Technologies, Salina, Kansas) or electromagnetic inductance (e.g., EM-38, Geonics Limited, Mississuaga, Ontario, Canada) methods. When the Veris[Æ] 3100 cart with a set of six coulter-electrodes is pulled through the field, it provides contact measurement of shallow (0 ñ 30 cm) and deep (0 ñ 90 cm) soil electrical conductivity (Lund and Christy, 1998). In the case of the Geonics EM-38, it provides non-contact measurement of apparent electrical conductivity and magnetic susceptibility to an effective depth of 1.5 m in vertical dipole mode. Some researchers documented correlations between measured electrical conductivity and soil chemical characteristics. However, most of these relationships were field-specific (Kitchen et al., 1999).

2.3.2 Optical and Radiometric Methods

Optical sensors are capable of measuring several soil properties based on the unique spectral signature of every material/property. Optical sensors work in a broad range of wavelengths (mid infra red, near infra red, visual, etc.) beyond the visible range to detect or distinguish the material or property of interest. Optical sensor systems have been successfully applied in chlorophyll determination in leaves, weed identification, yield monitoring, soil organic matter, and moisture measurement.

Varvel et al. (1999) attempted the determination of relationships between spectral data from an aerial image and intensive grid soil test results of soil organic matter and phosphorus. They concluded that aerial imagery could be used to improve soil-sampling strategies although it requires substantial inputs from other data layers and past management history.

Thomasson et al. (2001) studied the relationship between soil properties and

reflectance spectra along with the sources of variability of reflectance spectra. The soil properties of interest: soil nutrients and texture were predicted using diffuse reflectance in the range between 250 and 2500 nm. They found that certain sections of the spectrum were more useful for discriminating among soil samples with differing characteristics than others. They concluded that the regions of highest discriminatory power were both in 400 ñ 800 and 950 ñ 1500 nm.

Hummel et al. (2001) evaluated an earlier developed near infrared reflectance sensor to predict soil organic matter and soil moisture contents of surface and subsurface soils. They reported standard error (SE) of prediction for organic matter and soil moisture as 0.62 and 5.31%, respectively.

Bajwa et al. (2001) attempted soil characterization using hyper spectral images. They reported that soil parameters such as CEC, organic matter, calcium, and magnesium were related to spectral soil reflectance. However, they also found that different soil types had different reflectance characteristics related to soil fertility properties.

Ehsani et al. (2001) reported the feasibility study of detecting soil nitrate content using the mid-infrared (MIR) technique. They used a fourier transform infrared (FTIR)

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spectrophotometer to determine the MIR response to various concentrations of nitrate in solutions and soil samples. They reported the coefficient of determination (R^2) of 0.856 for nitrate prediction using the wavelet decomposition technique. To overcome specular reflection effects and band overlap, they utilized a continuous wavelet transform to deconvolute soil spectral data, resulting in a model with $R^2 = 0.878$ between soil nitrate content and MIR diffuse spectral reflectance. However, the results of this study were based on soil samples with nitrate contents ranging from 400 ñ 3000 mg kg^{-1} nitrate

nitrogen, which is not applicable to field measurement of soil nitrate in bulk soil.

Jahn et al. (2004) also utilized wavelet analysis to soil FTIR / attenuated total reflectance spectral data in order to predict nitrate contents. They reported that the volume of the nitrate peak for each spectra could be correlated to nitrate concentration with R^2 greater than 0.97 and relatively low standard error (SE < 25 mg kg^{-1} nitrate nitrogen) in laboratory evaluation. Similarly, field experiments resulted in R^2 greater than 0.92 and SE < 9 mg kg^{-1} nitrate-nitrogen. However, under approximately 20 mg kg^{-1} nitrate-nitrogen concentrations prediction of nitrate peak was difficult due to interfering peaks.

Bogrekci et al. (2003) used visible and near infrared spectroscopy to determine soil phosphorus concentrations, reporting values of 9.4% and 12.9% for SE of prediction using partial least square validation of dry and wet soil samples. Bogrekci and Lee (2005) reported spectral phosphorus mapping using diffuse reflectance of both soil and Bahia grass vegatation. Their investigation of the soil reflectance in ultra-violet, visible and near infrared regions resulted in prediction of spatial phosphorous distribution identifying areas with high and low phosphorus concentrations in soil. They reported an accuracy

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and precision for prediction of phosphorus concentration in Bahia grass. They were 334 and 188 mg kg^{-1}, respectively.

Viscara Rossel et al. (2006) qualitatively analyzed soil pH, lime requirement, organic carbon, clay, silt, sand, CEC, exchangeable calcium, exchangeable aluminum, residual nitrate, available phosphorus, exchangeable potassium and electrical conductivity in the visible (400 ñ 700 nm), near infrared (700 ñ 2500 nm) and mid infrared (2500 ñ 25000

nm) reflectance spectra. They compared the simultaneous predictions of soil properties in each spectral range and their combination. They implemented a partial least-squares regression decomposition technique and found that mid infrared range had the most high intensity spectral bands. However, only minor improvements in predictions of clay, silt and sand content were reported using the combination of all the three ranges. Soil properties studied were pH, lime requirement, organic carbon, clay, silt, sand, CEC, exchangeable calcium, exchangeable aluminum, nitrate-nitrogen, available phosphorus, exchangeable potassium, and electrical conductivity. They reported that accurate predictions using the mid-infrared reflectance for soil pH, lime requirement, organic carbon, clay, silt, sand contents, cation exchange capacity, phosphorus and electrical conductivity were possible. Also, in the near infrared region, accurate predictions of exchangeable aluminum and potassium were better than other properties. Conclusively, they demonstrated the potential of diffuse reflectance spectroscopy using the three regions for more efficient soil analysis and the acquisition of soil information.

Although optical sensors have gained widespread attention for their possible application for measurement of soil properties, there are several hurdles in the successful application of close range optical sensors in soils, including: the need for robust

measurement methodologies for on-the-go mapping, proper optical sensor - soil contact, and constant lighting conditions.

2.3.3 Electrochemical Methods

Direct electrochemical measurement of soil chemical properties, including pH, soluble potassium, and residual nitrate contents, has been the subject of considerable investigations. Several researchers have attempted measurement of three soil properties

based on both ISE and ISFET.

Farell and Scott (1987) studied the procedures using ISEs for accurate determination of exchangeable potassium in soil extracts. They measured exchangeable potassium in 30 soil samples using extraction solutions of 1M NH_4OAc and 0.5M $BaCl_2$. The soil samples were analyzed with 1:5 SWR and a constant ionic strength at pH 7. The exchangeable potassium measurements were correlated (r = 0.983 with no significant difference at $\alpha = 0.05$) with the AAS results using the same neutral extracts.

Wang et al. (1988) used ISEs to study potassium Q/I relationships. They found that ISEs offered a simple and rapid alternative to AAS. They detected compatible (r ≥ 0.999) potassium related characteristics measured in three Iowa soils.

Brouder et al. (2003) evaluated a rapid and inexpensive potassium ISE protocol for soil solutions. Their study included 32 agricultural soils with a 15 s agitations and 30 min settling period that proved sufficient to equilibrate potassium concentrations in a 1:1 SWR solution. The electrochemical measurement values closely correlated with the AAS (r = 0.93).

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Adamchuk et al. (2002) reported preliminary laboratory experiments to quantify potentials and the limitations of PVC membrane, combination, ISEs for measuring potassium and nitrate content in soils. The results of laboratory experiments indicated that it was feasible to use both nitrate and potassium ISEs to determine soluble potassium and residual nitrate contents on naturally moist soil samples with errors of up to 0.3 log (K^+) or log (NO_3^-), similar to soil pH. However, when comparing those errors to the total field variability, potassium and nitrate measurements have much lower relative accuracy than soil pH. They compared individual potassium and nitrate ISE-DSM measurements

with reference AAS and CR procedure on 15 different Nebraska soils, resulting in R^2 values 0.57 - 0.86 and 0.85 ñ 0.87, respectively.

Adsett and Zoerb (1991) reported on real-time nitrate sensing using ISEs. The limiting factors were the extraction time and measurement methodology of the system, and additional research was planned to improve the mixing and extraction phases.

Thottan et al. (1994) reported on the subsequent laboratory investigation of the suitability of nitrate ISE in an automated on-the-go soil nitrate monitoring system. They studied the effects of different soil:extract ratios and extract clarity on electrode response. There was no significant difference ($\alpha = 0.05$) among different soil:extractant ratios (1:15, 1:5, 1:3) and no significant difference among final nitrate concentration (decanted, filtered, and suspension samples). Analysis of time response showed that 80% of final concentration was consistently indicated within 12 s, 40% within 6 s and 10% within 4 s, which they felt was within the time required for rapid in-field measurements.

Nair and Talibudeen (1973) used an ISE for in-situ soil measurements and evaluated the rate and magnitude of depletion of potassium and nitrate activity in the root zone of winter wheat. They utilized a 1M NaCl salt bridge and KCl standards in water for potassium electrode and 1M KCl salt bridge and KNO_3 standards in water. They found out that for both electrodes, a 2:1 SWR and 30 s equilibration time were sufficient. The electrode readings were compared to flame photometry measurements used as a reference ($R^2 = 0.99$).

Wang and Huang (1990) studied the feasibility of using potassium ISE to monitor changes in potassium concentration in soil suspensions over time. They described factors

affecting the efficiency of the ISE method, including: the ISE response time, influence of suspended soil particles, shaking speed, and ionic strength of the system.

Loreto and Morgan (1996) reported the development of a system for field measurement of soil nitrate using ISFETs. The system was tested in laboratory as well as field conditions. In a laboratory soil bin study, correlations of ISFET response to a nitrate ISE and to laboratory colorimetric analysis were 0.65 and 0.43, respectively. Measurement of soil pH using ISFET sensors was attempted in field conditions with little success as the system had shortcomings in design.

Addsett et al. (1999) reported on the development of an automated on-the-go soil nitrate monitoring system. They developed a routine for predicting soil nitrate based on 6 s ISE responses with an error of 10% based on simulated field calibration tests. Though the system performance was acceptable in laboratory conditions, field-testing manifested in unacceptable electrode noise, mechanical and electrical issues.

Birrell and Hummel (1993) investigated the use of a multi-ISFET sensor chip to measure soil nitrate in a flow injection analysis system using different flowrates (0.057 - 0.236 ml s^{-1}), injection times (0.25 - 2 s) and washout times (0.75 - 2 s). They reported successful soil nitrates measurement in manually extracted soil solutions ($r^2 > 0.9$), and found that errors in prediction were caused by lack of repeatability in injection times and by variable flow parameters during the testing cycle of the automated soil extraction unit.

Birrell and Hummel (2001) investigated the optimization of flow rate, injection and washout time of an ISFET-based real-time soil nitrate sensing system coupled with the flow injection analysis. They reported the use 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. However, their automated soil solution extraction system required additional development to be adopted for field use.

Price et al. (2003) developed a real-time soil nitrate extraction system and optimized system parameters, such as texture, moisture, core density, nitrate concentration, core diameter, core length, and extraction solution flow rate, using a factorial statistical design. They reported 12 data descriptors to be statistically significant and suggested that a ëprioríí knowledge of soil type might be necessary for the ISFET technology to make accurate real-time measurements of soil nitrate-nitrogen.

