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Soil Nutrient Assessment Using Ion-Selective Electrode-Based Nutrient Analyzer for Precision Agriculture

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Abstract: Rapid and accurate soil nutrient assessment is critical for precision agriculture. This study presents a portable and intelligent soil nutrient analyzer based on ion-selective electrodes (ISE) for rapid, on-site estimation of potassium, nitrate, and chloride. Unlike image-based or machine learning approaches that rely on indirect inference, the proposed system directly measures ion activity using electrochemical sensing, ensuring higher reliability under field conditions. The device integrates sensing, signal conditioning, self-calibration using polynomial regression, and wireless data transmission for real-time soil health assessment. A total of 546 soil samples collected from diverse agricultural locations in Dhanbad district, India, were used for validation, with measurements compared against standard laboratory methods including flame photometry and UV-Vis (ultraviolet-visible) spectrophotometry. The developed system achieved high correlation coefficients of 0.994 (potassium), 0.933 (nitrate), and 0.946 (chloride). Statistical evaluation using RMSE (root mean square error), measurement uncertainty, and hypothesis testing confirms the robustness of the calibration model. The study highlights the advantages of direct sensing over image-based prediction methods, particularly in terms of accuracy, environmental robustness, and practical deployment. Limitations related to sensor drift, soil heterogeneity, and field conditions are also discussed. The proposed system provides a scalable and cost-effective solution for precision agriculture and real-time soil monitoring.

Keywords: Soil Nutrient Analysis; Ion-Selective Electrodes; Precision Agriculture; Soil Nutrient Prediction

1. Introduction

Soil fertility plays a fundamental role in agricultural productivity, influencing plant growth through the availability of essential nutrients, water, and physicochemical conditions [1]. Among the sixteen essential plant nutrients, thirteen are primarily derived from soil and are categorized into macronutrients and micronutrients based on plant requirements. Nitrogen, phosphorus, and potassium (NPK) are particularly critical macronutrients that regulate vegetative growth, biochemical processes, and nutrient transport within plants [2–4].

In the Indian agricultural context, maintaining soil fertility has become increasingly challenging due to intensive cultivation, imbalanced fertilizer use, and growing population pressure [5]. Government initiatives such as the Soil Health Card Scheme aim to promote periodic soil testing; however, conventional laboratory-based methods remain time-consuming, resource-intensive, and inaccessible to small-scale farmers. These limitations highlight the need for rapid, cost-effective, and field-deployable soil nutrient assessment technologies.

Assessments conducted through nutrient index and balance sheets have revealed that many regions in India suffer from nutrient deficiencies in the soil, primarily due to inadequate fertilization and composting practices [6].

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Consequently, regular soil nutrient testing is crucial to determine the appropriate amount of fertilizers required for specific crops in particular areas [7,8].

Different soil testing techniques are accessible in laboratories to analyze the presence of diverse nutrient elements in soil [9]. However, these methods come with certain drawbacks such as increased chemical usage, extended analysis duration, expensive per-sample analysis, and the need for specialized knowledge. Consequently, these techniques are impractical for farmers who lack the necessary time, financial resources, and expertise to conduct these analyses. Furthermore, it is important to note that these methods are primarily conducted in laboratory settings.

In recent times, a portable device for measuring nutrients has been developed and validated by various researchers, which eliminates or reduces the need for chemicals [10, 11]. The optical sensing method is the most commonly employed technique for nutrient measurement. This method, known as visual sensing, utilizes the visible and infrared range of the spectrum and is a form of spectroscopy [12]. By exploiting the distinctive spectral properties of soil nutrients, this method enables their identification and analysis [11]. Numerous devices have been developed using light-emitting diodes (LED) as transmitters and photodiodes as detectors [13]. The setup involves transmitting light of a specific wavelength from the LED, which then passes through the soil solution. During this process, a portion of the light is absorbed, while the remaining light is detected by the photodiode. The device subsequently employs the intensity of absorbed radiation to quantify specific nutrients based on the wavelength of the transmitter [10]. However, this method does have a significant drawback. The spectral range data for nutrients varies depending on the soil type and chemical reagent used, thereby limiting the applicability of this device to different soil types [13]. Another widely used method is the colorimetric technique. This approach involves utilizing soil testing kits to generate colour in the soil solution, which is then compared to a reference colour chart to determine the nutrient level [11].

