

# ADVANCES IN MEASUREMENT SYSTEMS



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Edited by  
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# In-field measurement of soil nitrate using an ion-selective electrode

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## 1. Introduction

Standard laboratory methods for measurement of soil nitrate ( $\text{NO}_3\text{-N}$ ) use various procedures and instruments to analyze soil samples taken from the field and transported to the laboratory. Concerns with these procedures range from delays in measurement time, the high cost of soil sampling and analysis, high labour requirements, and the need to aggregate samples. With recent advances in using the ion-selective electrode, as presented in this chapter, soil  $\text{NO}_3\text{-N}$  can now be measured directly, rapidly, accurately, at low cost, at a fine scale, and in real-time right in the field. This chapter describes the methodologies and procedures for how this can be done and provides experimental data and results from data analyses that validate measurements of soil  $\text{NO}_3\text{-N}$  obtained with a prototype soil nitrate mapping system (SNMS) developed at the Nova Scotia Agricultural College, Truro, Nova Scotia, Canada. These advances in the in-field use of the nitrate ion-selective electrode ( $\text{NO}_3^-$ -ISE) provide the ability for (i) assessing soil nitrate variation, (ii) linking soil nitrate variation to crop growth, (iii) developing site-specific crop management practices, and (iv) environmental monitoring of soil nitrate.

This chapter will begin with a discussion of the concerns with nitrate in the soil and environment, precision agriculture and site-specific crop management, variation in soil nitrate and its links to crop growth and yield, and issues with assessing soil nitrate variation in a field. Next will be a discussion of ion-selective electrode theory and application for measuring soil nitrate, followed by a presentation and discussion of early experiments conducted for determining electrode operating parameters to enable the electrode to be used in a soil slurry. The development and testing of the mechanical system used for soil nitrate extraction and measurement along with a description of the control sub-unit, measurement methodology, and operation of the nitrate extraction and measurement sub-unit (NEMS) for using the  $\text{NO}_3^-$ -ISE in the field will be presented. And the results of experiments used to validate in-field measurements of soil  $\text{NO}_3\text{-N}$  obtained with the ion-selective electrode will be presented and discussed. There will be a discussion of what is

significant about the new measurement advances presented along with some results of experiments conducted using the SNMS in wheat and carrot production systems. Finally, conclusions and recommendations for future research in this area will be made.

### **1.1 Soil nitrate is an environmental issue**

In addition to the fertility needs of farmers, it is important to deal with environmental issues associated with the use of nitrogen fertilizers. As agriculture continues its best efforts to provide the world's rising population with high-quality, safe, and nutritious food, water sources contamination and associated socio-economic costs indicate a great need for precise soil fertility management practices—using the right form of fertilizer, applied at the right time and place, in the right amount, and in the right way (Power & Schepers, 1989; Dinnes et al., 2002).

The seriousness and extent of  $\text{NO}_3^-$  contamination of water sources and its effect on drinking water quality has been documented and discussed by many researchers in Canada, the United States, and the European Community (USEPA, 1990; Reynolds et al., 1995; Oenema et al., 1998; Henkens & Van Keulen, 2001). As a result, policy makers are revising laws to ensure the safety of public water supplies. These include amendments to the Water Pollution Control Acts in Canada and the United States, the European Community Nitrate Directive, and the Mineral Policy in the Netherlands.

Nitrate leaching from soil into groundwater has been attributed to poor soil nitrogen management practices involving inorganic and manure fertilizer inputs (Geron et al., 1993; Campbell et al., 1994; Patni et al., 1998; Koroluk et al., 2000; Astatkie et al., 2001; Randall & Mulla, 2001; Dinnes et al., 2002). As such, better soil nitrogen management practices, including more accurate fertilizer recommendations and placement, could help minimize the contribution by agriculture to the  $\text{NO}_3^-$  pollution problem.

### **1.2 Precision agriculture and site-specific crop management**

The profitability of farmed crops can be severely affected if poor nitrogen management practices are used. Precision agriculture technology offers farmers the potential to more intensely and precisely analyze variations in numerous field conditions throughout the growing season, in association with environmental and crop response data in order to make the most sound, and site- and time- specific, management decisions possible. At the same time the public can be assured those practices are being conducted in the most environmentally friendly way (Adamchuk et al., 2004a; Bongiovanni & Lowenberg-DeBoer, 2004; Bourenanne et al., 2004).