Viscara Rossel and McBratney (1997) evaluated different potentiometric pH sensors for continuous on-the-go mapping. They selected ISFETs based on key parameters including pH range, fragility, precision, and response time. Further, they tested the

response time of ISFETs at two stirring rates and two SWR. It was reported that the speed of response increased with increased stirring speed, and with a higher SWR.

Viscara Rossel et al. (2004) developed an on-the-go soil pH and lime requirement measurement system prototype. They reported field testing results with accuracies of 0.37 and 0.60 pH using 0.01M $CaCl_2$ and de-ionized water solutions, respectively. The accuracy of estimated lime requirement was 0.60 Mg ha^{-1}. However, the prototype needed further improvements for field use.

An automated system for on-the-go mapping of soil pH based on direct soil measurement (DSM) approach has been developed and successfully tested by Adamchuk et al. (1999). The automated on-the-go soil sampling system obtained naturally moist soil samples at a fixed depth and placed then in firm contact with the electrodes. After

stabilization of the electrode output (5 ñ 15 s), measurements were completed and the system cleaned the electrode while taking another sample. Collins et al. (2003) modified the soil sampling mechanism to increase the reliability of the on-the-go soil pH mapping, and Veris Technologies Inc. (Saline, Kansas) commercialized the system as Veris^{Æ} Mobile Sensor Platform (MSP), shown in figure 2.1.

Soil Sampling

MSP
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Hydraulic Mechanism (SSHM)

Row Cleaners and Firming Wheel

DSM - ISE measurement

Soil Sampling Shoe Covering Disks
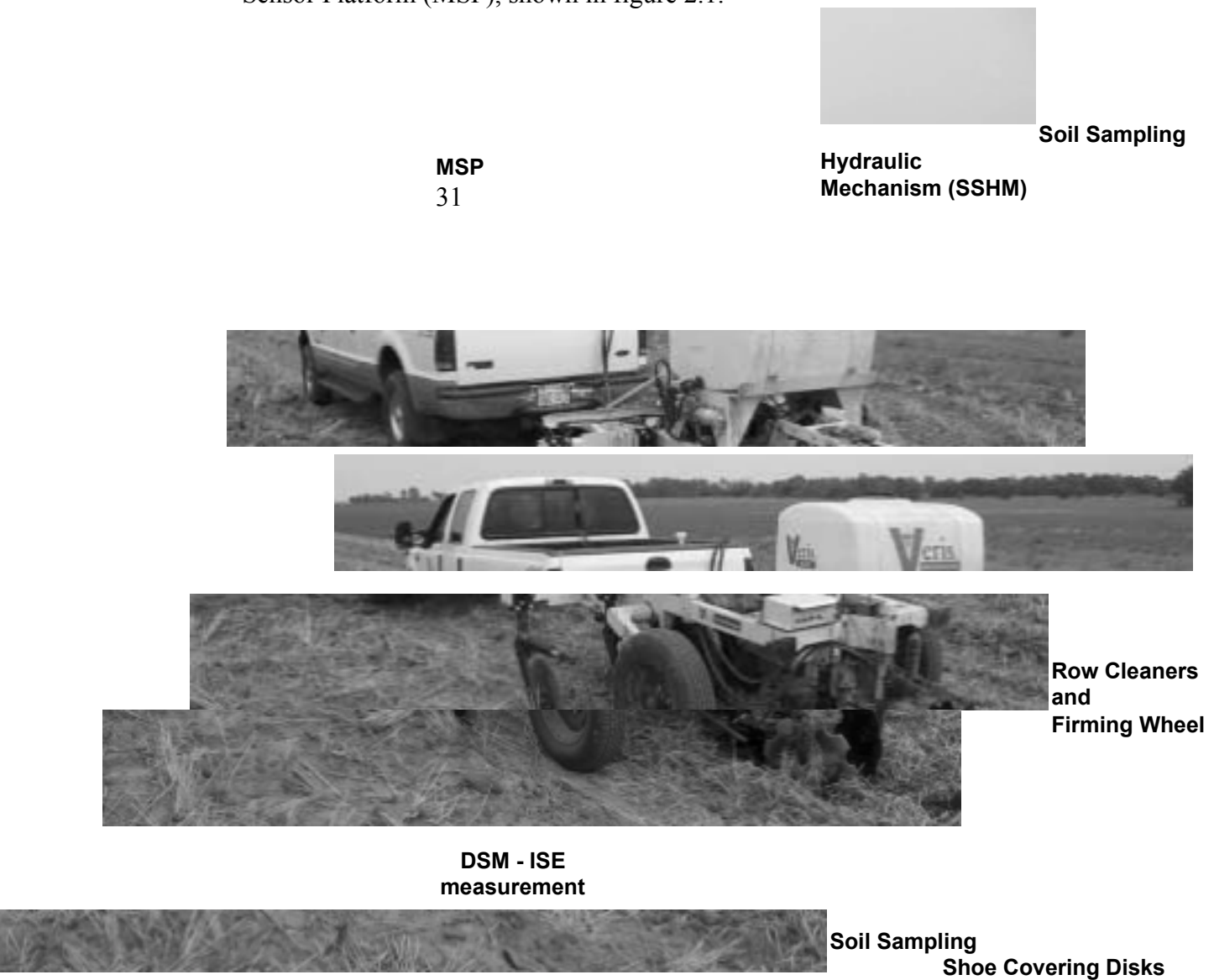
Figure 2. 1. Veris® mobile sensor platform with DSM capability.

MSP unit utilizes a soil sampling hydraulic mechanism (SSHM) and two independent ISEs to capture pH readings on soil samples collected by the sampling shoe in field

conditions every 10 s. Sampling densities of 10 - 20 samples ha^{-1} are usually mapped at a given speed and swath width. For example, at a speed of 15.84 km hr^{-1} and 18.2 m swath width, sampling densitis can be as high as 6 - 7 samples ha^{-1}. The apparatus is mounted on a toolbar pulled by a pickup or mounted on a tractor. Measurement depth is adjustable from 5 to 15 cm. While mapping a field, row cleaners remove crop residue, and firming wheel compacts loose soil for optimal flow into the sampling shoe. SSHM lowers the sampling shoe into the soil, collecting a soil core. After sample collection, SSHM raises the sampling shoe bringing the soil sample in contact with two pH ISEs. After recording

the measurements, the ISEs are washed with two flat fan nozzles while SSHM extends to collect the next soil sample. Covering disks fill the soil trench and cover the track.

An agroeconomic analysis was conducted to estimate the potential value of automated soil pH mapping (Adamchuk et al., 2004). They reported the difficulties associated with weighing economic benefits of soil pH adjustment as liming has indirect positive effects rather than direct ones. Although automated soil mapping did not provide more accurate soil analysis than the standard laboratory method, they found that increased sampling density resulted in higher quality of soil pH maps, while keeping data collection costs relatively low. They compared automated soil pH mapping against commonly used 2.5 acre (~ 1 ha) manual grid point sampling with soil lab test analysis. The results showed that automated soil pH mapping could result in $6.13 ha^{-1} higher net return over cost of liming during a four year growing cycle in a corn soybean rotation.

Based on this review, it becomes clear that the development of an innovative ISE based methodology for integrated on-the-go mapping of soil chemical properties (activity of H^{+}, K^{+}, and NO$_3^{-}$ ions) is required. The new methodology should provide simple and

inexpensive approach for on-the-go soil measurements with precision, accuracy and reliability adequate to map agricultural fields prior to variable rate application of mineral fertilizers and lime.

3. MATERIALS AND METHODS

Evaluation of the extendibility of the multi-probe DSM method to other soil chemical properties such as potassium and nitrate was the first step in the development of a robust integrated on-the-go soil sensing system. The commercial MSP implement was modified to allow the use of DSM methodology for integrated measurement of potassium and nitrate contents, in addition to soil pH. Based on the results of this preliminary study, the need for an improved interface between the electrodes and soil was recognized, and therefore a new ASM methodology was developed. To define the proper measurement technique, the following factors affecting measurement precision and accuracy were considered: SWR, ISA, stirring (agitation), quality of water used for extraction (QWE), and quality of water used for rinsing (QWR). Practical implementation of ASM methodology required development of an integrated agitation chamber module (IACM) to be attached to the existing Veris^{Æ} MSP unit (figure 2.1). A series of laboratory experiments was conducted to evaluate the potential for both DSM and ASM methodologies applied for integrated on-the-go mapping of important chemical soil properties (pH as well as potassium and nitrate contents).

3.1 Experimental Materials

3.1.1 Electrode Calibration

ISE calibration was performed using chemical solutions with known ionic concentration to define the relationship between voltage output and the activity of targeted ions in a tested solution. Replicated calibrations between sets of soil

measurements provided the ability to monitor possible changes in calibration parameters that could indicate ISE malfunctioning if reasonable limits were exceeded.

The ion selective electrodes used in this research are listed in table 3.1. Standard pH buffer solutions (pHCS) were used for calibration of pH ISEs, which included pH 4, 7 and 10 standards (table 3.2). In the case of potassium and nitrate ISEs, potassium calibration solution (KCS) and nitrate calibration solution (NCS) with recommended ionic strength adjustor (ISA) additions were used during DSM and other preliminary studies. For the rest of the experiments (ASM), new integrated calibration solution (ICS) was prepared using KNO_3, which allowed for simultaneous calibration of both potassium and nitrate electrodes (table 3.2).

Table 3. 1. Ion-selective electrodes used throughout the study.

Electrode ID	ions Targeted	Model[*]	Type	Expt.	Group
pH Probe 1	H^+	p17[1]	Combination	DSM	II
pH Probe 2	H^+	EID-E-FPH-DOME[2]	Combination	DSM	II
pH Probe 3	H^+	EID-E-FPH-A001[2]	Combination	DSM	II
pH Probe 4	H^+	ASI H028-001[3]	Combination	ASM	III
pH Probe 5	H^+	Veris ISE pH 23458[4]	Combination	ASM[5]	III
K Probe 1	K^+	detectION™ 3031BN[1]	Combination	DSM	I
K Probe 2	K^+	EID-E-CIX-A0KT[2]	Combination	DSM	I
K Probe 3	K^+	detectION™ 1031BN[1]	Half Cell	ASM	III
K Probe 4	K^+	detectION™ 1031BN[1]	Half Cell	ASM	III
N Probe 1	NO_3^-	detectION™ 3021BN[1]	Combination	DSM	I
N Probe 2	NO_3^-	EID-E-CIX-A0NO[2]	Combination	DSM	I
N Probe 3	NO_3^-	detectION™ 1021BN[1]	Half Cell	ASM	III
N Probe 4	NO_3^-	detectION™ 1021BN[1]	Half Cell	ASM	III
N Probe 5	NO_3^-	detectION™ 1021BN[1]	Half Cell	ASM	III

[1] Nico Scientific, Inc., Huntingdon Valley, Pennsylvania, USA
[2] Erlich Industrial Development (EID) Corporation, Westport, Connecticut, USA
[3] Innovative Sensors Inc., (ISI), Anaheim, California, USA
[4] Veris Technologies Inc., Salina, Kansas, USA
[5] Field simulation tests only.

* Mention of a trade name, proprietary product, or company name is for presentation clarity and does not imply endorsement by the authors, University of Nebraska-Lincoln, or exclusion of other products that may also be suitable.

Na$_2$SO$_4$ was used to prepare ISA for ICS since it contained both the anions (SO$_4^{2-}$) and cations (Na$^+$), which would not cause the interference. pH was excluded from ICS as pH buffering compounds have caused malfunctioning of nitrate PVC membranes. Three point calibration of each ISE was performed during both DSM and ASM experiments.

