



การพัฒนาเครื่องตรวจวัดไนเตรทในดินแบบพกพาอัตโนมัติสำหรับการทำแผนที่ดินโดยใช้ Nitrate Ion Selective Electrodes (ISEs)

Development of a Portable Automated Detector of Soil Nitrate for Mapping Using Nitrate Ion-Selective Electrodes

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บทคัดย่อ

การจัดการธาตุอาหารพืชให้เหมาะสมกับสภาพดินในแต่ละพื้นที่ย่อยเฉพาะของแปลง (Site-Specific Management, SSM) นั้นมีความสำคัญอย่างยิ่งต่อการผลิตพืชอย่างมีประสิทธิภาพ เนื่องจากการใส่ปุ๋ยที่มากเกินไปจนเกินความจำเป็นนั้น นอกจากจะทำให้ต้นทุนในการผลิตพืชของเกษตรกรสูงขึ้นแล้ว ยังทำให้เกิดการเสื่อมสภาพของดินและการปนเปื้อนในแหล่งน้ำใต้ดิน การวิเคราะห์ดินด้วยการใช้เซนเซอร์นั้นมีความเหมาะสมในการวิเคราะห์ตัวอย่างดินจำนวนมาก ๆ เนื่องจากมีค่าใช้จ่ายที่ต่ำ ทำงานได้รวดเร็ว และสามารถนำไปใช้งานในแปลงเกษตรได้ วัตถุประสงค์หลักของงานวิจัยนี้ เพื่อพัฒนาเครื่องมือวัดความเข้มข้นไนเตรทในดินด้วยการใช้เซนเซอร์แบบ Nitrate Ion-Selective Electrode (Nitrate-ISE) ร่วมกับระบบบันทึกตำแหน่งพิกัดดาวเทียม (GPS) มีการทำงานและบันทึกข้อมูลลงในการ์ดจัดเก็บข้อมูล (SD card) แบบอัตโนมัติ ควบคุมการทำงานด้วยบอร์ดสมองกลฝังตัว (Arduino mega 2560) โดยประกอบด้วยการทำงาน 5 ระบบ ได้แก่ 1.การสกัดดิน 2.การวัดค่า 3.การทำความสะอาด 4.การระบุพิกัดดาวเทียม และ 5.การควบคุมและบันทึกผล ใช้น้ำประมาณ 0.5 ลิตรและเวลาในการวิเคราะห์ประมาณ 5 นาทีต่อตัวอย่าง อัตราส่วนผลระหว่างดิน-น้ำ ที่เหมาะสมคือ 1:10 ระยะเวลาที่ใช้ในการวัด 30 s สามารถวิเคราะห์ได้อย่างมีความถูกต้องเฉลี่ยมากกว่า 80 % โดยมีค่า $R^2 = 0.80$ และค่า RMSE = 1.44 เทียบกับวิธีทางห้องปฏิบัติการ ลดต้นทุนค่าใช้จ่ายในการวิเคราะห์ดินลง 5-6 เท่า ข้อมูลที่ได้จากเครื่องต้นแบบนี้ สามารถนำมาสร้างเป็นแผนที่ดิน ช่วยเกษตรกรให้สามารถตัดสินใจสำหรับการจัดการปุ๋ยในโตรเจนของแปลงเพาะปลูกให้เหมาะสมต่อไป

คำสำคัญ: ไนเตรท, เซนเซอร์วัดดิน, แผนที่ดิน

Abstract

Management of plant nutrients to suit soil conditions in each specific sub-area of a plot (Site-Specific Management, SSM) is crucial for efficient crop production. Excessive fertilizer application not only increases production costs for farmers but also leads to soil degradation and contamination of groundwater sources. Soil analysis using sensors is suitable for analyzing a large number of soil samples due to its low cost, quick operation, and applicability in agricultural fields. The main objective of this research is to develop a tool for measuring nitrate concentration in soil using a Nitrate Ion-Selective Electrode (Nitrate-ISE) along with a GPS system for automatic data recording on a secure digital card (SD card). The system is controlled by an Embedded Board (Arduino mega 2560) and consists of five main operations: 1. Soil extraction, 2. Measurement, 3. Cleaning, 4. Satellite coordinate detection, and 5. Controller and data logger. The analysis requires approximately 0.5 liters of clean water, and the