The inability to assess soil and plant data rapidly and inexpensively in the field, however, remains one of the biggest limitations of precision agriculture (Adamchuk et al., 2004b). In particular, the lack of a soil  $\text{NO}_3\text{-N}$  measurement system is a major roadblock (Ehsani et al., 1999). If this roadblock could be overcome, a positive contribution toward improving precision agriculture technology would be made.

### **1.3 Variation in soil nitrate and its links to crop growth and yield**

Soil  $\text{NO}_3\text{-N}$  levels in agricultural fields, as well as other chemical and soil physical properties, exhibit high variation spatially and temporally and at different measurement scales and levels of aggregation (Heuvelink & Pebesma, 1999). Much research has been dedicated to assessing



and characterizing this variation to improve our understanding of the effects of soil  $\text{NO}_3\text{-N}$  on crop growth and yield within agro-ecosystems (Almekinders et al., 1995).

Growing plants utilize varying amounts of soil  $\text{NO}_3\text{-N}$  during different phenological (growth) stages and its availability should ideally be in response to the plant's need. In wheat, for example, the level of available soil  $\text{NO}_3\text{-N}$  during early plant growth determines yield for the most part by influencing population density and the degree of stimulation of tiller fertility, spikelet initiation, and floret fertility. Soil  $\text{NO}_3\text{-N}$  uptake is greatly reduced shortly after anthesis, and nitrogen is re-translocated from leaves primarily, and other vegetative organs secondarily, to the ears to meet the need of the filling grains (Simpson et al., 1983). The reduction in soil  $\text{NO}_3\text{-N}$  uptake during grain filling varies with weather conditions, disease pressures, and subsequent management practices (i.e. irrigation or chemical applications) which put stress on the plants. Physiologically, soil  $\text{NO}_3\text{-N}$  and crop yields are linked via nitrate uptake and its conversion into proteins and chlorophylls during plant growth (Engel et al., 1999; Schröder et al., 2000) and photosynthesis buffering against soil nitrogen deficits by an abundance of RuBP carboxylase that serves as a reserve of protein in the leaves during unfavourable weather conditions (Hay & Walker, 1989).

The availability and distribution of  $\text{NO}_3\text{-N}$  in the soil depends on many soil forming, chemical, microbial, plant growth, environmental, and management factors that influence soil crop dynamics (Addiscott, 1983; Wagenet & Rao, 1983; Trangmar et al., 1985). Because the effects of these factors and their interactions are highly variable (Almekinders et al., 1995), they also lead to the characteristic behavior of  $\text{NO}_3\text{-N}$  being highly variable within the soil.

Studying the levels of nitrogen in various plant tissues and organs at the various phenological stages simultaneously with the availability of soil  $\text{NO}_3\text{-N}$ , and on a fine-scale, could provide information to researchers and farmers useful for developing better site-specific nitrogen management (SSCM) practices. Collecting this information at the required sampling intensity, however, has been found to be very tedious and generally cost and time prohibitive using current methods (Engel et al., 1999; Ehsani et al., 2001; Adamchuk et al., 2004a).

#### 1.4 Assessing soil nitrate variation

Geostatistical techniques have been developed to provide practical mathematical tools for assessing spatial and temporal variation, and spatial structure of soil properties including soil  $\text{NO}_3\text{-N}$  (Burgess & Webster, 1980; Webster & Burgess, 1984; Webster & McBratney, 1989; McBratney & Pringle, 1999).

Research applying these tools on a field-scale, such as through SSCM-experimentation (Pringle et al., 2004), has led to the development of a multitude of methods for determining minimum soil sample spacing, sampling grid layout and cell size (Russo, 1984; Han et al., 1994; Van Meirvenne, 2003; Lauzon et al., 2005), optimum number of samples (Webster & Burgess, 1984), sampling schemes and protocols for pre-planning experimental designs (Trangmar et al., 1985; Chang et al., 1999; Ruffo et al., 2005) and sample bulking strategies (Webster & Burgess, 1984).

However, when using these methods for implementing precision agriculture practices related to soil nitrogen management, the "most serious obstacles" are still the need to know the spatial structure in advance and the cost of obtaining this information even though the sampling effort required is much less than for full-scale sampling (Lark, 1997; McBratney & Pringle, 1999; Jung et al., 2006).