Several studies have employed electronic devices to automate the process of manual colour comparison [14]. One commonly used colour sensor in these studies is the TCS3200 sensor. However, a drawback of this approach is its reliance on pre-made colour developing kits. If these kits are not readily available, the device becomes unusable which makes it difficult for farmers to use [15].

In recent years, computer vision and machine learning approaches have been explored for soil nutrient estimation using image-based features such as color, texture, and spectral reflectance [16]. While these methods offer scalability and rapid analysis, their performance is highly dependent on imaging conditions, dataset quality, and model generalization. Variability in lighting, soil moisture, and texture often limits their reliability in field conditions. Nevertheless, this method also requires expertise, making it impractical for farmers [15].

In contrast, electrochemical sensing using ion-selective electrodes provides direct measurement of ion activity, reducing dependency on environmental factors and eliminating the need for large labelled datasets [17–21]. Therefore, the present study focuses on a sensor-based approach while acknowledging the potential of hybrid systems integrating sensing with data-driven models. Ion-selective electrode (ISE) uses electrochemical sensors to create a cost-effective, user-friendly, and portable soil nutrient testing device [22–25].

Despite numerous research studies conducted on ion-selective electrode (ISE), it is still primarily used in laboratory settings. This is mainly due to the issues of drifting sensitivity, calibration, and accuracy associated with ISE [26]. To enhance accuracy and minimize drifting errors, a self-calibration approach combined with statistical methodology should be implemented. The present study proposes the development of an ISE-based soil nutrient analyzer that incorporates self-calibration functionality. The effectiveness of this device was validated by comparing its analysis results with those obtained from established laboratory-based testing methods such as flame photometry, spectrophotometry, and manual titration techniques. It is important to note that the developed device requires calibration each time it is switched off and restarted, as the phenomenon of drift can cause deviations in sensor response voltage over extended measurement periods [27]. Thus, the hypothesis, objectives and novelty of the present study are as follows:

1. Hypothesis
   The hypothesis of the present study is that the development of a smart portable ISE-based soil nutrient analyzer, coupled with advanced calibration methods and software modelling, will lead to accurate and efficient measurement of soil nutrients in both field and laboratory settings.
2. Objectives

The objectives of the study were to:

- Develop a smart portable ISE-based soil nutrient analyser.
- Accurately measure potassium, nitrate, and chloride levels in soil samples in both field and laboratory environments.
- Validate the device using a diverse range of field soil samples and conventional laboratory methods.

3. Novelty

- Development of a portable ISE-based soil nutrient analyzer with integrated self-calibration.
- Implementation of polynomial regression for improved sensor accuracy and drift compensation.
- Extensive validation using 546 real soil samples with laboratory-grade reference methods.
- Demonstration of superior reliability compared to indirect image-based estimation methods.
- Integration of sensing, data logging, and wireless communication for precision agriculture applications.

4. Core Ideas

- A smart portable ion-selective electrode-based soil nutrient analyzer has been developed.
- The device accurately measures potassium, nitrate, and chloride of soil both in the field and laboratory.
- The device's precision has been enhanced by integrating a self-calibration process and polynomial fitting model.
- The developed software model generates soil health cards and fertilizer doze recommendation for different crops.
- The device is thoroughly validated using a wide range of field soil samples and conventional laboratory methods.

2. Soil Nutrient Analyzer

The portable soil nutrient analyzer that has been developed can measure the concentration of nutrients in soil and present the results on its own display. Additionally, this device is equipped with a self-calibration feature, ensuring precise and reliable measurements.