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time for each sample is around 5 minutes. The optimal soil-water ratio is 1:10, and the measurement time is 30 seconds. The average accuracy of the measurements is more than 80%, with an $R^2 = 0.80$ and RMSE = 1.44 compared to laboratory methods. This prototype reduces soil analysis costs by 5-6 times, providing reliable data for creating soil maps. This information can be used to support farmers in making decisions for nitrogen fertilizer management in subsequent crop cultivation.

Keywords: Nitrate, Soil Sensors, Soil Map

1 Introduction

Soil is a critical factor for plant growth and agriculture because it provides a foundation for plant roots, moisture, and essential nutrients for growth. It acts as a medium that supports plant roots, retains water, and supplies essential nutrients necessary for plant development. Without healthy soil, plants cannot thrive, which in turn affects agricultural productivity and food security. However, in modern commercial agriculture, chemical or organic fertilizers are commonly used to supplement essential nutrients like nitrogen (N), phosphorus (P), and potassium (K). These fertilizers are vital in enhancing soil fertility and ensuring that crops receive the nutrients required for optimal growth and yield.

The global use of nitrogen fertilizers has continuously increased between 1961 and 2014 (FAO, 2019), with Asia experiencing the highest increase compared to other regions. This trend reflects the intensification of agricultural practices aimed at boosting crop yields to meet the demands of growing populations and improving food security. In Thailand, for instance, fertilizers are typically applied at the same rate across entire fields, despite variations in nutrient levels and soil conditions within different areas of a field. This uniform application method is often inefficient and can lead to several adverse outcomes, both economically and environmentally.

Inefficient fertilizer use not only increases agricultural production costs, making it difficult to compete globally, but also leads to nutrient runoff, which pollutes surface and groundwater sources, and long-term soil degradation. Excessive fertilizer application can result in the leaching of nitrates into groundwater, posing health risks such as methemoglobinemia or "blue baby syndrome," and contributing to environmental hazards like eutrophication. Proper fertilizer application in specific

sub-areas within a field can help plants grow uniformly, increase yields, and improve soil organic matter and fertility over time (Haneklaus et al., 2010; Pamapolino et al., 2007). By tailoring fertilizer applications to the specific needs of different parts of a field, farmers can optimize resource use, enhance crop performance, and protect the environment.

However, appropriate fertilizer application requires soil analysis to assess nutrient concentrations. Traditional laboratory methods, while accurate, are expensive, require skilled operators, and are not economically viable for analyzing large numbers of soil samples. This reduces farmers' acceptance of precision agriculture practices (Heiniger et al., 2003). Additionally, there are costs associated with maintaining soil sample integrity during transportation and storage. The logistical challenges of collecting, transporting, and analyzing numerous soil samples can be prohibitive for many farmers, particularly those with limited resources or access to laboratory facilities.

Nitrate ions (NO_3^-) are a form of inorganic nitrogen in soil, easily dissolved in water, making them readily available for plant uptake (Soil Science Faculty, 2005). Nitrate is a crucial nutrient for plant growth, influencing protein synthesis and overall plant health. The presence or absence of nitrate nitrogen ($\text{NO}_3^- - \text{N}$) in the topsoil at a depth of approximately 30 cm often indicates whether plants can absorb enough nitrogen from the soil and how they will respond to additional fertilization (Fox et al., 1989). Generally, $\text{NO}_3^- - \text{N}$ in soil is absorbed by plants first (Schröder et al., 2000), making it a reliable indicator of soil fertility and the effectiveness of fertilization strategies.