### 1.5 Concept of a soil nitrate mapping system

Development of an SNMS could contribute to the advancement of precision agriculture by providing a way to quickly, accurately, and affordably collect the data necessary to analyze small-scale variation in soil nitrate in time and space while crops are being grown, thus enabling this variation to be linked to crop growth and yield. Ideally, an SNMS would automatically collect a soil sample in the field and directly measure nitrate concentration in real-time. Moreover, global positioning system (GPS) geo-referenced data could be simultaneously recorded at each sampling location to enable a nitrate map to be created for the field. An SNMS, thus, would overcome many of the impediments, roadblocks, and serious obstacles of measuring and assessing soil  $\text{NO}_3\text{-N}$  variation using conventional methods in terms of sample analysis lag time, high labour requirements, and high costs as discussed above. The overall objective of the experimental work described in this chapter was to develop and validate such an advanced soil  $\text{NO}_3\text{-N}$  measurement and mapping system.

## 2. Attempts by others to develop methods for in-field measurement of soil nitrate

Over the last 20 years or so, attempts to develop a real time soil  $\text{NO}_3\text{-N}$  measurement system by other researchers have been based on three types of sensors: (i) ion-selective field effect transistor (ISFET), (ii) ISE, and (iii) spectrophotometer. The majority of this research work has not progressed past laboratory feasibility studies and testing in soil-bins. A brief review of these works is presented below. Details can be obtained by reviewing the cited papers directly, or the summaries contained in the comprehensive review paper recently published by Adamchuk et al. (2004a) who concluded that "sensor prototypes capable of accomplishing this task are relatively complex and still under development."

### 2.1 Ion-selective field effect transistor sensor based systems

Loreto & Morgan (1996) developed a prototype real time soil  $\text{NO}_3\text{-N}$  measurement system that consisted of a soil core sampling wheel, indexing and processing table, and a data acquisition and control system. This system was quite similar to that of Adsett & Zoerb (1991); however it used a specially developed prototype ISFET as the  $\text{NO}_3^-$  analysis instrument. In soil bin tests, correlations between ISFET measurements with a  $\text{NO}_3^-$ -ISE and laboratory colorimetric analysis measurements had an  $R^2$  between 0.65 and 0.43, respectively. The system worked reasonably well as a first attempt, but issues with the ISFET's response characteristics and calibration drift were apparent. Work has continued focusing on the development of ISFET technology and its use in combination with novel soil extraction and flow injection analysis (FIA) systems as a potential method of real-time measurement of  $\text{NO}_3^-$  in filtered soil extracts (Birrell & Hummel, 1997, 2000, 2001; Price et al., 2003). This work has resulted in the development of a promising combination ISFET/FIA system that gives reasonable results compared to a cadmium reduction method using a Lachat FIA (Slope 1:1,  $R^2 = 0.78$ ) with a measurement time ranging between 3–5 s (Price et al., 2003), but it is still at the laboratory level.

## 2.2 Ion-selective electrode sensor based systems

A prototype nitrate monitoring system (NMS), was developed by Adsett (1990) and Adsett & Zoerb (1991). It used a specially designed unit for  $\text{NO}_3^-$  extraction wherein the soil was mixed with de-ionized water and then the liquid fraction was clarified before being presented to the electrode for  $\text{NO}_3^-$  measurement. Although the system functioned reasonably well as a first attempt, it had major difficulties with collecting a soil sample and obtaining a clear extractant for  $\text{NO}_3^-$  measurement on a consistent basis. This early work was the starting point from which improvements have been steadily made by Thottan et al. (1994), Thottan (1995), Adsett et al. (1999), Khanna & Adsett (2001), and Sibley (2008) that have advanced the system to the form described below in sections 5 and 6 into a fully functioning and field-validated prototype SNMS.