2.1. Device Design

The ISE was utilized in the development of the device. To enable wireless data transmission from the field to the cloud server, a wireless fidelity (Wi-Fi) module (ESP-01) was incorporated. The overall soil nutrient analyzer is illustrated in **Figure 1**. This device comprises various components, including the input unit, ISE, sensing, calibration, control unit, display unit, data logger, and wireless module. The ISE produces a minute direct current (DC) electrical signal, which is amplified and then analyzed and calibrated by a microcontroller. The sensing, calibration, and control unit is specifically designed to gather data from the ISE. Additionally, the device is equipped with a 4 × 3 keypad, which allows the user to input commands for device operation and calibration. The 20 × 4 liquid crystal display (LCD) screen displays the nutrient concentration and serves as an interface for user interaction during the calibration process. The hardware component comprises various elements such as an ISE, a data acquisition module, an integrated power module, an input interface, an output/LCD interface, a data logger interface, and a wireless module.

2.2. Ion-Selective Electrode

ISEs are used for analyzing specific ions in a liquid solution by relating the measured ions to the electrical potential generated at the electrode [28]. These electrodes are a form of electrochemical sensors and comprise an ion-selective electrode, a reference electrode, and an ion-selective membrane. The following Nernst equation [29] is employed to calculate the potential difference corresponding to the concentration of ions to be measured:

$$E = E^{\circ} + (2.030\ RT/nF) logC \tag{1}$$

where, E = measured potential (mV) between the ion-selective and the reference electrode, E° = measured potential (mV) at the lower concentration standard, R = gas constant (8.314 joules/mole-Kelvin), T = temperature (in °K), n = charge of the target ion, F = Faraday constant (96,485 coulomb/mol), and C = concentration of target ion.

The ISEs used have polyvinyl chloride (PVC) membranes which have exceptional durability. The design of the PVC-based ion-selective electrode employed in this research endeavor is illustrated in **Figure 2**.

Figure 1. View of the developed soil nutrient analyzer.

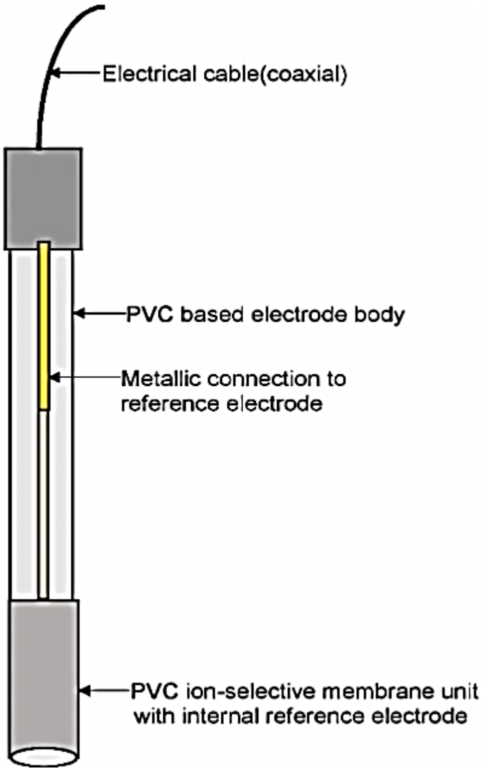


Figure 2. Polyvinyl chloride-based ion-selective electrode.

Various ISEs exhibit distinct measuring ranges, as indicated in **Table 1**. It also highlights the presence of numerous ions that can potentially interfere with the electrode membranes. In order to address this concern and ensure the device's accuracy, various soil extracting solutions were tested and evaluated.

Table 1. Specification of ion-selective electrodes.