Table 3. 2. ISE calibration solutions.

Electrode	Calibration solutions	ISA	Experiment
pH	pH calibration solution[+] (pHCS) 10, 7, and 4	N/A	DSM/ASM
Potassium Nitrate	(7.221g/L KNO$_3$) 3, 30, and 300 mg kg^{-1} nitrate calibration solution (NCS) obtained from 1000 mg kg^{-1} as NO$_3^-$ standard (1.631 g/L KNO$_3$) 5.74, 57.4, and 574 mg kg^{-1} (K$^+$) corresponding to 9.11, 91.1, and 911 mg kg^{-1} (NO$_3^-$) integrated	calibration solution (ICS) obtained from 574 mg kg^{-1} (K$^+$) and 911 mg kg^{-1} (NO$_3^-$) integrated standard as (1.5 g/L KNO$_3$) · 30 ml of 0.06M Na$_2$SO$_4$ per 100 ml of standard solution · 2 ml of 5M NaCl per 100 ml of standard solution · 2 ml of 1M Al$_2$(SO$_4$)$_3$ x 18H$_2$O per 100 ml of standard solution	DSM DSM ASM
Potassium and nitrate 3, 30, and 300 mg kg^{-1} potassium calibration solution (KCS) obtained from 1000 mg kg^{-1} as K$^+$ standard			

[+] Acros Organics, Fairlawn, New Jersey, USA

Although soils in each experiment were analyzed in random order, ISE calibration was always performed from low to high concentration of targeted ions. This resulted in the order 10 >> 7 >> 4 for pHCS, and Low >> Medium >> High concentrations for KCS, NCS and ICS. The output of ISEs representing an electrostatic potential difference (E) is theoretically defined by the Nernst equation as in (1) and could also be expressed as a function of the logarithm of the specific ion activity pX (similarly to pH). Therefore, a

generalized ISE calibration equation can be written as:

$$E = E_0 \pm S \cdot pX \quad (8)$$

where E_0 ñ initial ISE potential or intercept (mV)

    S ñ Nernst coefficient or slope (mV pX^{-1})

    pX ñ activity of X ions (e.g., pH, pK, or pNO$_3$) given by:

$$\vdots = \frac{-_X a}{}$$

$$pX^3 \; 10 \log \; \rho \quad (9)$$

$$\frac{_{i\,W}}{M}$$

where ρ_W ñ water density (1 g cm^{-3})

    M_X ñ molar weight (H$^+$: 1 g mole^{-1}, K$^+$: 39 g mole^{-1}, and NO$_3^-$: 62 g mole^{-1}) A

simple linear regression was applied to the three-point calibration data to determine the

slope (S) and intercept (E_0) for each ISE. While the initial ISE potential is attributed to

the type and design of the ISE, theoretical slope of calibration equation typically remains

similar and depends on the targeted ionís valence and temperature. On the other hand,

ISE aging and mechanical wear of sensitive membrane may result in significant reduction

of the slope. Periodical measurement of ion activity in buffered calibration solution is a

common practice to assess ISE performance (acceptable slope) and to adjust the

electrode-specific calibration equation accordingly.

3.1.2 Soil Samples

Fifteen different soils from across Nebraska were used for laboratory evaluation of

soil sensors. Soil names according to the USDA survey, average organic matter content,

and ranges of test reports for soil pH, exchangeable potassium, and nitrate contents are

listed in table 3.3. These soils were air dried, sieved (2 mm mesh) and stored at 40 °C.

Prior to this study, six samples of each soil were analyzed in different commercial

laboratories.

Although minor differences in laboratory test procedures and equipment might exist, it was expected that every commercial soil analytical laboratory followed standard test procedures. Thus, reported % organic matter represents weight loss-on-ignition (LOI) measurements (Combs and Nathan, 1998).

Table 3. 3. Results of soils analyses performed by six commercial laboratories.

ID % OM[1] CEC[+]

Soil   Potassium[2], mg kg^{-1} mg kg^{-1} USDA soil survey
meq 100g^{-1} Soil pH[2]   Nitrate N[3],

1 2.9 25 5.6 - 6.0 213 - 329 16 - 19 Zook Silty Clay Loam 2 2.6 17 6.4 - 7.0 409 - 503 12 - 16 Hasting Silt Loam 3 2.9 22 6.3 - 6.6 522 - 606 7 - 10 Fillmore Silt Loam 4 2.9 23 6.4 - 6.8 477 - 619 24 - 30 Crete Silt Loam 5 2.3 31 6.7 - 7.3 200 - 329 6 - 8 Wymore Silty Clay Loam 6 3.2 27 6.1 - 6.5 307 - 426 13 - 16 Sharpsburg Silty Clay Loam 7 3.6 23 5.9 - 6.4 332 - 455 14 - 16 Kennebec Silt Loam 8 1.2 9 4.8 - 5.3 121 - 184 13 - 16 Brocksburg Sandy Loam 9 1.2 8 5.7 - 6.2 135 - 210 8 - 11 Thurman Loamy Fine Sand 10 2.5 16 5.2 - 5.8 253 - 325 18 - 21 Muir Silt Loam 11 2.8 24 6.7 - 7.2 513 - 605 21 - 25 Wood River Silt Loam 12 2.3 16 6.7 - 7.2 361 - 494 15 - 19 Hall Silt Loam 13 2.5 19 5.0 - 5.3 420 - 582 12 - 17 Hall Silt Loam 14 1.3 7 4.4 - 4.9 273 - 379 15 - 19 Thurman-Anselmo Fine Sandy Loam 15 0.9 5 4.9 - 5.8 121 - 349 5 - 6 Valentine Fine Sand [+]ñ Average of five test reports
[2]ñ Range of reports from six commercial soil laboratories
[3]ñ Range of reports from three commercial soil laboratories

Soil pH was determined using pH ISEs to measure hydrogen ion activity in 1:1 SWR

solution (Watson and Brown, 1998). Determination of pre-plant nitrate-nitrogen involved

preparing 1:2.5 to 1:10 SWR solution with following CR flow injection analysis

(Gelderman and Beegle, 1998). Although potassium content can be sensed in both exchangeable and water-soluble forms, exchangeable (sometimes called extractable) content of potassium ion is commonly reported by commercial labs (Warncke and Brown, 1998). Therefore, 1:10 soil - extractor (neutral 1M NH4OAc) solutions were prepared and filtrates of such mixtures were then analyzed by either AAS or by inductively coupled plasma atomic emission spectrometer.

3.2 Experimental Methods

During all experiments presented in this dissertation, the output from each ISE was recorded for 60 s (300 readings at 5 samples per second) after its contact with a soil sample or calibration solution. The average of the last five seconds was assumed to be the best estimate of ISE steady-state output that was used to evaluate each ISEís precision and accuracy. The evaluation criteria used to quantify the performance of the ISEs were calibration, measurement precision and accuracy.

Measurement precision was quantified by the precision error that represents repeatability of ISE output while measuring the same soil. Variance of ISE output was determined for each soil through three replicated measurements (three sets of soil samples). According to the Levene test, these variances were significantly different between ISEs, but relatively constant between soils. Therefore, precision error (quantification of precision) was calculated as the square root of the mean of these variances for each ISE. Feasibility to distinguish between soils with different levels of activity of selected ions was determined using the F-statistic calculated as the ratio of between soils to within soil variance estimates (single-factor analysis of variance approach).

Measurement accuracy was evaluated through a simple linear regression between corresponding values of pX determined using a tested methodology and a corresponding reference. Coefficient of determination (R^2), F-statistic, and accuracy error were used as primary quantitative indicators. In this case, the accuracy error was calculated as the standard error of the predicted measurement for each reference pX using the set of ISE specific linear regression equations.

Reliability of ISEs indicate their performance during useful life. The consistency of ISE calibration parameters serves as the main indicator of satisfactory performance. Although, none of the ISEs failed during a particular experiment and their calibration parameters did not change significantly, except for the cases discussed, the life expectancy of PVC membrane ISEs remain a concern while performing soil measurements.

3.2.1 Ionic Strength Adjuster Experiment

The effect of the new and conventional ISA dissolved in calibration standards was studied using a two factorial (fixed factors) experimental design. It included four types of the ISAs (table 3.4) and four levels of concentration: 10, 30, 100, and 300 mg kg^{-1} (K^+), and 5.9, 47.6, 158.6, and 475.6 mg kg^{-1} (NO^{3-}). To prepare calibration standards, 2 ml of selected ISA was added to 100 ml of KNO_3 calibration standard with appropriate concentration. While the calibration order in each set of standards remained from low to high concentration, types of ISA used in these standards were randomized. During this test, K probe 4 and N probe 4 were used with pH probe 4 as the reference. The entire experiment was replicated twice.

Table 3. 4. Ionic strength adjusters tested.

Type of ISA	Used salt	Mass of salt added g L^{-1}
No ISA	N/A	N/A
Integrated ISA	3 M Na_2SO_4	426.12
Std. K ISA	5 M NaCl	292.21
Std. NO_3 ISA	1 M $Al_2(SO_4)_3 \cdot 18H_2O$	666.38

3.2.2 Multi-Probe DSM Test – Field Simulation Experiment

During the DSM test, soil samples were prepared by adding DDW according to soil texture class as shown in table 3.5. Prior to the DSM test, six replications (A, B, C, D, E, and F) of 15 soil samples were prepared. Each of the samples consisted of 60 g of soil and DDW added according to targeted gravimetric water content (θg) calculated based on the following equation and stored overnight:

$$\theta_g = \left(\frac{\theta_{v_{field}}}{2.65} \right) \left(\frac{1}{\theta_{v_{saturated}}} \right) \tag{10}$$

where $\theta_{v_{field}}$ ñ field capacity volumetric water content (ASCE, 1990) $\theta_{v_{saturated}}$ ñ volumetric water content of saturated soil (Schaap, 1999) Eight ISEs were combined in two groups of four (Group I and Group II), according to table 3.1 plus a sodium probe was added to Group II. Group I consisted of two potassium and the nitrate electrodes while Group II contained three pH and a sodium electrodes. ISEs in Group I were used to measure soil samples from replications A, B, and C. Similarly, probes in Group II were placed in contact with soil samples from replications D, E, and F.

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Table 3. 5. Particle size (texture) analysis and gravimetric water content used during the laboratory experiment for DSM.

Sample ID	% Particles[1]			Texture Class	Gravimetric water content, g/g	
	Sand	Silt	Clay		Targeted	Measured after the DSM test[2]
1	14	54	31	Silty Clay Loam	0.25	0.29 (0.008)
2	19	63	18	Silt Loam	0.20	0.23 (0.009)
3	16	58	25	Silt Loam	0.20	0.24 (0.003)
4	15	56	28	Silty Clay Loam	0.25	0.29 (0.005)
5	15	44	41	Silty Clay	0.26	0.32 (0.010)
6	13	51	36	Silty Clay Loam	0.25	0.30 (0.008)
7	15	61	24	Silt Loam	0.20	0.23 (0.007)
8	78	12	9	Loamy Sand	0.09	0.11 (0.007)
9	76	14	9	Sandy Loam	0.14	0.16 (0.011)
10	54	28	18	Sandy Loam	0.14	0.17 (0.005)
11	25	48	26	Loam	0.16	0.20 (0.006)
12	29	55	15	Loam	0.16	0.19 (0.009)
13	28	50	22	Silt Loam	0.20	0.23 (0.004)
14	72	21	8	Sandy Loam	0.14	0.16 (0.006)
15	87	7	6	Loamy Sand	0.09	0.11 (0.001)

[1] - Average of results reported from six commercial soil laboratories   [2] - Average (standard deviation) of three measurements (Soil Sets C, E, and F)

During DSM field simulation tests, prepared soil samples were taken in plastic cups and placed on a holder mounted on the top of soil sampling shoe. The electrode holder with four ISEs (figure 3.1a) was engaged in direct contact with each soil sample placed on the top of the sampling shoe (figure 3.1b). The ISEs were pressed against the soil using a spring-loaded ISE holder that ensured consistent soil-ISE contact pressure. ISEs were rinsed using DDW after each measurement. All measurements were conducted during the same day. Soil preparation was done approximately 14 hours before the first measurement. In this test, each ISE was calibrated four times (after each replication of 15 soil samples and before the experiment).