As part of an investigation into the feasibility of a real time soil K and  $\text{NO}_3\text{-N}$  mapping system, Adamchuk et al. (2002a) performed laboratory tests on four commercially available  $\text{NO}_3^-$ -ISEs to simulate the direct soil measurement technique used in an automated soil pH measurement system developed by Adamchuk et al. (1999, 2002b). In the laboratory, manually remoistened previously air dried soil samples were pressed into contact with the sensing membrane of each  $\text{NO}_3^-$ -ISE to determine  $\text{NO}_3^-$  concentration (liquid basis of  $\text{mg L}^{-1}$  reported as ppm). These results were compared to a standard cadmium reduction laboratory analysis technique to give an indication of the accuracy of the  $\text{NO}_3^-$ -ISEs. For individual soil samples,  $R^2$  values ranging 0.38–0.63 were obtained, depending on the ISE, while averaging of three repeated measurements yielded  $R^2$  values ranging 0.57–0.86. It was concluded that it is feasible to use a  $\text{NO}_3^-$ -ISE for measuring soluble nitrate concentration of naturally moist soil samples, but one of the main limitations of the proposed method reported was difficulty in maintaining high quality contact between soil and electrode. It should also be noted that use of the proposed method in the field in combination with the pH measurement system's soil sampling mechanism would not enable the  $\text{NO}_3\text{-N}$  content ( $\text{mg kg}^{-1}$ ) of the sample to be directly computed since the 'weight' (mass) of the soil sample would not be known.

## 2.3 Spectrophotometer sensor based systems

Laboratory testing and field-based experimentation of a near-infrared (NIR) spectrophotometer conducted by Ehsani et al. (1999) using soils samples spiked with ammonium sulfate, ammonium nitrate, and calcium nitrate (10–100 ppm) revealed that soil  $\text{NO}_3\text{-N}$  could be detected with  $R^2$  ranging 0.76–0.99 using partial least squares regression with each data point being an average of 10 sub-samples. However, the calibration equation must be derived from samples taken from the same location, otherwise the analysis procedure fails. Further laboratory-based research work (Ehsani et al., 2001) using soil samples spiked with ammonium nitrate and calcium nitrate (400–3000 ppm) and a spectrophotometer equipped with a deuterated triglycine sulfate (DTGS) sensor showed that the ratio of area under the nitrate peak to area under the water peak in the mid-infrared (MIR) spectra is proportional to  $\text{NO}_3^-$  concentration ( $R^2 = 0.81$ ), and that the analysis technique is not dependent on the time of measurement, soil type, or nitrate source. However, as the authors themselves note, the range of  $\text{NO}_3^-$  concentration in agricultural soils is usually less than 100 ppm so the practicality of this sensing method is questionable unless a more sensitive mercury cadmium telluride (MCT) type sensor can be used.

Use of a real-time portable spectrophotometer using a multi-spectral approach has been

investigated by Shibusawa et al. (1999, 2003). They reported that NIR reflectance could be used to detect soil  $\text{NO}_3\text{-N}$  with an  $R^2$  of 0.50.

Christy et al. (2003) have conducted preliminary field testing of a prototype soil reflectance mapping unit utilizing a NIR spectrophotometer for simultaneously measuring total N, total carbon, pH, and moisture content. Results from testing in a single field indicated the system could repeatably produce clear definition of patterns in these soil parameters related to spectral reflectance with an  $R^2$  of 0.86, 0.87, 0.72, and 0.82, respectively.

### 3. Ion-selective electrode theory and application for measuring soil nitrate

The nitrate ion-selective electrode ( $\text{NO}_3^-$ -ISE) (Fig. 1) provides a rapid and reliable method for quantitative analysis of soil nitrate. Nitrate ISEs, which are highly selective to  $\text{NO}_3^-$  ions in solution, were first used around 1967 as quick and reliable alternatives to chemical-based laboratory methods for nitrate measurement (Dahnke, 1971). The  $\text{NO}_3^-$ -ISE electrochemically generates a voltage across its organophilic membrane that varies with ionic strength (molarity) of the solution according to the Nernst equation (Morf, 1981).

$$E = E_0 + S \log (A) \quad (1)$$

where  $E$  is the electrochemical cell potential (mV),  $E_0$  is the standard potential (mV) in a 1M solution, ideally a constant,  $S$  is the electrode slope ( $-mV$  per decade of concentration), and  $A$  is the nitrate activity (effective concentration moles  $\text{L}^{-1}$ ) in the solution.

Through calibration with known standards, the logarithm of solution molarity is related to electrode output voltage to determine a linear calibration curve for determining nitrate concentration ( $\text{mg L}^{-1}$  or ppm) of subsequent soil samples.

