An automated system for rapid in-field soil nutrient testing

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Abstract
This paper outlines the laboratory experimentation and development of a multi-ion measuring system (MIMS) for proximal sensing of soil nitrate, potassium and sodium using Ion Selective Electrodes (ISEs). We present work conducted for characterising ion exchange reactions using multiple ISEs and a universal extracting solution. The use of ion exchange kinetics and prediction models for rapid estimation of soil extractable nutrient concentration was evaluated. Using these techniques the prototype laboratory and field portable MIMS was developed to provide rapid in-field soil nutrient analysis in less than 30 seconds. The system automates the measurement process including ISE calibration, temperature compensation, and soil analysis with nutrient estimation. Finally we describe the hardware and the performance of the MIMS under laboratory and field conditions.

Key Words
Proximal soil sensing, Ion Selective Electrodes (ISE), ion exchange kinetics, precision agriculture.

Introduction
The implementation of Precision Agriculture (PA) is important for optimising crop production and economic return to farmers, and reducing the environmental impact of farming operations. More precise and accurate resource application (e.g. fertiliser, lime, etc) both spatially and temporally may reduce their over or under application, thereby ensuring optimum productivity for any given unit of land. This management philosophy requires the collection of high resolution soil chemical and physical information, which can not be met by conventional sampling and laboratory analysis. The reason is the large labor requirements, the expense and time needed, making conventional methods inefficient (Viscarra Rossel & Walter 2004). For this reason the development of Proximal Soil Sensors (PSS) is important. These sensors should be rapid, inexpensive, robust and capable of repeatable measurements. A number of proximal soil sensors have been developed and are commercially available. For example electromagnetic induction (EMI) instruments (Sudduth \textit{et al.} 2001), electrical conductivity systems (e.g. Lund \textit{et al.} 1999) and a pH sensor (Adamchuk \textit{et al.} 1999). Currently, there are no commercially available proximal soil sensors that measure soil nutrient concentration directly.

Our sensor is novel in that it aims to bridge the gap between conventional sampling and analysis and current proximal soil sensors by providing direct chemical measurements of soil nutrients at intermediate resolutions. We developed the system with the view that it should be versatile enough to be used as:

1) A field portable sensor for site specific nutrient analysis, soil core analysis, or screening of critical nutrient concentrations.
2) The analytical unit for an automated on-the-go sampling system for high resolution mapping of soil nitrate, sodium and potassium

The first will provide rapid, low cost analysis of nutrient concentrations through the soil profile, for example, allowing a larger number of soil cores to be analyzed in the field and minimising the need for returning samples to the laboratory. The second will provide information on the spatial variability of soil nutrient concentrations within approximately the top 20 cm of the soil profile.

Ion Selective Electrodes for soil nutrient sensing
Ion Selective Electrodes (ISEs) are capable of providing direct measurements in unfiltered soil extract or slurries, making them attractive options for proximal soil sensing. They are small, economical and require little supporting hardware. Proximal sensing of soil pH using ISEs has been demonstrated by (Adamchuk \textit{et al.} 1999) and commercially available (Veris pH manager – Veris Technologies). Initial techniques employing ISE technology such as Direct Soil Sampling (DSM) for measurement of K\textsuperscript{+}, Na\textsuperscript{+} and NO\textsubscript{3}\textsuperscript{-} on naturally moist soil samples (Adamchuk \textit{et al.} 2005) have experienced limited success. These studies demonstrate the applicability of ISEs for proximal soil nutrient sensing, however the rather rudimentary techniques used to make the measurements and the consequent inconsistencies in the measurements are their major drawback and accountable for their limited success.

Previous work has also inherently been limited to soluble or plant available ion concentrations. Information
on both soluble and exchangeable components is important in management decisions due to the buffering nature of the soil, for example in the measurement of lime requirement (LR) and fertilizer application. However, this requires a lengthy soil extract procedure which creates the rate limiting component of the measurement process.

**Ion Exchange Kinetics – Observation and steady state prediction**

To overcome the rate limiting ion exchange processes it is proposed that the observation of the ion exchange kinetics on addition of soil to the extracting solution will yield sufficient information to predict the steady state or equilibrium concentration. Conceptually, this work continues from that of Viscarra Rossel and McBratney (2003) and Viscarra Rossel et al. (2005) where the monitoring of the kinetics of pH reactions in a batch system was used to estimate LR in a prototype on-the-go proximal sensor.

A series of half-cell ISEs selective for nitrate, sodium and potassium using a shared lithium acetate double junction reference electrode were used in a batch processing system for the real-time monitoring of initial ion exchange kinetics. To improve extraction rates and sensor performance an extracting solution of 0.1M Magnesium Sulphate was chosen. Choices were limited by ISE interferences and selectivity.

![Figure 1. Nitrate, sodium and potassium ion exchange kinetics for 25 seconds after soil addition (selected samples for clarity).](image)

Due to ISE calibration requirements, the ion exchange kinetics (Figure 1) and equilibrium concentrations were obtained using two subsamples and separate batch processes. It was found that the kinetics could be successfully modeled empirically and the extracted nutrient concentration (40 minute extraction) could be adequately predicted using the initial 15 seconds of the exchange reaction. There were no significant improvements by extending the initial measurement to 30 seconds (Table 1).

<table>
<thead>
<tr>
<th>Soil nutrient</th>
<th>Concentration Range (mg/kg)</th>
<th>Prediction R² (15s)</th>
<th>Prediction MRE(%) (15s)</th>
<th>Prediction R² (30s)</th>
<th>Prediction MRE(%) (30s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate</td>
<td>8.86-80.18</td>
<td>0.85</td>
<td>37.1</td>
<td>0.92</td>
<td>21.5</td>
</tr>
<tr>
<td>Sodium</td>
<td>1.62-121.99</td>
<td>0.98</td>
<td>17.4</td>
<td>0.99</td>
<td>16</td>
</tr>
<tr>
<td>Potassium</td>
<td>7.41-316.80</td>
<td>0.99</td>
<td>8.7</td>
<td>0.99</td>
<td>9.0</td>
</tr>
</tbody>
</table>

**Multi-Ion Measurement System (MIMS)**

A Multi-Ion Measurement System was developed to implement the ion exchange equilibrium technique in a field portable device. The system is capable of analyzing a nominal 5g sieved sample (< 2 mm). The MIMS is a mechatronic system that contains all necessary hardware, electronics and software to provide fully
autonomous sample analysis including reagent injection, agitation, kinetics monitoring and soil nutrient predictions (Figure 2 and Figure 3). ISE calibration is also performed automatically and includes ‘quality’ control of the ISEs.

Figure 2. The Multi-Ion Measurement System (MIMS)

Figure 3. MIMS system overview

We are currently field testing the MIMS (Figure 4) with an integrated GPS for automatic referencing of sample locations. The hardware for the automation of soil collection, sieving and volumetric sampling for integration of the MIMS into an on-the-go nutrient sensor is currently being developed. The improved system is based on the mechanical sampling mechanism developed by Viscarra Rossel et al. (2005).

Figure 4. Field operation of the MIMS
Conclusion
The MIMS system was developed to automate the analytical components of soil nutrient testing with the goal of providing: (i) a field portable system for simple and rapid estimation of soil nutrient concentrations through the soil profile and (ii) to characterize the spatial variability of nutrient concentrations in surface soil. In both these roles this sensor will provide an improved understanding of soil nutrient variability both spatially and temporally. It will provide sensing capabilities for more effective continuous and site specific nutrient management.

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References