Given the problems of improper fertilization and the limitations of laboratory soil analysis, the Agricultural Engineering Research Institute has developed a portable electrochemical device for nitrate concentration mapping using Ion-Selective Electrode (ISE) sensors. These sensors are commercially available and known

for their simplicity, reliability, and rapid response. The developed device integrates an Embedded Board for controlling its operations and data logging. This innovative approach aims to provide a cost-effective, accurate, and user-friendly solution for farmers to monitor soil nitrate levels rapidly, facilitating more precise and efficient fertilizer application. By enabling farmers to quickly and accurately assess the nitrate levels in their soil, this device helps to optimize fertilization practices, reduce environmental impact, and improve crop yields. The integration of GPS technology also allows for precise mapping of nitrate concentrations across different areas of a field, further enhancing the ability to apply fertilizers in a targeted manner.

2 Materials and Methods

2.1 Prototype Development

The prototype was developed with a focus on automating the entire process of nitrate concentration measurement in soil samples. The device integrates multiple components to perform soil extraction, measurement, cleaning, satellite coordinate detection, and data logging. The detailed design of the prototype's operational cycle is shown in Figure 1.

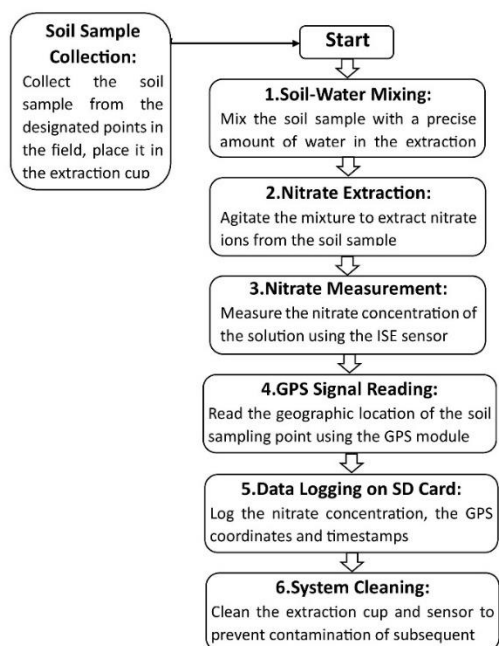


Figure 1 Workflow Chart of the prototype.

The core of the prototype's control system is an Arduino Mega 2560 microcontroller, chosen for its versatility and ample input/output capabilities. This

microcontroller coordinates the functions of various components, including pumps, sensors, and data storage devices.

Key Components and Their Functions:

1. Soil Extraction System: This system involves a mechanism for mixing soil samples with water to extract nitrate ions. The soil sample is placed in an extraction cup, and a precise amount of water is added. The mixture is then agitated to ensure thorough extraction of nitrates. The extraction process is critical for ensuring that the nitrate ions are sufficiently dissolved in the water for accurate measurement.

2. Measurement System: The core measurement component is the Sentek UK Nitrate 3021 Combination Ion Selective Electrode (ISE). This solid-state sensor is durable, easy to maintain, and provides rapid and reliable measurements. The sensor is connected to a 16-bits of analog-to-digital converter (ADC) before to the Arduino board, which digitizes the voltage readings. The Nitrate-ISE sensor operates based on the principle of ion-selective permeability, which allows it to specifically measure the concentration of nitrate ions in the soil extract.

3. Cleaning System: After each measurement, the extraction cup and electrode must be cleaned to prevent contamination of subsequent samples. The cleaning system includes a water pump and nozzles that thoroughly rinse the components. This step is automated to ensure consistency and efficiency, reducing the likelihood of cross-contamination and maintaining the integrity of subsequent measurements.

4. Satellite Coordinate Detection: A GPS module is integrated to record the geographic location of each soil sample. This data is crucial for creating precise nitrate concentration maps. The GPS coordinates are logged along with the nitrate concentration data, allowing for the creation of spatially accurate nutrient maps that can guide site-specific fertilizer application.