Typically in the laboratory, measurement of nitrate concentration of a soil sample then proceeds by mixing together a known 'weight' (mass) of soil with a known volume of deionized or distilled water (e.g. soil:extractant ratio). After an appropriate extraction time, the extractant in the mixture is decanted from the soil particles and clarified by filtration. Then the molarity of the clarified extractant is measured with the  $\text{NO}_3^-$ -ISE. The resulting electrode voltage output is mathematically converted to concentration via the calibration curve, and subsequently to content ( $\text{mg kg}^{-1}$ ) via the soil:extractant ratio.

Many researchers over the years have studied various aspects of  $\text{NO}_3^-$ -ISE performance (accuracy, repeatability, stability, reliability), the potential for measurement interference by other ions, solution ionic strength, and use of deionized or distilled water as an extractant, for a multitude of use conditions, and in comparison with other chemical-based laboratory methods of soil nitrate determination (Myers & Paul, 1968; Mahendrappa, 1969; Milham et al., 1970; Onken & Sunderman, 1970; Dahnke, 1971; Mack & Sanderson, 1971; Yu, 1985; Sah, 1994).

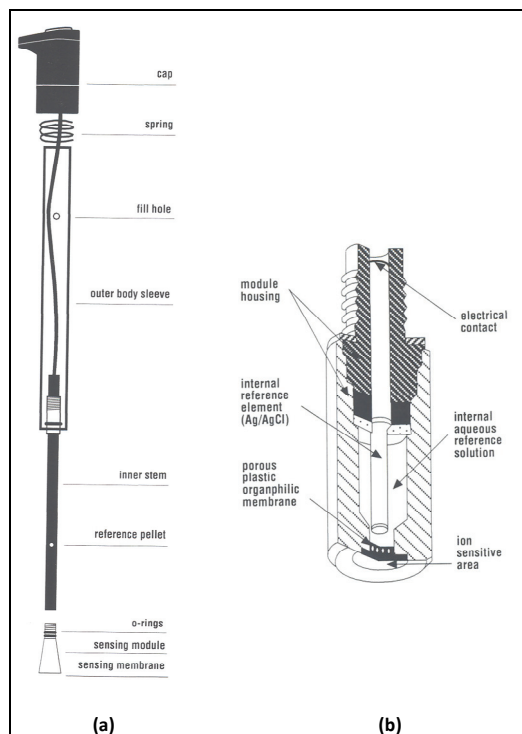


Fig. 1. The Orion 97-07 ionplus nitrate ion-selective electrode. (a) Pictorial diagram, (b) cross-section diagram of the electrode's nitrate sensing module (Orion, 2005).

As a result,  $\text{NO}_3^-$ -ISEs have enjoyed wide acceptability because the results obtained are comparable to other chemical-based methods' results, and they are quick and simple to use. Today, several types of  $\text{NO}_3^-$ -ISEs are manufactured commercially, and they are widely used in laboratories around the world for water quality monitoring and plant tissue sap nitrate measurement in addition to soil nitrate measurement. It is because of their well-defined operating characteristics, reliability, and commercial availability that a  $\text{NO}_3^-$ -ISE was chosen as the analysis instrument for the SNMS to perform direct in-field measurement of  $\text{NO}_3^-$  in a soil slurry.

#### 4. Experiments conducted for determining electrode operating variable parameters

Laboratory work conducted by Thottan et al. (1994) and Thottan (1995) determined that a  $\text{NO}_3^-$ -ISE could be used in a soil slurry whilst investigating operating variables of soil:extractant ratio, slurry clarity, and electrode response time, repeatability and output signal stability.

Soil samples of sandy loam, silty clay loam, and clay loam were taken from the surface layer (15 cm) of fields in Cumberland and Colchester counties of Nova Scotia, Canada (45° N, 63° W). The results reported in this chapter relate to Chaswood clay loam, since of the three

soils tested it is considered to be more difficult to analyze because of the higher clay content than the coarser textured soils. The Chaswood soil is of the gleysolic order, of the subgroup RegoGleysol. Particle size analysis revealed a composition of 34.0% sand, 37.9% silt, and 28.1% clay. The sampled A horizon was a fine textured alluvial formation which had been deposited above loamy sand.

Testing of the soil:extractant ratio revealed that there was no significant difference ( $\alpha = 0.05$ ) between final  $\text{NO}_3^-$  concentrations for the three ratios tested. The mean  $\text{NO}_3^-$  concentrations determined at soil:extractant ratios of 1:15, 1:5 and 1:3 were 18.6, 18.6, and 19.3 ppm, respectively. In terms of mechanical extractor design, these results indicated that any of the three ratios may be used in the field when extracting  $\text{NO}_3^-$  from soil with equal effectiveness.