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a) b)

**Spring Loaded
ISE Holder**

**Water
Nozzles**

Soil Sampling **Soil
Shoe
Sample** **Plastic Cup
Holder**
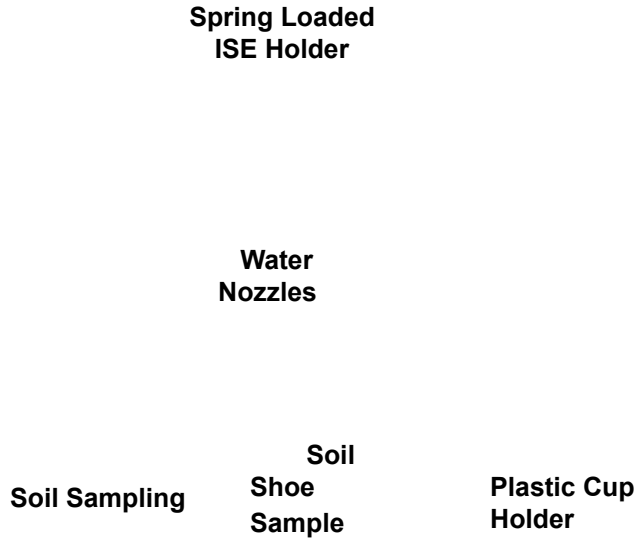
Figure 3. 1. Veris® MSP with implemented direct soil measurement (DSM) technique, when (a) mapping soil pH and (b) during field simulation test.

While performing DSM, detected activity of potassium ions relate to the soluble potassium content rather than exchangeable. Also, activity of nitrate ions is very dynamic and may significantly change over time. Therefore, additional commercial soil laboratory tests were requested the day following the described laboratory experiment. Soil Set A was sent to prepare 1:10 SWR solutions that were used to measure nitrate-nitrogen content (CR method) and soluble potassium (AAS).

3.2.3 Multi-Probe ASM Factorial Experiment - Methodology Development

To optimize the new ASM technique, several factors that could affect the measurements were studied. Firstly, a one half replication of a 4×2^5 factorial experiment was conducted in the laboratory to analyze the effects of 1) SWR, 2) QWE, 3) QWR, 4)

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addition of ISA, 5) agitation, and their interactions on the random errors associated with

measurements of four soils (Soil IDs 3, 8, 11, and 14). Each of the five factors had two

levels: 1) weight-based SWR of 1:1 versus 1:5, 2) DDW versus tap water for ion

extraction, 3) DDW versus tap water for rinsing, 4) presence versus absence of ISA, and

5) agitated (stirring) versus non-agitated measurements.

pH probe 4, K probe 3, and N probe 3 (table 3.1) were used during this experiment.

Sixty-four soil samples were prepared based on the treatment combinations dictated by

the one half replication of 4 x 2^5 factorial experiment design (table 3.6).

Table 3. 6. Treatment combinations for the soils.

Test ID	Soil 3	Soil 8	Soil 11	Soil 14
1	a*	1	1	a
2	b	ab	ab	b
3	c	ac	ac	c
4	abc	bc	bc	abc
5	d	ad	ad	d
6	abd	bd	bd	abd
7	acd	cd	cd	acd
8	bcd	abcd	abcd	bcd
9	e	ae	ae	e
10	abe	be	be	abe
11	ace	ce	ce	ace
12	bce	abce	abce	bce
13	ade	de	de	ade
14	bde	abde	abde	bde
15	cde	acde	acde	Cde
16	abcde	bcde	bcde	Abcde

* - ëaí means 1:5 versus 1:1 SWR, ëbí means tap versus DDW QWR, ëcí means tap
versus DDW QWE, ëdí means present versus absent ISA, and ëeí means stirred versus
non-stirred solution.

The experiment was performed during one day, which restricted testing every

possible combination of influential factors with a complete statistical design. The effects

of main factors were aliased with the four-factor interactions. Based on prior experience,

it was assumed that these four-factor interactions were insignificant. A PROC GLM

procedure (SAS Institute Inc., Cary, North Carolina) was utilized to analyze the sources of measurement variation caused by all the factors. The statistical analysis was performed at α = 0.05 rejection level. Electrode calibration (ICS and pHCS) was performed at the beginning of the experiment at after 16 consecutive measurements.

3.2.4 Soil - Water Ratio Experiment

It was found that SWR was the major influencing factor (excluding soils) based on the results of the 4 x 2^5 factorial experiment to be discussed later. Therefore another experiment was conducted using four levels of SWR (2:1, 1:1, 1:2.6, and 1:5) on four different soils (Soil IDs 3, 8, 11 & 14). This experiment was conducted based on the randomized complete block design and was replicated three times resulting in 48 total measurements per ISE. As during the previous experiment, pH probe 4, K probe 3, and N probe 3 (table 3.1) were used. The electrode calibration (ICS and pHCS) was performed once before the start of the experiment and after 16 consecutive measurements. The mean squared error (MSE) weighted across all three electrodes was used to select the SWR producing the most repeatable measurements. The relative changes of ISE outputs caused by inconsistent SWR were evaluated and discussed.

3.2.5 Soil as a Buffer Experiment

An experiment was conducted to analyze the buffering characteristics of the soils, and therefore verify the need for ISA during soil solution measurements. The experiment followed a factorial design with two levels of the SWR and four levels of concentration of solutions added to each of four soils (soil IDs 3, 8, 11, and 14). Four different KNO_3

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solutions had concentrations of 0, 30, 100, and 300 mg kg^{-1} of K^+, which corresponded to

0, 47.6, 158.6, and 475.57 mg kg^{-1} of NO_3^-. The experiment was replicated two times and therefore, the total of 64 measurements were accomplished by each electrode (pH probe 4, K probe 3, and N probe 3). Electrode calibrations (ICS and pHCS) were performed once before the start of the experiment followed by every 36 measurements.

3.3 Integrated Agitation Chamber Module (IACM) System Design When applying DSM, soil is brought into a direct contact with ISEs. This caused severe electrode abuse and other potential drawbacks to be discussed later. Therefore, the suggested ASM technique was pursued. To facilitate ASM, IACM has become a part of the system that engages with soil collected by the MSP sampling mechanism (figure 3.2).

**Sampling
Hydraulic Mechanism (SSHM)**

Soil

**MSP Soil
Sampling Shoe**

Figure 3. 2. Veris® mobile sensor platform with integrated agitation chamber module (IACM).

The IACM encompasses an electrode holder with agitated chamber system, water supply system, and DAQ and control system.

3.3.1 Electrode Holder with Agitated Chamber System

The electrode holder with agitated chamber system (figure 3.3a) includes a motor stirrer unit (figure 3.3b), Teflon^{Æ} electrode holder, and an agitation chamber (figure 3.3c).

b) c)

Stirrer

Bearing

Shaft

Motor

Electrode Holder

Agitation Chamber

a)   **ISEs**
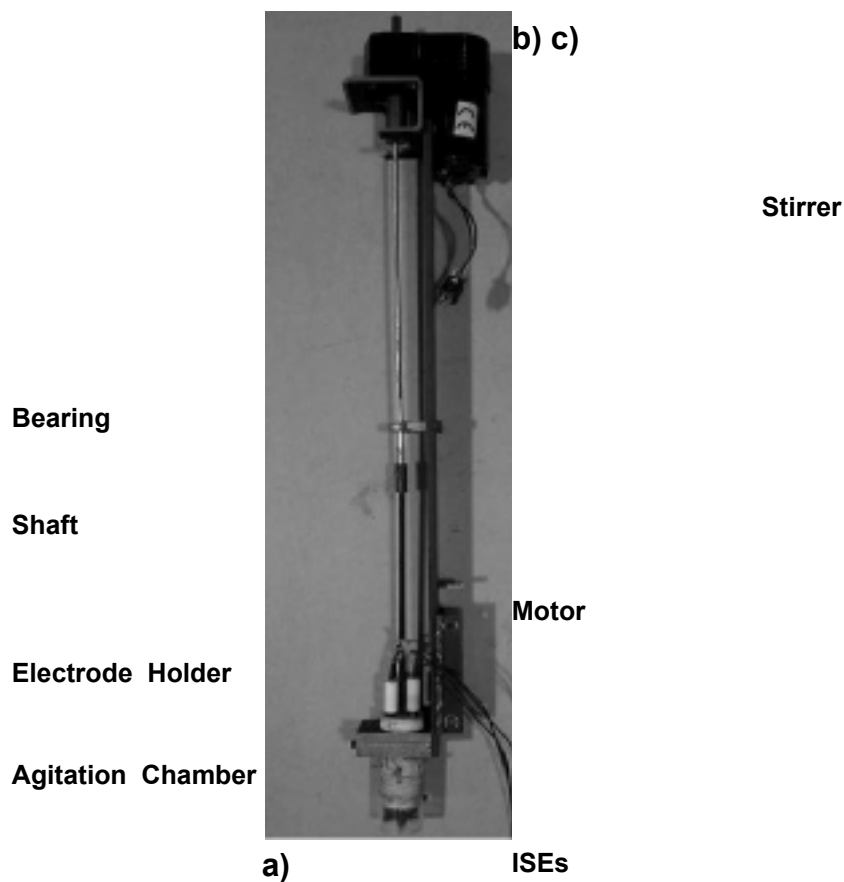
Figure 3. 3. Assembly of a) integrated agitation chamber module (IACM) with, b) DC motor, and c) electrode holder with agitation chamber.

The motor-stirrer unit includes a continuous duty electric motor (12 VDC, 20 A, 150 rpm, model 5-1524, Warner Electric Motor, South Beloit, Illinois), die cast pillow block bearing, and 6.35 mm shaft welded with a 45° twisted plastic blade. The choice of

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the high torque motor among other high speed motors used during the initial stages of

system development was due to the requirement of sufficient torque to agitate mixtures of soil with high clay contents. A Delrin^{Æ} plastic shaft and twisted blade were used to avoid electrical interferences with the ISEs during measurement, which was observed when stainless steel components were used. The electrode holder is a solid cylinder with four lateral holes equidistant from the center of the cylinder capable of holding conventional laboratory ISEs using plastic setscrews. It also has two other lateral holes, one at the center of the cylinder for the motor shaft and the other offset from the center for the flow of extraction solution from the water supply system.

The agitation chamber is a transparent cylindrical plastic tube that fits at the lower end of the electrode holder. The agitation chamber is spline shaped to seal the curved insides of sampling shoe watertight while operating in the field. For laboratory testing, a flat clear plastic tube was used as the agitation chamber was placed into plastic cups. Proper ISE - soil contact was visually monitored.