Parameter	**Values**		
	Potassium	**Nitrate**	**Chloride**
Range	1–39,000 mg/L (or ppm)	1 to 14,000 mg/L (or ppm)	10 to 20,000 mg/L (or ppm)
Interfering ions	Rb^{2+}, Cs^{2+}, NH_4^+, Ca^{2+}, Mg^{2+}, Li^+	ClO_4^-, I^-, ClO_3^-, CN^-, BF_4^-	CN^-, Br^-, I^-, S^{2-}
pH range	2–12	2–11	2–12
Temperature range	0 to 40 °C (not compensated)	0 to 40 °C (not compensated)	0 to 40 °C (not compensated)
Reproducibility (precision)	± 11% of full scale	± 10% of full scale (calibrated 1 to 100 mg/L)	± 10% of full scale (calibrated 10 to 1,000 mg/L)

2.3. Data Acquisition Module

This module comprises ion-selective electrodes, an electrode interfacing board with an operational amplifier, a 4:1 analog or digital multiplexer/demultiplexer, and a microcontroller, as illustrated in **Figure 3**. The Arduino Mega development board, which possesses a flash memory of 256 KB, is utilized for this purpose. The weak signals (in mV) received from the electrode are amplified by an operational amplifier (LM358). The resulting electrical voltage signal from the ion-selective electrode is then transmitted to the analog pin of the microcontroller. Additionally, an analog/digital multiplexer/de-multiplexer is incorporated into the electrode interfacing board to enable the selection of different electrodes for connection to various analog pins on the board. This allows for the simultaneous interfacing of up to four electrodes. However, to prevent electromagnetic or power-line interference between the electrodes, a dedicated data acquisition module has been designed for each individual electrode [30].

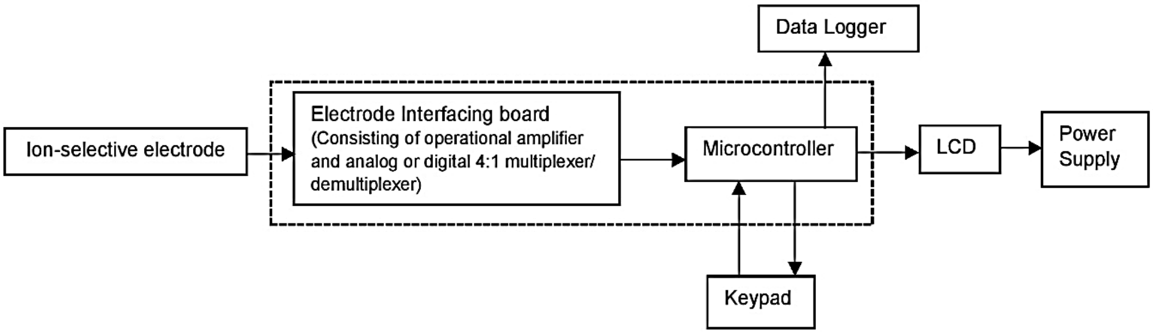


Figure 3. Block diagram of the data acquisition module.

The data acquisition module operates on a +5 V power supply provided by an integrated power module through the integrated circuit (IC: LM7805). The Arduino Mega features a 16-channel, 10-bit analog-to-digital (A/D) converter. The analog pin to which the electrode's output is connected is further linked to the on-board converter, which scales the output to integer values ranging from 0 to 1,023.

2.4. Device Operation

The block diagram presented in **Figure 3** illustrates the components of the soil nutrient analyzer. These components include an external power source, ISE, electrode interface module, Wi-Fi module (ESP-01), microcontroller, keypad, LCD, and data logger.

Upon activation of the device, the user must first perform calibration. This involves entering the number of standards and subsequently testing each standard individually, following the instructions displayed on the LCD. Once calibration is completed, the device prompts the user to enter the sample number for testing. The measured values of the samples are then recorded in the data logger, along with their respective sample numbers. Additionally, the measured values are transmitted to a cloud database via the Wi-Fi module. Following this, the data obtained from soil tests are employed to generate soil health cards.

3. Materials and Methods

The developed device has been calibrated for better accuracy. Further, performance assessment has been carried out by comparing the sensors' data of various soil samples with other available standard testing methods.