Tests to determine the effect of clarity on electrode performance showed that there was no significant difference ( $\alpha = 0.05$ ) between mean final  $\text{NO}_3^-$  concentration measured in either slurry (34.1 ppm), decanted (32.0 ppm), or filtered (33.8 ppm) soil samples. This result confirmed the hypothesis that the  $\text{NO}_3^-$ -ISE could be used in a soil slurry during in-field use—obviating the need for time consuming filtering of soil extracts required by other nitrate determination methods that would complicate mechanical system design and slow down operation. Using a  $\text{NO}_3^-$ -ISE, Paul & Carlson (1968), Myers & Paul (1968), Dahnke (1971) and Yu (1985) also found that there was no significant difference between nitrate determinations made in a slurry or filtrate.

Fig. 2. shows a typical response curve of the  $\text{NO}_3^-$ -ISE in a soil slurry. The electrode potential drops sharply indicating a rapid release of nitrate into solution. It was found that the electrode detects a large percentage of the nitrate concentration in less than 20 s, but it takes up to two minutes to detect the total nitrate concentration as the electrode signal stabilizes. Electrode signal stability was considered to be achieved when a signal drift of less than  $1 \text{ mV min}^{-1}$  was obtained. It was also found that the electrode had very consistent response time curves. Therefore, it was hypothesized that it was not necessary to wait until 100% of the  $\text{NO}_3^-$  in a soil sample is extracted before taking a measurement. This characteristic was utilized to create normalized response curves (Adsett et al., 1999) to speed up the measurement cycle. Accurate and reliable estimates of the sample's total  $\text{NO}_3^-$  concentration could be made in six seconds, which is within the time required for rapid in-field measurements. A successful mechanical system, however, would depend not only on a properly functioning and calibrated electrode, but also on properly functioning mechanical components, electronics, and controls to enable it to be reliably used in the field.

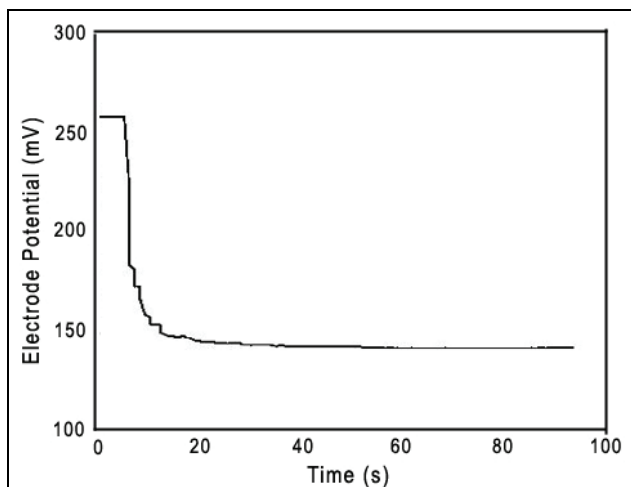


Fig. 2. Typical electrode response in soil slurry during nitrate extraction and measurement (Thottan et al., 2004).

## 5. Systems developed for in-field measurement and mapping of soil nitrate

In this section, a description of the mechanical systems and their operation for soil nitrate extraction and measurement are presented and discussed. First will be a description of the SNMS, followed by a description of the nitrate extraction and measurement sub-unit (NEMS).

### 5.1 Soil nitrate mapping system

Sibley (2008) and others (e.g., Thottan, 1995; Adsett et al., 1999; Khanna & Adsett, 2001) have developed a SNMS (Fig. 3) that uses a nitrate ion-selective electrode ( $\text{NO}_3^-$ -ISE) (Orion Model 9707 ionplus, Thermo Electron Corp., Massachusetts, USA) as the measurement instrument. It is an electro-mechanical machine that automatically collects a soil sample (0–15-cm depth), mixes it with water, and directly analyzes it electrochemically for nitrate concentration in real-time (6 s). Additionally, global positioning system (GPS) geo-referenced position data are simultaneously recorded at each sampling location to enable a nitrate map to be created for the field being sampled.

The SNMS consists of six sub-units: (1) soil sampler, (2) soil metering and conveying, (3) nitrate extraction and measurement, (4) auto-calibration, (5) control, and (6) GPS as indicated in Fig 3.