5. Controller and Data Logger: All operations are controlled by the Arduino board (Arduino mega 2560), which also logs data onto a secure digital (SD) card. The logged data includes point number, nitrate concentration (voltage, mV), GPS coordinates, and timestamps. The data logging system ensures that all relevant information is captured and stored for further analysis and mapping.

2.2 Sensor Calibration

Before deployment, the Nitrate ISE sensor is required for calibration with standard nitrate solutions of known concentrations. Solutions with concentrations of 1 ppm, 10 ppm, and 100 ppm were prepared. The voltage readings from the sensor for each solution were recorded, and a calibration curve was plotted.

The calibration curve is based on the Nernst equation (Morf, 1981; Adumchuk et al., 2002) as indicated by equation (1):

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

where E is the measured voltage (mV), E_0 is the standard constant potential, S is the slope (related to the sensor's sensitivity), and A is the activity (concentration) of the nitrate ions. This calibration curve allows conversion of voltage readings from soil samples into nitrate concentrations. The calibration process is essential to ensure that the sensor readings are accurate and reliable across the range of expected nitrate concentrations.

2.3 Testing for Key Factors in Laboratory

2.3.1 Optimal Soil-Water Ratio

To determine the optimal soil-to-water ratio for accurate nitrate extraction, 45 soil samples were collected from agricultural plots. Each sample was tested with three different soil-to-water ratios: 1:5, 1:10, and 1:20. Each sample was divided into two parts: one for testing with the prototype and one for standard laboratory analysis using 1.0 M KCl as the extractant. The results from the prototype were compared to the standard method to evaluate accuracy. This comparison ensured that the prototype's measurements were reliable and comparable to established laboratory methods.

2.3.2 Repeatability Testing

The repeatability of the prototype was tested by analyzing three soil samples, each divided into five portions. The soil-to-water ratio was set at 1:10, and the extraction time was 30 seconds. The consistency of voltage readings across replicates was evaluated to ensure reliable performance. High repeatability indicates that the prototype can produce consistent

results under the same conditions, which is crucial for its practical application in the field.

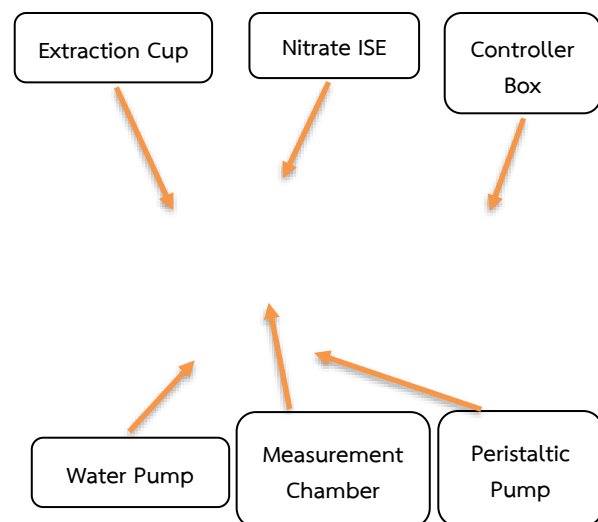
2.4 Field Testing

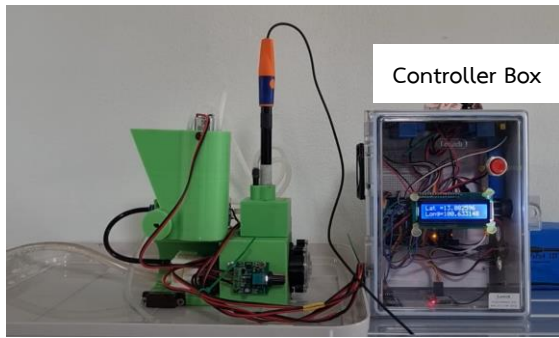
The field testing was conducted in a 1.6-hectare sugarcane field in U Thong District, Suphan Buri Province, Thailand. Measurement points were spaced approximately 15-30 meters apart. Soil samples were collected at a depth of 15-30 cm, homogenized, and divided into two parts: one for laboratory analysis and one for prototype testing. Each 10 g soil sample was mixed with 100 ml of clean water in the prototype, which then automatically performed the extraction, measurement, GPS recording, and data logging. The system cleaned itself after each sample to ensure accuracy for subsequent tests. Field testing in a real agricultural setting was essential to evaluate the prototype's performance under practical conditions and to identify any potential issues that might arise during actual use.