3.1. Calibration Method

Calibration involves the comparison of known standards with the measurement results obtained from the calibrated device [31]. It necessitates the use of various standard solutions. Therefore, the materials and procedures for preparing the extraction solution for calibration are elucidated subsequently.

3.1.1. Extracting Solutions

To determine the available potassium content in the soil, a 0.5 M (molar) barium chloride ($BaCl_2$) solution was used for extraction [32,33]. For nitrate, the soil was extracted using 0.5 M copper sulfate ($CuSO_4$) and 0.6% silver sulfate (Ag_2SO_4) solutions. For chloride extraction, a solution was prepared using 0.01 M calcium nitrate ($Ca(NO_3)_2$) [34].

3.1.2. Preparation of Standard Solution for Calibration

The standard solutions were prepared for potassium, nitrate, and chloride soil nutrients following the steps summarized in **Table 2**.

Table 2. Steps for standard preparation for calibration.

Step No.	Process	Potassium	Nitrate	Chloride
1	The standard solution was prepared by adding X to Y extracting solution as mentioned in **Table 2**	X = KCl Y = Potassium	X = KNO_3 Y = Nitrate	X = KCl Y = Chloride
2	Calibration of the ISE sensor was done following the standard values (μg/mL)	5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, and 100	1, 2, 4, 6, 8, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, and 20	5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, and 100

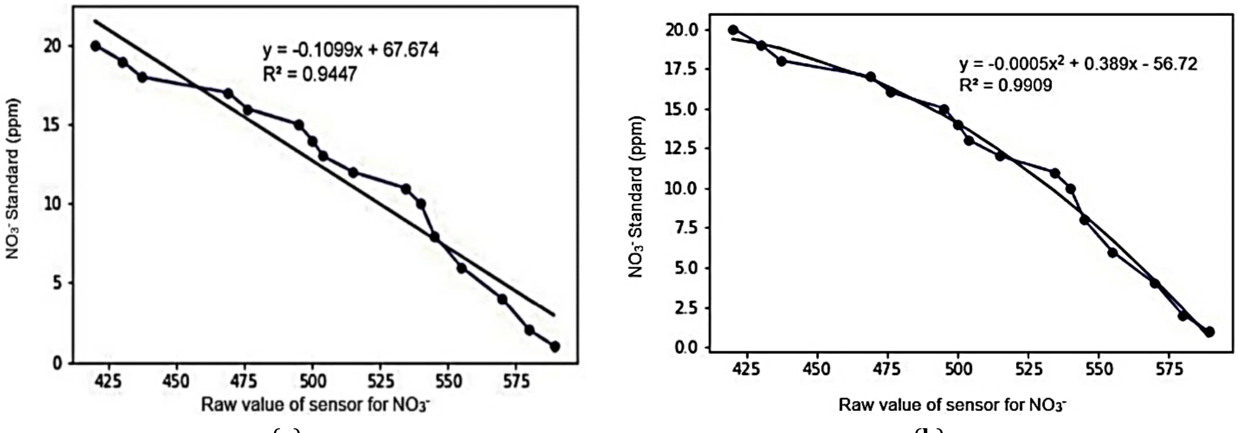
3.1.3. Calibration Model Selection

Equation (1) provides a means to anticipate the correlation between the potential difference observed at the electrode and the concentration of the specific nutrient being measured in ISE [29]. It can be deduced that the potential generated at the electrode is directly proportional to the logarithm of the nutrient's concentration ($\log C$). However, it is important to acknowledge that other ions present in the soil can interfere with the electrodes, causing them to react. While Equation (1) predicts the activity of the desired nutrient by solely considering its presence in the solution, it is crucial to account for the influence of interfering ions when predicting the behavior of an ion-selective electrode. Therefore, the Nikolsky-Eisenman equation [35], presented as Equation (2), should be employed to forecast the behavior of ion-selective electrodes.