3.3.2 Water Supply System

The water supply system (figure 3.4) includes an electrical pump, a reciprocating piston type water pump, water tanks, an intermediate chamber, nozzles, a manual flow control valve, and a fork shaped actuator.

Water tank (rinsing water)

Electrode holder with agitation chamber

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Water pump

Intermediate reservoir

Secondary tank (extraction solution)

piston pump

Reciprocating

Nozzle 1 Nozzle 2

Water supply system.

Outlet Port

Cylinder

Inlet Port

Piston

Variable
Displacement
Setting

Figure 3. 5. Reciprocating piston water pump.

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The water supply system could either use the water tank of the MSP or supply

purified water or another extraction solution from a secondary water tank. The

reciprocating piston type water pump (figure 3.5) has a variable piston stroke setting to meter the required amount of water to the agitation chamber through the intermediate chamber and manual flow control valve (figure 3.4). The piston of the water pump is moved by fork shaped actuator attached to the SSHM of MSP through a spring loaded threaded rod with variable displacement settings. The electrical pump of the MSP supplies water to the nozzles for rinsing of ISEs.

3.3.3 Data Acquisition (DAQ) and Control

The data acquisition (DAQ) system (figure 3.6) was developed to accommodate a maximum of four ISEs (table 3.1) for simultaneous soil measurements.

Amplification   **Solutions**   **ISEs**
Circuit   **Connector Block**
                                                      Graphical
                                                      interface

Calibration

PCMCIA Card

Laptop with

Figure 3. 6. Data acquisition system.

Several pH, potassium and nitrate ISE were used at different phases of experiment. These electrodes were of-the-shelf items and were treated according to manufacturerís recommendations. The DAQ included a laptop computer with DAQ 1200 PCMCIA input/output (I/O) card (National Instruments, Corp., Austin, Texas), four signal amplification circuits (AMPER PH-1 pH/ORP unity gain amplifiers, Development, Corp., Bridgeport, Connecticut), CB 50LP I/O connector Instruments, Corp., Austin, Texas), external power supply, and tional Instruments, Corp., Austin, Texas) software interface (figure 3.7).
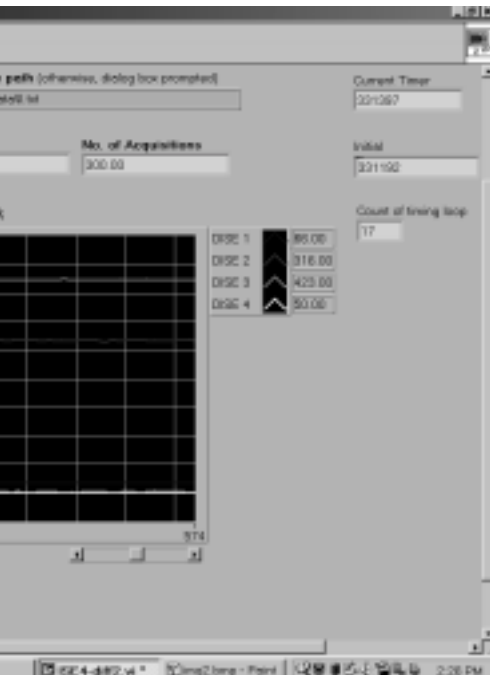
Digital display

Data logging

Figure 3. 7. LabVIEW graphical user interface.

For the multi-probe DSM experiment, each channel was individually grounded with a single ended input (figure 3.8a). So, the four channels utilized all combination ISEs. In the case of ASM experiments, a differential input circuit (figure 3.8b) was utilized with

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channel 1 as the reference for channels 2 and 3, while channel 4 was individually grounded.

Com

ISE 4
Com

-

+

8
Channel 0

-

+ -

ISE 3
Com

ISE 1
Com

Channel 1

-

Channel 2

1

+

2 3

+ -

Channel 7

+

+

Measured
Voltage

+

ISE 2

+

9 Analog Input Ground

a)

Com ñ Combination electrode HC ñ Half-cell
electrode

11 Analog Output Ground

ISE 1 Com

3 5

Channel 6

-

+

ISE 2* HC

7
Channel 0

Channel 2

+

Channel 4

+

1

+

ISE 3*
HC

Com

2
+

6
-

8
+

-

4
ISE 4

Channel 1

Channel 3   Channel 7

Channel 5

                                                              -

                                          Measured Voltage

                        11 Analog Output Ground

100 KΩ 100 KΩ b)
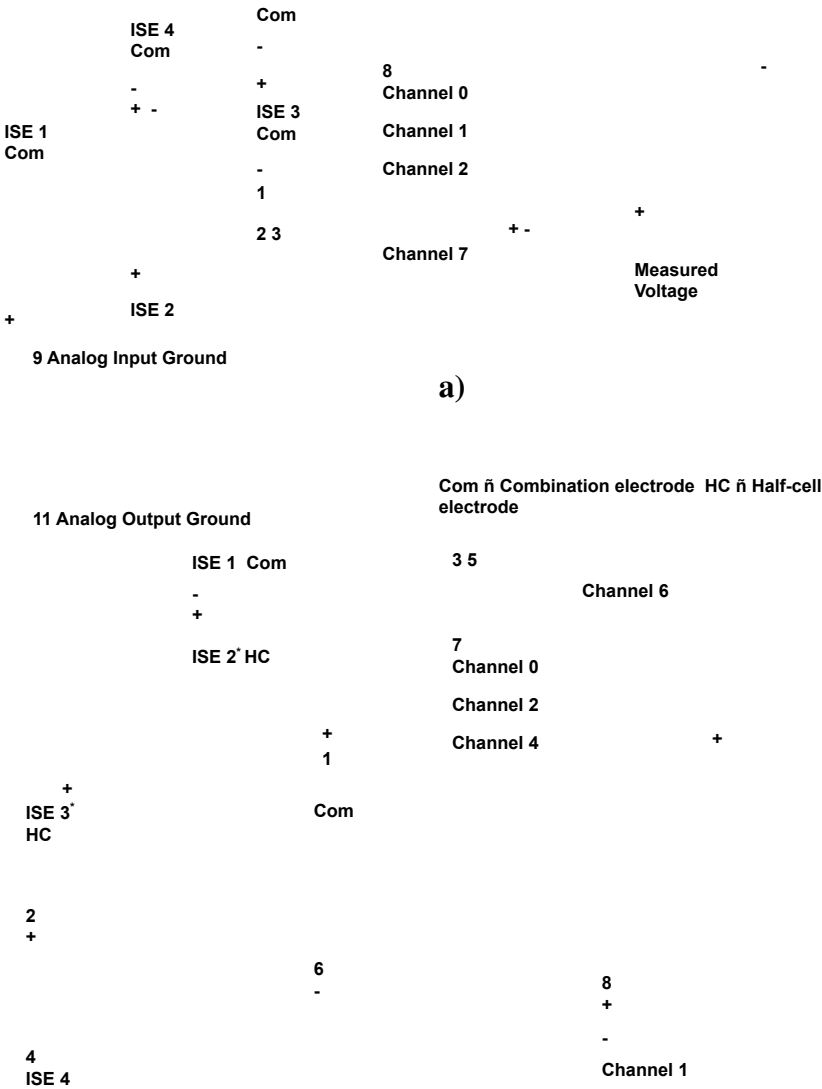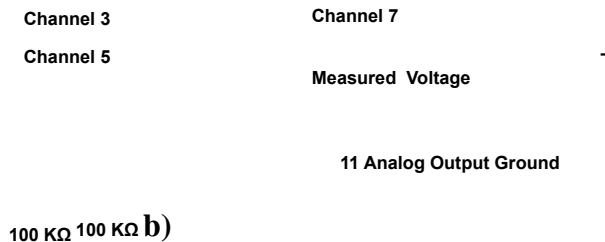
**Figure 3. 8. Data Acquisition circuit configured as: a) single-ended input (DSM Method) and
b) differential input (ASM Method).**

So, channels 1 and 4 were used for combination ISEs (both pH) and channels 2 and 3
were used for half-cell ISEs (potassium and nitrate). The DAQ system (figure 3.7) was
set to sample each sensor output at approximately 1000 Hz and averaging the response
over the specified time interval (200 ms) resulting in data logging at 5 Hz.

                              Starter Relay Limit Switch

                        NO
                         C
                        NC
           Cut-off Switch   NO   Stirring

                                                                        Motor +

   C
                                          +
   12 V
   Battery
   -
                                          -

   NC
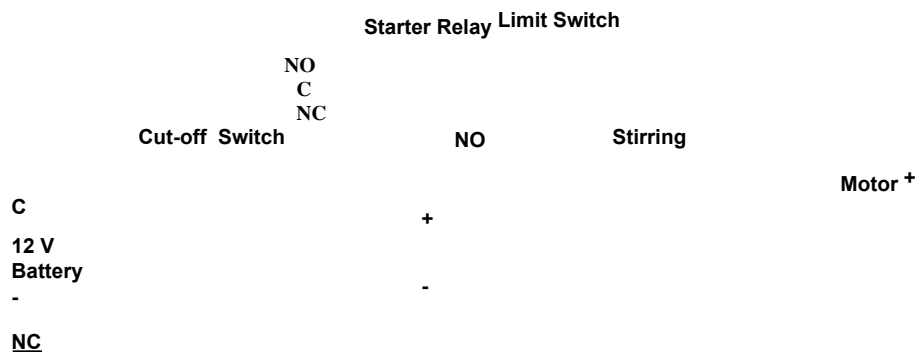
Figure 3. 9. Electrical control system circuit.

The control system comprises of the pick up/tractor battery, starter relay, normally
open limit switch, and safety cut off switch (figure 3.9). The power for the motor-stirrer
system is routed through the starter relay to avoid high amperage current passing through

the limit switch. The normally open limit switch is mechanically closed by SSHM, controlling the motor on/off timing to prevent overheating. As was mentioned above, the supply of purified water or extraction solution to the agitation chamber is achieved through a simple automated mechanical control.

3.3.4 ASM Operation

While mapping a field using the modified MSP implementing the ASM methodology, operation cycle summarized in table 3.7 was followed. First, the SSHM lowered the

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sampling shoe to collect a soil core. During this motion, the fork shaped actuator charged the piston type water pump with water or extracting solution from the tank. Simultaneously, electrode surfaces were rinsed with water and the motor-stirrer was turned off. After a sample was obtained, the SSHM raises the sampling shoe with soil toward the agitation chamber. Simultaneously, the fork shaped actuator moved the piston pump supplying water to a reservoir located above the agitation chamber and the limit switch turns the motor-stirrer on. As the agitation chamber secured and sealed the soil against the sampling shoe and the agitation process began with the retained extraction solution filling the chamber, four ISEs secured in the electrode holder came in contact with the soil slurry and ASM was performed. After the measurement, SSHM lowered the sampling shoe to collect the next soil core and prepare the system for a new measurement.