3 Results and Discussion

3.1 Prototype Design and Construction

The prototype's design was created using SolidWorks, and components were manufactured using a 3D printer. The assembly of the prototype for field testing is shown in Figures 2 and 3. The modular design allows easy assembly and maintenance. The use of 3D printing for component fabrication enabled rapid prototyping and iterative improvements, ensuring that the final design was both functional and practical for field use.





Figures 2 The extraction and measurement systems and controller box.



Figure 3 The prototype for field testing.

3.2 Sensor Calibration Results

Calibration with standard nitrate solutions showed a linear relationship between the measured voltage and the logarithm of nitrate concentration (Figure 4). The calibration equation derived from these results was used for converting voltage readings to nitrate concentrations during field and laboratory tests. The calibration curve demonstrated the sensor's ability to accurately measure nitrate concentrations across a wide range, providing confidence in the prototype's measurements.

Calibration by Standard Solution 1, 10 and 100 ppm

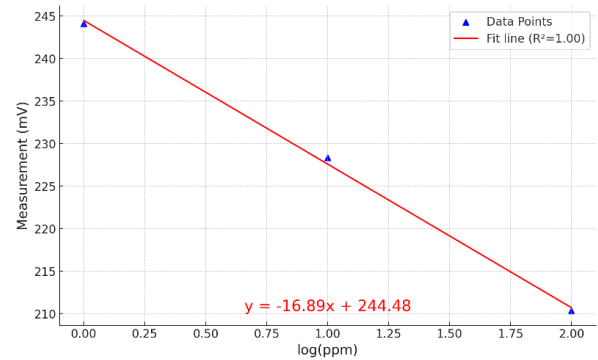
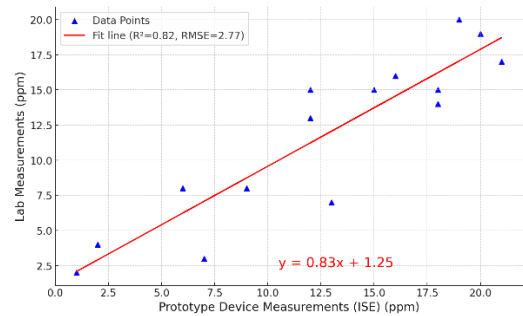


Figure 4 Nitrate-ISE calibration curve.

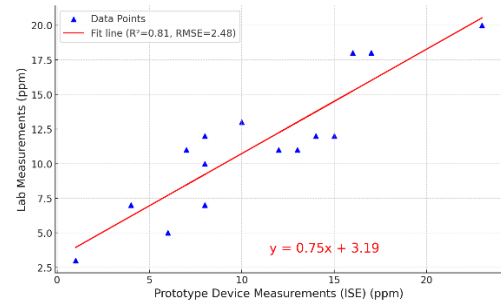
3.3 Optimal Soil-Water Ratio

Correlation between Prototype Device and Lab Measurements (1 : 5 Soil-water ratio)



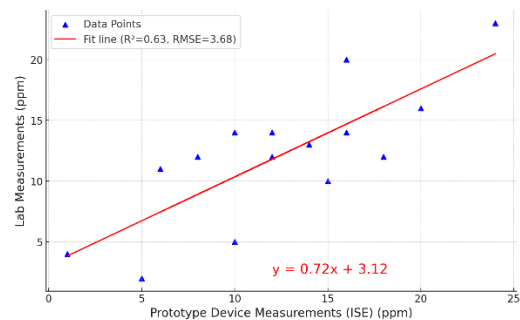
(a)

Correlation between Prototype Device and Lab Measurements (1 : 10 Soil-water ratio)



(b)

Correlation between Prototype Device and Lab Measurements (1 : 20 Soil-water ratio)



(c)

Figure 5 Comparison of soil: water ratio in the extraction process (a) 1:5 (b) 1:10 and (c) 1:20.