$$E = Constant + \left(2.030\frac{RT}{z_A F}\right) log \left[a_A + K_{A,B}^{pot} \times a_B^{\frac{z_A}{z_B}} + K_{A,C}^{pot} \times a_C^{\frac{z_A}{z_C}} + \ldots + K_{A,n}^{pot} \times a_n^{\frac{z_A}{z_n}}\right] \tag{2}$$

Where, E = experimentally measured galvanic potential change of ISE cell (in mV) when only variables are active in the test solution; R = gas constant equal to 8.314510 joules/mole-Kelvin; T = absolute temperature in °K; F = Faraday constant, 96,485 coulomb/mol; a_A = activity of the desired ion; a_B and a_C = activities of the interfering ions, B and C, respectively; $K_{A,B}^{pot}$ through $K_{A,n}^{pot}$ = potentiometric selectivity coefficients for ions B through nth concerning the primary ion A; Z_A = charge number, an integer with a sign and magnitude analogous to the charge of the principal ion, A; and Z_B through Zn = charge numbers analogous to the charge of interfering ions, B through nth, respectively.

Based on the equation provided, it can be deduced that the potential generated at the electrode is not directly proportional to the concentration of the desired nutrient. Consequently, employing a linear regression model for calibration is not the most suitable approach. To enhance the calibration of the developed device, researchers conducted experiments using both linear and polynomial regression modeling [36]. The outcomes of these regression models are applied for nitrate, potassium, and chloride calibration of ISEs. **Figure 4** presents regression analysis results for nitrate.



(**a**) (**b**)

Figure 4. Regression analysis results for nitrate, (**a**) linear regression, and (**b**) polynomial regression.

The determination coefficient (R^2) obtained from the linear and polynomial regression analysis for nitrate were 0.945 and 0.990, for potassium were 0.947 and 0.988, and for chloride were 0.998 and 0.999, respectively. The comparative evaluation of linear and polynomial regression models across nitrate, potassium, and chloride datasets demonstrated consistently higher coefficients of determination (R^2 > 0.98) for polynomial fitting. This confirms the non-linear response behavior of ion-selective electrodes and justifies the selection of second-order polynomial models for calibration.

3.1.4. Calibration Procedure

A comprehensive overview of the calibration steps can be found in **Table 3**.

Table 3. Steps for calibration of the developed ISE-based device.

Calibration Step	Required Action
1	Switch on the device.
2	Press 2 to select calibration mode.
3	Enter number of standards through keypad.
4	Enter the value of first standard followed by # and put the sensor in relative standard solution simultaneously.
5	Wait till the analysis duration as required by the device.
6	After analysis, the device will ask to enter the value of next stand solution.
7	Follow steps from 4 to 5 for all the other standard solutions.
8	The standard values entered should be in a sequence either in ascending or descending manner.
9	Device calculates the calibration coefficients and develops a polynomial regression equation for unknown solutions.
10	Calibration is completed.

Given the curvilinear path followed by the electrode's measurement behavior, a calibration approach utilizing second-order polynomial regression models was employed. Equation (3) represents the specific form of the second-order polynomial regression model in one variable.

$$y = \beta_2 x^2 + \beta_1 x + \beta_0 \tag{3}$$

Where, y = nutrient concentration, x = ISE's output converted into digital from on board A/D converter on microcontroller, β_2 = quadratic effect parameter, β_1 = linear effect parameter, and β_0 = y, when x = 0. The flowchart for calibration coefficient calculation procedure of the device is depicted in **Figure 5**.