Fig. 3. Soil nitrate mapping system with six sub-units: (1) soil sampler, (2) soil metering and conveying, (3) nitrate extraction and measurement, (4) auto-calibration, (5) control and (6) global positioning system, with (7) inset showing Orion 97-07 ionplus  $\text{NO}_3^-$ -ISE used for measuring soil nitrate (adapted from Sibley, 2008).

Prior to use, the  $\text{NO}_3^-$ -ISE is calibrated using pre-prepared reagent-grade  $\text{NO}_3^-$  standards placed into the calibration cups of the auto-calibration sub-unit. As well, a field (soil condition) calibration is completed to enable rapid measurements of  $\text{NO}_3^-$  concentration to be taken during system operation. As the tractor moves forward, the SNMS collects a soil sample via the combination of soil sampler and soil metering and conveying sub-units. During sampling, the hydraulic-powered wood-saw blade is lowered into the soil by the carrying frame. Over a travel distance of approximately 0.5 m, the blade cuts a 15-cm deep slot and throws a spray of finely chopped soil onto the head-end area of an automatically positioned flat-belt transfer conveyor. This action creates a sample of uniform bulk density and finely-granulated particles to facilitate the subsequent nitrate extraction process (Sibley et al., 2008). The conveyor belt has an oblong fixed-volume pocket milled into its surface to collect a sample from the soil landing on the conveyor. A specially designed scraper placed above the belt levels the soil sample in the pocket without compaction and removes excess soil from the belt as the belt moves to deliver the soil sample to the NEMS. During delivery, the pocket stretches lengthwise as it passes around the conveyor's tail-end roller to facilitate complete emptying of the pocket.

Just prior to soil sample delivery, water for  $\text{NO}_3^-$  extraction is pumped into a nitrate extractor to completely submerge the sensing module of the  $\text{NO}_3^-$ -ISE and the stirrer is activated. The soil sample is received into the extractor where vigorous mixing takes place



creating a soil slurry. Nitrate in the soil sample is rapidly extracted into the slurry. The  $\text{NO}_3^-$  concentration of the mixture is measured by the  $\text{NO}_3^-$ -ISE and stored in the control system's computer memory. Geo-referenced position data are simultaneously recorded by the GPS sub-unit at each sampling location to enable a nitrate map to be subsequently created for the field. All data collected are downloaded to a computer for post-sampling processing via the computer-interface facility built into the control system.

The SNMS can be used to analyze soil samples automatically in real time, or manually while stationary by hand-placing samples into the NEMS. It is envisioned that two configurations of the system will eventually be used in practice—a tractor-mounted version (Fig. 3.) and a 'suitcase' (portable) version. Initial research on developing a 'suitcase version' was completed by Brothers et al., (1997). The prototype developed was capable of measuring  $\text{NO}_3^-$  and pH with the same mechanical system and control hardware.

## 5.2 Nitrate extraction and measurement sub-unit

The heart of the SNMS is the NEMS (Fig.4). It consists of an extractor, an impeller and drive motor, a spray nozzle, a gate valve and drive actuator, and the  $\text{NO}_3^-$ -ISE. The electrode and the sample, plus associated electrode circuitry, comprise an electrochemical cell. The extractor was constructed using 9.5 cm ID clear acrylic tubing so that the extraction process could be viewed.

A 7.6 cm ID sliding-knife gate valve was installed to act as the bottom of the extraction chamber, forming the extraction chamber outlet. This arrangement gives a nearly full-diameter chamber pass-through capability for efficient clean-out of each sample and prevents potential jamming by small stones or field debris that might enter the chamber with the soil sample. A 12Vdc linear actuator is used to open and close the valve between samples.

In normal position, the extraction chamber outlet is kept closed by the actuator. When the actuator is powered, it opens the extraction chamber outlet. The extraction chamber was electrically isolated from other components to eliminate any stray voltages that may interfere with the  $\text{NO}_3^-$ -ISE signal.

The added advantage of having the extraction chamber outlet normally closed was that the extraction chamber could be used as a storage unit for the electrode in a dilute  $\text{NO}_3^-$  standard solution when not being used. To the lower end of the valve, a 3.5-cm diameter polyvinyl chloride (PVC) pipe was connected. The PVC pipe provided structural support and electrical isolation for the extraction chamber, as well as being an extension of the extraction chamber outlet.

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