It can be seen from these figures that the analysis of the provided graphs elucidates the relationship between the prototype's nitrate concentration measurements and standard laboratory measurements for soil-to-water ratios of 1:5, 1:10, and 1:20. Each ratio was meticulously examined to ascertain the optimal balance between measurement accuracy and practical usability. The 1:5 ratio, characterized by the equation $y=0.83x+1.25$ and an R^2 value of 0.82, demonstrates a very strong correlation between the prototype's readings and the reference measurements, with a Root Mean Square Error (RMSE) of 2.77. This high accuracy indicates reliable performance; however, the elevated soil concentration complicates the cleaning process, rendering it less practical for repeated use in field settings where operational efficiency is paramount.

In contrast, the 1:10 ratio, represented by the equation $y=0.75x+3.19$ and an R^2 value of 0.81, also exhibits a strong correlation, nearly matching the accuracy observed with the 1:5 ratio. It has a lower RMSE of 2.48, indicating improved precision. This ratio is particularly noteworthy because it balances accuracy with practicality, maintaining reliable measurement precision while simplifying the cleaning and maintenance process. Consequently, the 1:10 ratio is more suitable for field conditions where ease of operation and time efficiency are critical considerations.

Conversely, the 1:20 ratio, depicted by the equation $y=0.72x+3.12$ and an R^2 value of 0.63, exhibits a significantly weaker correlation compared to the other two ratios. With the highest RMSE of 3.68, this ratio highlights its lower precision and reliability for nitrate detection. The increased dilution of the soil sample at this ratio adversely affects the accuracy of nitrate detection, rendering it less reliable for precise nutrient management. This reduced accuracy is likely due to the diminished concentration of nitrate ions in the solution, potentially falling below the sensitivity threshold of the sensor.

Therefore, considering both the accuracy of the measurements and the practicality of use, the 1:10 ratio emerges as the optimal choice for the prototype. It offers a robust correlation with reference measurements, ensuring reliable data collection, while also facilitating easier and quicker cleaning procedures, which are essential for efficient field operations. The

lower RMSE at this ratio indicates greater precision in nitrate measurement. This balance of accuracy and practicality underscores the suitability of the 1:10 ratio for authentic agricultural applications in actual field conditions.

3.4 Repeatability Testing

The prototype demonstrated high repeatability with consistent voltage readings across five replicates for each of the three soil samples. The standard deviation was low, indicating reliable performance (Table 1). High repeatability is essential for any analytical device, as it ensures that the results are consistent and reproducible, which is crucial for building confidence in the measurements and their subsequent use in decision-making.

Table 1 Testing for repeatability of the prototype.

	Measured Voltage (mV)		
	Samp.1	Samp.2	Samp.3
Rep. 1	233	230	233
Rep. 2	234	230	232
Rep. 3	231	230	235
Rep. 4	232	231	234
Rep. 5	230	231	235
Mean	232	230	234
Standard Deviation	1.58	0.55	1.30
Degree of freedom	4	4	4
Repeatability (pooled standard deviation)	1.22		

3.5 Field Testing Results

Field testing results showed good agreement between the prototype's measurements and laboratory analysis, with an accuracy of $R^2=0.80$ and $RMSE = 1.44$. The average accuracy was approximately 80%, confirming the prototype's reliability in practical applications (Figures 7). This high level of agreement between the prototype and laboratory measurements indicates that the device can consistently produce accurate results, making it a valuable tool for farmers and agricultural professionals.