Table 3. 7. Operational steps of MSP with IACM during ASM

Step	Sampling Shoe	Water Nozzle	Motor	Water Pump	Operation
New Sample	Down	On	Off	Charge	Sample Extraction
	Moves up	Off	On	Discharge Stroke	Measurement
	Up	Off	On	Empty	Sample discard
	Moves Down				

3.4 ASM Test

3.4.1 ASM - Laboratory Experiment

After establishing the final ASM protocol (1:1 SWR, DDW as the extraction solution, tap water for rinsing, no addition of ISA and presence of solution agitation) a laboratory ASM test was performed following similar experimental design as DSM. Fifteen

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different soils were tested with three ISEs, including pH probe 4, K probe 4, and N probe 5 (table 3.1). The 1:1 SWR (60 g soil and 60 ml DDW) solutions were prepared and placed on a magnetic stirrer 30 s before the ISEs were inserted. Stirring was continued through the measurement during the following 60 s. Each set of 15 soils was randomized. Electrode calibration (pHCS and ICS) was performed once before the experiment and after each set of soils. This experiment represented ìbest case scenarioî related to the established ASM

3.4.2 ASM - Field Simulation Experiment

The ASM field simulation tests were followed the same experimental procedure as previous DSM test. In this case, pH probe 4, K probe 4, N probe 5, and pH probe 5 were used (table 3.1). A 60 g soil sample was placed into the plastic cups and 60 ml DDW were added using the water supply system developed. The cap with soil sample (figure 3.10a) was pressed against a spring loaded IACM (figure 3.10b). The operation of MSP with IACM was performed similarly to the DSM test. The electrode configuration and data analysis, on the other hand, were the same as during the laboratory ASM. The test was repeated during two different days. In addition, three separate sub samples of each

fifteen soils were sent to a commercial soil test laboratory (Soil and Plant Analytical Lab, University of Nebraska-Lincoln, Lincoln, Nebraska) for measurement of soil pH, residual nitrate (CR method) and soluble potassium (AAS method) contents in 1:1 soil solutions.
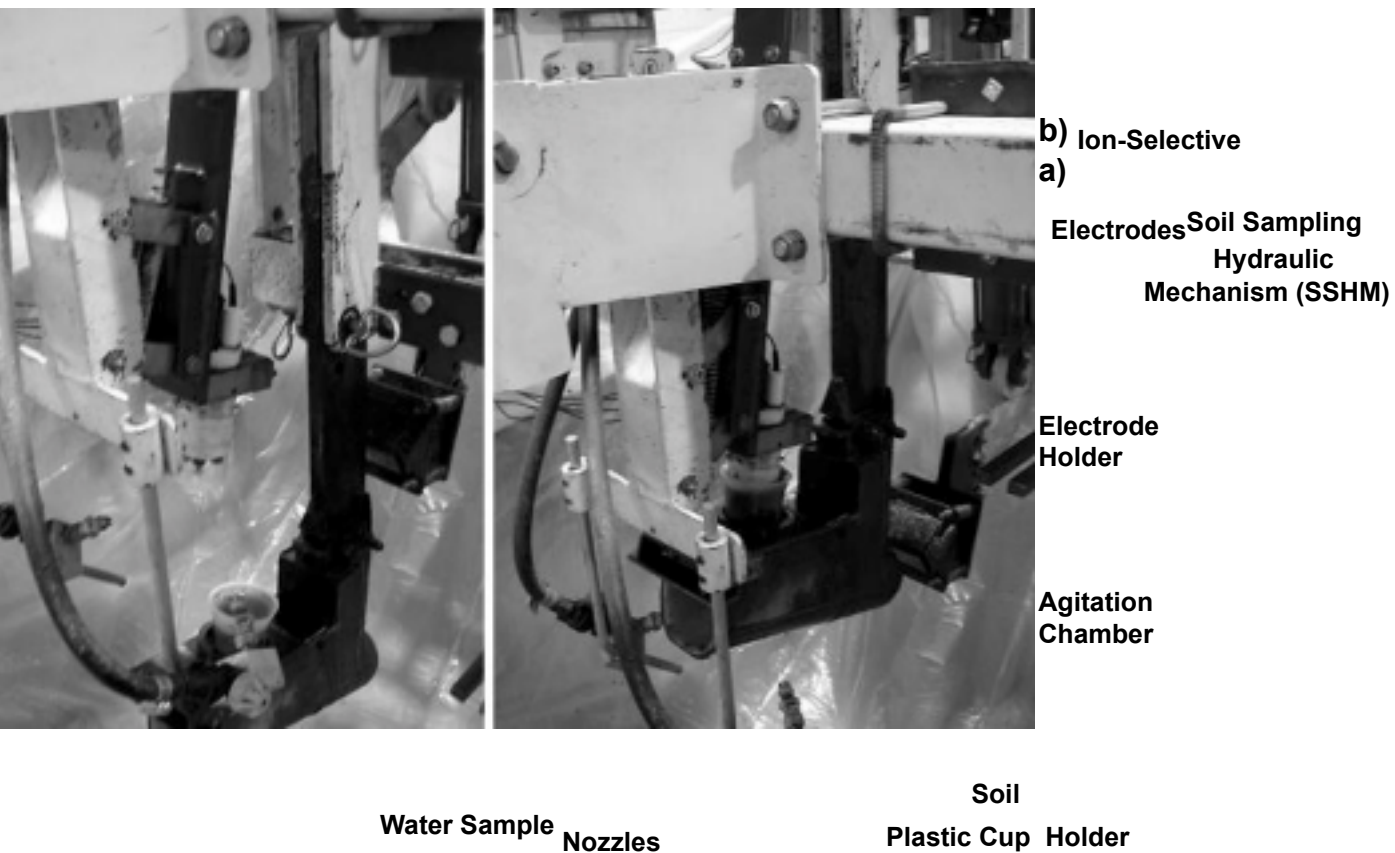
Figure 3. 10. Integrated agitation chamber module a) before and b) during ASM measurement.

3.5 Agronomic Evaluation

On-the-go sensing of soil chemical properties using DSM and ASM methods result in water pH, soluble potassium and residual nitrate measurements. Water pH and soluble potassium are not adequate for lime and potassium fertilizer application rate prescription. As described before, soil pH buffering characteristics defined by the buffer pH is required to prescribe lime application rates. Similarly, exchangeable component of soil potassium is necessary to use current potassium fertilizer prescription recommendations.

Based on previously cited literature, some soil properties, such as CEC, are related to soil buffering. Therefore, CEC could be used to predict buffer pH based on measured water pH and exchangeable based on soluble potassium. The percent clay and organic matter contents, either directly measured or indirectly estimated, could be used to define

CEC. Soil test reports from various commercial laboratories were analyzed for feasibility of predicting CEC (six commercial laboratories) based on clay and organic matter contents reported from five commercial laboratories.

To evaluate these hypotheses, ISE measurements of water pH and soluble potassium based on commercial soil laboratory report (table 3.8), and ASM laboratory and DSM/ASM field simulation tests were analyzed along with soil laboratory CEC data, using general linear model approach to predict buffer pH and exchangeable potassium, respectively.

Table 3. 8. Results of soils analyses performed by commercial laboratories.

	Soil	Exchangeable Potassium[2]	Buffer	CEC[3] meq 100g^{-1}	% Clay[4]	% OM[4]
ID	pH[1]	mg kg^{-1}	pX			
1	6.5	278	2.15	25	31	2.9
2	7.0	461	1.93	17	18	2.6
3	6.9	569	1.84	22	25	2.9
4	7.0	552	1.85	23	28	2.9
5	7.0	276	2.15	31	41	2.3
6	6.6	374	2.02	27	36	3.2
7	6.6	397	1.99	23	24	3.6
8	6.6	147	2.42	9	9	1.2
9	6.9	179	2.34	8	9	1.2
10	6.6	299	2.12	16	18	2.5
11	7.0	571	1.84	24	26	2.8
12	7.0	426	1.96	16	15	2.3

<div align="center">
13 6.4 502 1.89 19 22 2.5
14 6.5 328 2.08 7 8 1.3
15 6.9 185 2.33 5 6 0.9
</div>

[1] ñ Average of reports from two commercial soil laboratories
[2] ñ Average of reports from six commercial soil laboratories
[3] ñ Average of reports from five commercial soil laboratories
[4] ñ Same as table 3.3

After applying multivariate regression models, previously reported by commercial

laboratories buffer pH and exchangeable potassium values were compared with

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corresponding predictions. The regression parameters were used to evaluate the

performance of different prediction methods.

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4. RESULTS AND DISCUSSION

4.1 ISE Calibration

4.1.1 Stability of ISE Calibration

Since calibration of ISEs was a part of every experiment, it is essential to discuss

variability in calibration parameters. Practically every ISE (especially nitrate) had some

change in calibration parameters between the initial calibration and after the first set of

soils. It was hypothesized that contamination of sensitive membranes and reference

junctions with soil particles was the main cause for such change. On the other hand,

further variability of ISE outputs in calibration solutions was relatively small and

random. Therefore, average and standard deviation for slopes and intercepts

corresponding to each ISE and every experiment are listed in table 4.1.

The slopes of nitrate (and sometimes potassium) ISEs were less than 90% of the

theoretical (Nernst) slope. According to the manufacturers, this may indicate some degree

of ISE malfunctioning. However, it also was noted that, once reduced, slopes did not

significantly change throughout the experiment. Thus, among all ISEs, the maximum standard deviation between three pairs of calibration parameters was for half-cell N Probe 5 during IACM 2 test and corresponded to 7.75 mV pNO_3^{-1} (16.8%) for slope and 15.75 mV (0.27 pNO_3) for intercept. For combination ISEís the least stable calibration was for pH probe 2 during the multi-probe DSM test and corresponded to only 0.67 mV pH^{-1} (1.1%) for slope and 4.26 mV (0.07 pH) for intercept. For practical applications, extreme differences in calibration parameters (drift) can cause the reduction in ISE precision. Generally, compensation for changes in calibration parameters is appropriate when it can reduce the error associated with precision (repeatability).

Table 4. 1. ISE calibration parameters – combination ISEs

ISE ID ISE	intercept E_0, mV	ISE slope S, mV pX^{-1}	Nernst slope[2] % of Reference ISE	Cabn. Soln.

Multi-Probe DSM Test ñ Field Simulation Experiment

pH Probe 1 404 (0.58)[1] -59.2 (0.16) 102% NA pHCS pH Probe 2 385 (4.26) -56.5 (0.67) 97% NA pHCS pH Probe 3 408 (0.68) -59.3 (0.03) 102% NA pHCS K Probe 1 395 (0.91) -54.9 (0.19) 94% NA KCS K Probe 2 183 (3.88) -57.3 (0.91) 98% NA KCS N Probe 1 109 (2.72) 43.5 (0.24) 75% NA NCS N Probe 2 -64 (2.14) 41.1 (0.15) 71% NA NCS

Multi-Probe ASM Factorial Test ñ Methodology Development Experiment pH Probe 4 411 (2.07) -58.5 (0.20) 102% NA pHCS K Probe 3 487 (5.70) -47.5 (2.64) 83% pH Probe 4 ICS N Probe 3 248 (8.66) 41.7 (4.24) 73% pH Probe 4 ICS SWR Experiment

pH Probe 4 402 (-1.48) -56.7 (0.26) 99% NA pHCS K Probe 3 475 (2.23) -45.1 (0.81) 79% pH Probe 4 ICS N Probe 3 224 (5.56) 41.5 (3.47) 73% pH Probe 4 ICS Soil as a Buffer Experiment

pH Probe 4 pH Probe 4 -57.7 (0.31) 101% NA pHCS K Probe 3 478 (3.44) -48.2 (1.85) 84% pH Probe 4 ICS N Probe 3 228 (10.61) 44.1 (4.99) 77% pH Probe 4 ICS Ionic Strength Adjuster Experiment

K Probe 4 491 (10.93) -54.2 (1.04) 95% pH Probe 4 ICS N Probe 4 218 (7.29) 53.2 (2.75) 93% pH Probe 4 ICS Lab-ASM Test ñ Laboratory Experiment

pH Probe 4 406 (2.65) -56.0 (0.19) 98% NA pHCS K Probe 4 483 (1.04) -56.9 (0.24) 100% pH Probe 4 ICS N Probe 5 301 (14.49) 46.4 (7.75) 81% pH Probe 4 ICS IACM 1 Test - Field Simulation Experiment

pH Probe 4 415 (2.24) -58.6 (0.17) 103% NA pHCS K Probe 4 468 (3.16) -53.0 (0.91) 93% pH Probe 4 ICS N Probe 5 304 (9.72) 41.9 (4.55) 73% pH Probe 4 ICS pH Probe 5 383 (2.28) -55.1 (0.09) 96% NA pHCS IACM 2 Test - Field Simulation Experiment

pH Probe 4 405 (1.47) -57.0 (0.15) 100% NA pHCS K Probe 4 473 (2.95) -56.0 (0.93) 98% pH Probe 4 ICS N Probe 5 303 (15.75) 42.2 (6.98) 74% pH Probe 4 ICS

pH Probe 5 370 (2.72) -53.2 (0.32) 93% NA pHCS [1] ñ Averages calibration parameters with standard deviations indicated in parenthesis [2] ñ Nernst (theoretical) slope of for each ISE at 20 °C was 58.2 mV/pX

Based on this general rule, N probe 5 was the only ISE with significant changes of calibration parameters. To determine pX values (pH, pK, and pNO_3) for the rest of the ISEs, average calibration parameters were used. In every case, results of calibration conducted prior to the first soil measurement were excluded.

4.1.2 Ionic Strength Adjuster (ISA) Experiment

Both potassium and nitrate ISEs were calibrated in the same solutions with addition of different ISAs, including blank (nothing), Na_2SO_4 (recommended for ICS), NaCl (recommended for KCS), and $Al_2(SO_4)_3$ (recommended for NCS). Both calibration parameters were affected by the type of ISA implemented (table 4.2).

Table 4. 2. Summary of regression parameters.

KNO Potassium ISE Nitrate ISE $_3$ Cabn.

Solutions with RMSE,	pX Slope, mV	pX^{-1} Intercept,	mV RMSE, pX	Slope, mV	pX^{-1} Intercept,	mV

No ISA 0.028 -56.1 (0.02) 502 (0.05) 0.046 52.9 (0.03) 229 (0.08) Integrated ISA 0.094[2] -57.3 (0.06)[1] 491 (0.17) 0.008[2] 56.1 (0.01) 225 (0.02) Std. K ISA 0.012[2] -57.2 (0.01) 494 (0.02) 0.088 31.3 (0.06) 279 (0.16) Std. NO$_3$ ISA 0.040 -56.6 (0.03) 491 (0.07) 0.029[2] 61.0 (0.02) 210 (0.05) [+] ñ standard errors for calibration parameters are given in parenthesis [2] ñ proper ISA was used

However, the RMSE values showed no significant improvement in the use of either type of ISA versus the blank. Also there was no significant difference in RMSE pooled for each calibration standard (table 4.3), which supports the assumption of constant variance and need to apply pX scale when analyzing ISE measurements.

Table 4. 3. Summary of precision parameters for each level of concentration

K+ added, mg kg^{-1}	NO$_3^-$ added, mg kg^{-1}	ISE (Potassium)	pX	RMSE ISE	RMSE pX
10		15.9	3.59	0.070	0.047
30		47.6	3.11	0.065	0.030
100		158.6	2.59	0.060	0.026
300		475.7	2.11	0.061	0.024

[1] ñ RMSE (repeatability) pooled across different ISA

4.2 Direct Soil Measurement (DSM) Test

While evaluating ISE precision through replicated measurements their accuracy was assessed with respect to reference measurements summarized in table 4.4. **Table 4. 4. Reference measurements of targeted chemical soil properties**

Sample ID	Soil pH[1]	Potassium[2] mg kg^{-1}	pK	Nitrate N[2] mg kg^{-1}	pNO$_3$
1	5.82	55	2.85	15	2.98
2	6.74	94	2.62	14	2.99
3	6.48	121	2.51	11	3.12
4	6.63	103	2.58	7	3.28
5	7.03	59	2.82	9	3.19
6	6.26	59	2.82	12	3.08
7	6.18	71	2.74	17	2.93
8	5.10	43	2.96	11	3.09
9	6.00	58	2.83	10	3.16
10	5.45	65	2.78	18	2.90
11	7.01	127	2.49	25	2.75
12	6.98	100	2.59	15	2.97
13	5.22	136	2.46	16	2.94
14	4.74	122	2.50	13	3.03
15	5.45	46	2.93	6	3.38

[1] ñ Average values based on data referred to in table 3.4

[2] ñ Available potassium and nitrate-nitrogen determined from the 1:1 water-based extract in a commercial soil laboratory

As mentioned earlier, potassium and nitrate measurements were obtained for a

single set of 15 soils, and were expected to differ from commercial soil test reports summarized in table 3.3. These data were also used to estimate errors associated with the

precision of conventional laboratory analyses. figure 4.1 shows the relationship between these two reference measurements (table 3.3 and 4.4).
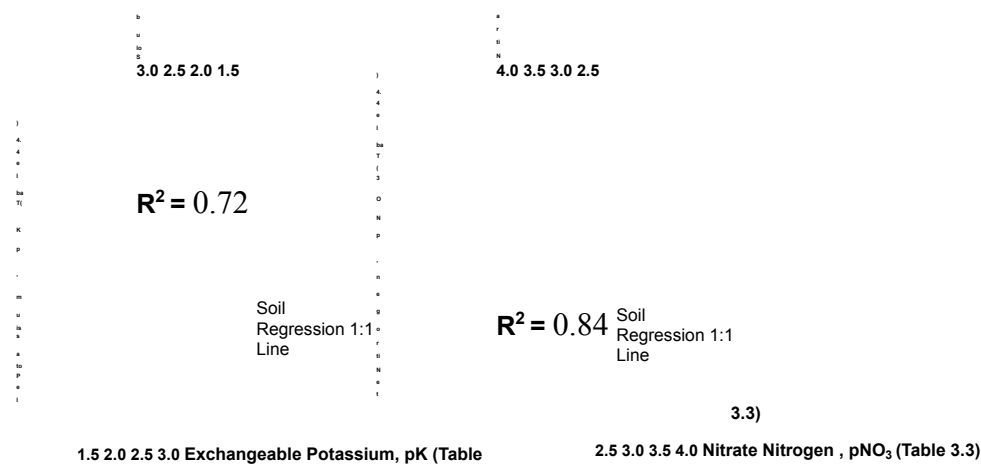
Figure 4. 1. Relationship between a) exchangeable AAS measurements and soluble potassium and b) CR nitrate and nitrate-nitrogen measurements obtained three years apart.

4.2.1 Measurement Precision

Analysis of measurement precision addressed using three replicated measurements for each ISE-soil combination is summarized in table 4.5. As mentioned earlier, the estimated variance of measurements performed on the same soil sample (MSE), differed significantly for different ISEs. A set of F-tests was used to distinguish ISEs with different levels of precision. Standard deviations of three ISE outputs obtained in soils and calibration solutions as well as the calculated precision error values (soils only) are shown in figure 4.2. For every ISE, there was no identifiable correlation between these standard deviations and pX, which supported the assumption of constant variance.

Table 4. 5. Summary of ion selective electrode precision assessments

ISE ID	Range[1]	Soil variability[2]	MSE[3]	F-stat[4]	Precision Error[5]
pH Probe 1	2.32	1.666	0.0154^{a}	108.02^{**}	0.12
pH Probe 2	2.35	1.431	0.0134^{a}	106.86^{**}	0.12
pH Probe 3	2.29	1.462	0.0116^{a}	126.48^{**}	0.11
K Probe 1	1.10	0.174	0.0165^{ab}	10.53^{**}	0.13
K Probe 2	1.26	0.129	0.0293^{bc}	4.40^{**}	0.17
N Probe 1	0.93	0.109	0.0369^{cd}	2.95^{*}	0.19
N Probe 2	1.24	0.165	0.0493^{cd}	3.35^{*}	0.22

[1] ñ Range of all 45 measurements
[2] ñ Variance component due to the variability of per soil averages of measurements [3] ñ Mean squared error (MSE), variance component due to three soil sets; MSE estimates with the same letters ([a, b, c, d]) do not differ from each other significantly ($\alpha = 0.05$) [4] ñ If the ability to distinguish between soils is significant, F-stat values are marked with [**] ($\alpha = 0.0001$), or [*] ($\alpha = 0.05$)
[5] ñ Precision error (ISE precision estimate in physical units)

It appears that all pH ISEs had good repeatability despite the differences in their design. The maximum observed standard deviation in soils was 0.23 pH (precision error = 0.11 - 0.12 pH) and in calibration solutions 0.08 pH. For comparison, precision error of reports from commercial soil laboratories was 0.21 pH (calculated for data used to produce table 3.3).

Potassium ISEs showed performance similar to pH ISEs with slightly greater standard deviations when measuring the same soil. Thus, the maximum observed standard deviation in soils was 0.28 pK (precision error = 0.13 and 0.17 pK) and in calibration solutions 0.07 pK. For comparison, precision error of reports on exchangeable potassium from commercial laboratories (table 3.3) was 0.07 pK.

Probe 1 - Calibration
Probe 1 - RMSE (Soil)
Probe 2 - Soil
Probe 2 - Calibration
Probe 2 - RMSE (Soil)
Probe 3 - Soil
Probe 3 - Calibration
Probe 3 - RMSE (Soil)

0.50 0.45 0.40 0.35 0.30 0.25 0.20 0.15 0.10 0.05

0.00 a)

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Probe 1 - Soil

3 5 7 9 11 Average pH (pH

0.50 0.45 0.40 0.35   Probe 2 - RMSE

0.30 0.25 0.20 0.15   (Soil)

0.10 0.05 0.00

Probe 1 - Soil
Probe 1 -
Calibration
Probe 1 - RMSE
(Soil)

Probe 2 - Soil
Probe 2 -
Calibration

Probe 2 -
Calibration
Probe 2 - RMSE
(Soil)

1.5 2.5 3.5 4.5

0.50 0.45 0.40 0.35

0.30 0.25 0.20 0.15

0.10 0.05 0.00

Probe 1 - Soil
Probe 1 -
Calibration
Probe 1 - RMSE
(Soil)
Probe 2 - Soil

1.5 2.5 3.5 4.5

b) c)

Average pK (potassium ISEs)

Average pNO₃ (nitrate ISEs)

Figure 4. 2. Precision (repeatability) assessment for a) pH, b) potassium, and c) nitrate ISEs during the multi-probe DSM test.

Nitrate ISEs, on the other hand, produced a greater number of results with high standard deviations for three measurements (up to 0.43 pNO_3 in soils and 0.12 pNO_3 in calibration solutions). Therefore, precision errors for the two ISEs were 0.19 and 0.22 pNO_3. For comparison, precision error of reports on nitrate-nitrogen from commercial laboratories (table 3.3) was 0.05 pNO_3.