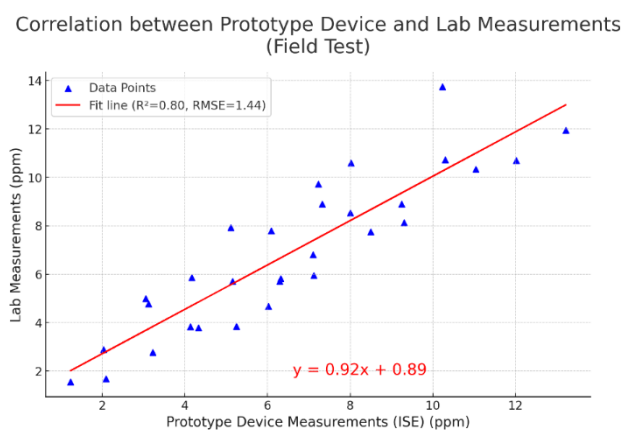


Figure 7 field test result.

The field-testing process involved collecting soil samples from a 1.6-hectare sugarcane field, ensuring that the prototype could handle large-scale operations. This was particularly important because the prototype allows for the flexibility to set the distance between sampling points as needed. By being able to specify the distance between each sampling point, we could ensure a comprehensive analysis of the field's nutrient distribution. This capability allows for tailored data collection strategies, accommodating the unique needs of different crops and field layouts.

Each sample was carefully analyzed, and the data were logged for comparison with traditional laboratory methods. The results not only validated the accuracy of the prototype but also showcased its efficiency in terms of time and cost savings. The quick operation time for obtaining results from the prototype allows for timely decision-making, which is essential for effective nutrient management.

Furthermore, the integration of GPS technology in the prototype provided precise location data for each soil sample. This feature enabled the creation of detailed nitrate concentration maps, which are invaluable for site-specific management practices as shown in figure 8. By using these maps, farmers can apply fertilizers more efficiently, targeting specific areas that require additional nutrients and reducing the overall amount of fertilizer needed. This targeted approach helps to minimize environmental impact, conserve resources, and optimize crop yields.

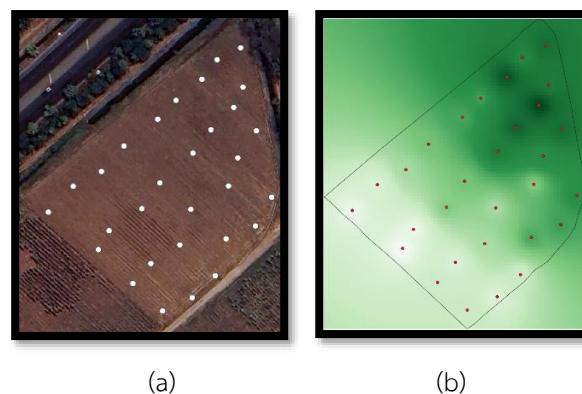


Figure 8 (a) measuring points in the field and (b) nitrate concentration maps generated by the dataset from the prototype.

4 Conclusion

The research successfully developed a portable automated nitrate concentration meter using Ion-Selective Electrodes (ISEs) for nitrate concentration mapping in soil. The prototype integrates an Embedded Board for automated operation and data logging, providing reliable and rapid nitrate measurements. The compact design allows easy field use, enabling farmers to make timely and informed decisions on nitrogen fertilizer management. Compared to traditional laboratory methods, the prototype significantly reduces analysis time and costs, enhancing the feasibility of precision agriculture practices.

The device's development and field testing indicate that it can effectively support precision nutrient management in agriculture. Future improvements may include enhancing sensor sensitivity, reducing sample preparation time, and integrating additional functionalities for comprehensive soil health monitoring. Potential advancements could also involve the development of a multi-parameter sensor system that could simultaneously measure other critical soil nutrients, further enhancing the tool's utility for precision agriculture.

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