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Although, the three types of ISEs produced different values of precision error declining in the order: pH < pK < pNO_3 (statistical difference was determined through comparison of corresponding MSEs), all precision errors had a similar magnitude. On the other hand, the range of ion activity (pX scale) measured by the ISEs varied significantly

from 2.35 pH to only 0.93 pNO_3 (table 4.5). This changed the ratio between soil variability and corresponding MSE (F-stat) for different types of ISEs. Every ISE could distinguish between different soils. However, separation of soils with different pH was relatively easier (higher F-stat values) than potassium, and nitrate. This indicates potential inapplicability of DSM to distinguish between different levels of pK, and pNO_3 when the range of these properties will be smaller than what was found in the experimental set of soils.

4.2.2 Measurement Accuracy

The accuracy of ISE quantified through simple linear regression between individual DSMs and the corresponding reference values listed in table 4.4 are summarized in table 4.6. For all ISEs, regression equations had statistically significant slopes. The R^2 values were equal to 0.90-0.93 for pH, 0.28 and 0.52 for pK, and 0.31 and 0.35 for pNO_3.

The accuracy (quantifying accuracy) between pX values determined using regression analysis and actual measurements ranged between 0.18 and 0.37 pX, with the highest value corresponding to the nitrate ISE (similar to precision error). In addition, coefficients of determination of simple linear regression between means of three measurements and corresponding reference values (figure 4.3) were determined. Based on these results, we conclude that every pH ISE had an excellent correlation with the

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reference measurements ($R^2 > 0.9$) with slight (< 0.5 pH) underestimation of soil pH along the entire range.

a)

6.0
1:1 line

5.5

5.0

pH Probe 1
7.0
4.5
Regression 1
pH Probe 2
6.5
4.0
Regression 2
pH Probe 3
4.5 5.0 5.5 6.0 6.5 7.0 7.5 Reference
Regression 3

pH

Regression 1
3.5 3.0 2.5 2.0
K Probe 2
Regression 2
1:1 line

4.0 3.5 3.0 2.5
1.5

2.0
N Probe 1
Regression 1 N
Probe 2
Regression 2
K Probe 1
2.0 2.5 3.0
1:1 line

2.5 3.0 3.5
Reference pNO3

b)
c) Reference pK

Figure 4. 3. Accuracy assessment for a) pH, b) potassium, and c) nitrate ISE

On the other hand, a relatively low ($R^2 > 0.2$) correlation with the reference measurements was obtained for potassium and nitrate ISEs. These low correlations can be attributed to: a) differences between ion activity in naturally moist soil and ion concentration in water-based extracts, b) ion mobility and potential change due to

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overnight storage of samples, and c) the relatively low range of ion activity represented in

the set of Nebraska soils.

Table 4. 6. Summary of ion selective electrode accuracy assessment

ISE ID	R^2	Intercept[1]	Slope[1]	F-stat[2]	R^2–means[3]	Accuracy Error[4]
pH Probe 1	0.93	-0.30 (0.24)	0.97 (0.04)	599.75**	0.96	0.164
pH Probe 2	0.90	0.34 (0.27)	0.89 (0.04)	397.33**	0.93	0.195
pH Probe 3	0.91	0.26 (0.27)	0.90 (0.04)	416.31**	0.93	0.196
K Probe 1	0.52	0.04 (0.44)	1.11 (0.16)	45.67**	0.62	0.154
K Probe 2	0.28	1.07 (0.52)	0.78 (0.19)	16.33**	0.41	0.165
N Probe 1	0.35	-0.64 (0.59)	0.93 (0.19)	23.53**	0.61	0.123
N Probe 2	0.31	-1.12 (0.73)	1.04 (0.24)	19.28**	0.51	0.171

[1] ñ Estimates and standard errors for parameters of regressions between DSM measurements and reference values

[2] ñ If linear regression is significant, F-stat values are marked with ** ($\alpha = 0.0001$), or * ($\alpha = 0.05$)

[3] ñ R^2 of a linear regression between per soil averages rather than individual measurements and reference values

In addition to the limited correlation, both the potassium and nitrate ISEs have shown almost a magnitude difference between the sensed ion activity and the reference ion concentration (approximately 0.5 pK increase and 1.0 pNO_3 decrease). The cause of this difference is unknown, but it was hypothesized that high nitrate anion activity was observed due to its high mobility and extremely low dilution during DSM.

The majority of potassium cations, on the other hand, are not released into soil solution at field moisture contents, which were lower than the moisture content used for the reference measurement. Although the potassium ISE measures the actual K^+ in soil solution, in a DSM approach this represents only a fraction of the potentially available (exchangeable) potassium.

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4.2.3 Discussion

Both precision and accuracy (as estimated using precision and accuracy errors) of

ISEs used to directly measure ion activity on moist soil had similar magnitude. The estimated errors ranged from 0.11 to 0.26 pX (precision) and from 0.12 to 0.19 pX (accuracy), as shown in figure 4.4. The pH ISEs showed better precision than the accuracy. Potassium and nitrate ISEs, on the other hand, had approximately the same errors for precision and accuracy.

From a practical viewpoint, modifying the measurement approach, the reference measurement procedure, or the method of their comparison can reduce relatively high accuracy error. On the other hand, there is absolutely no possibility to successfully implement on-the-go mapping technology using a sensor with relatively high error for precision. In such a case, the measurement technique itself must be improved.
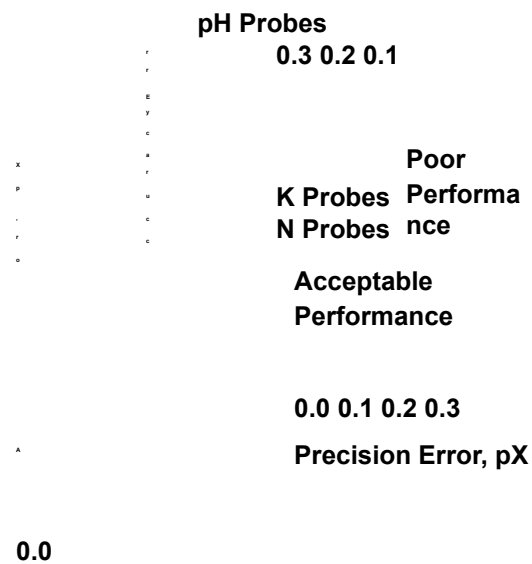

pH Probes
0.3 0.2 0.1

Poor
K Probes Performa
N Probes nce

Acceptable
Performance

0.0 0.1 0.2 0.3
Precision Error, pX

0.0

Figure 4. 4. Illustration of comparison between estimated errors of precision and accuracy for DSM tests.

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Based on the results of this test, glass-membrane pH ISEs showed the best performance. It is safe to anticipate that soil pH measurements obtained on-the-go will resemble conventional measurements performed on the same soil samples. However, in certain field conditions (e.g., sandy soils) the ISE lifetime can be shortened by physical

abuse of sensitive membranes, and additional spatial information (e.g., CEC estimates) will be needed to define lime requirement based on soil pH measurement.

Potassium ISEs have different sensitive membranes than pH ISEs. PVC seems to be more fragile in direct contact with soil than glass. However, relatively low precision errors suggest that potassium ISEs can also provide consistent measurements. Despite the fact that the range of pK measurements was more than two times smaller than the range of pH measurements, potassium ISEs can be used to separate field areas with very high and very low potassium ion activity. Similar to pH, exchangeable potassium required to develop prescription maps could be predicted using the soluble potassium from ISE measurement and sparse CEC data, as further discussed.

Nitrate ISEs were similar in design to potassium ISEs, but resulted in slightly higher precision errors while detecting a slightly lower range of pNO_3 than pK. This made the ISEís ability to separate low and high nitrate content more difficult. On the other hand, the conventional method is similar in nature to the measurements that can be conducted on-the-go (no chemical extraction is performed). This means that the maps obtained could potentially be used to provide nitrogen fertilizer credit in areas where very high residual nitrate nitrogen in subsurface soil samples has been detected.

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Based on concerns related to ISE reliability and marginally acceptable precision and accuracy errors obtained during the DSM test, an alternative technique for interaction between soil samples and ISE membranes was needed. Further explorations leading to the agitated soil measurements (ASM) are discussed throughout this dissertation.

4.3 Development of Multi-Probe Agitated Soil Measurement Methodology (ASM)

4.3.1 Multi-Probe ASM Factorial Experiment

The results of 64 different treatment combinations involving five factors (SWR, QWE, QWR, ISA, and Stir) applied to four soils (Soil IDs: 3, 8, 11, and 14) were analyzed using normal probability plots and a general linear model (GLM) statistical procedure. The normal probability plots of main effects (including individual soils) and two-factor interactions are shown in figure 4.5 (Kuehl, 2000). As anticipated, selected soils had the greatest effect on ISE output due to the different activity of targeted ions. The results from the GLM statistical analysis of the sources of variation are listed in table 4.7.

Despite soils, the major factors affecting the quality of ISE measurements were SWR and the addition of ISA, which were consistently significant among all three ISEs. QWE was critical only for the pH ISE and use of tap water as the extraction medium resulted in lower mV measurements (higher pH) compared to DDW due to the relatively high pH of the tap water source. The QWE factor was marginally significant for the nitrate ISE (p value of 0.0471). Because QWE did not appear significant with other factors in two factor interactions of the nitrate ISE, extraction was not considered to affect nitrate or potassium measurements.

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QWR also did not significantly influence the three ISEs, i.e., as long as the ISEs were cleaned well, tap water could be used. Stirring affected the quality of measurements by half-cell (potassium and nitrate) ISEs, but not pH ISE.

Table 4. 7. Results of ½ replication of the 4 X 2^5 fractional factorial experiment.

Factors	ISEs					
	Potassium		Nitrate		pH	
	F-stat	p-value	F-stat	p-value	F-stat	p-value
Soil	89.62*	<.0001	19.01*	<.0001	185.46*	<.0001
SWR	125.14*	<.0001				

97.52* <.0001 38.32* <.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* <.0001

ISA 23.86* <.0001 57.85* <.0001 6.09* 0.0195 Stir 12.38* 0.0014 10.15* 0.0034 0.75 0.3924 Soil x SWR 1.25 0.3099 3.54 0.0262 2.66 0.0663 Soil x QWR 0.24 0.8703 0.71 0.5544 0.07 0.973 SWR x QWR 1.86 0.1822 0.41 0.5289 0.07 0.789 Soil x QWE 0.73 0.5422 3.08 0.0423 14.57* <.0001 SWR x QWE 0.33 0.5678 1.94 0.1736 20.54* <.0001 QWR x QWE 1.46 0.2365 0.41 0.5289 0.4 0.5294

Soil x ISA 1.27 0.3025 2.26 0.1022 0.63 0.6014 SWR x ISA 0.10 0.7549 0.23 0.6362 3.36 0.0769 QWR x ISA 1.59 0.2172 0.00 0.9685 0.57 0.4579 QWE x ISA 1.00 0.3263 0.51 0.4791 0.0 0.9695

Soil x Stir 1.38 0.2668 0.51 0.6752 0.69 0.5642 SWR x Stir 14.30* 0.0007 5.15* 0.0306 11.52* 0.002 QWR x Stir 0.04 0.8350 0.23 0.6362 0.12 0.7309 QWE x Stir 0.62 0.4370 1.33 0.2573 1.29 0.2642

ISA x Stir 0.01 0.9170 0.16 0.6933 0.46 0.5049 SWR x ISA x Stir 0.75 0.3906 1.98 0.1667 0.02 0.8951 SWR x QWE x ISA 0.1 0.7592 0.03 0.8635 0.01 0.9879 * - significance at α=0.05