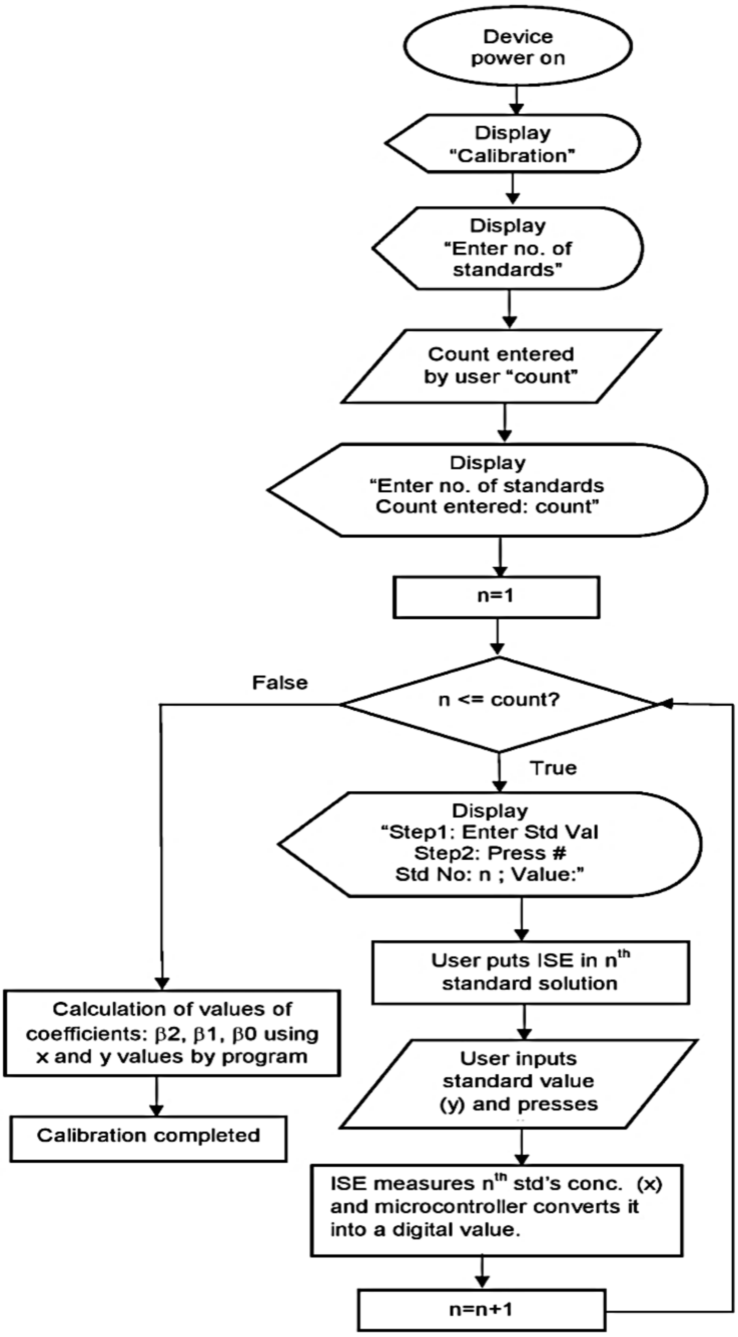


Figure 5. Flowchart for the calculation of calibration coefficients during calibration on device.

3.1.5. Calibration Coefficients Calculation

In order to calculate the sensor value using a second-order polynomial regression model, three coefficients (β_2, β_1, and β_0) need to be determined. The minimum number of calibration points needed for this model is four, which is determined by using the lowest degree of the polynomial for the electrode's characteristic. These coefficients can be obtained by solving a quadratic system of equations with four equations (considering the minimum number of points). It is important to note that increasing the number of calibration points will result in longer calibration time [37].

Let the four calibration points or standards be y_1, y_2, y_3, and y_4, with sensor's raw output be x_1, x_2, x_3, and x_4. Thus, a quadratic polynomial equation passing through these points: (x_1, y_1), (x_2, y_2), (x_3, y_3), and (x_4, y_4) is required to be found based on the following equations:

$$y_1 = \beta_2 x_1^2 + \beta_1 x_1 + \beta_0 \tag{4}$$

$$y_2 = \beta_2 x_2^2 + \beta_1 x_2 + \beta_0 \tag{5}$$

$$y_3 = \beta_2 x_3^2 + \beta_1 x_3 + \beta_0 \tag{6}$$

$$y_4 = \beta_2 x_4^2 + \beta_1 x_4 + \beta_0 \tag{7}$$

The coefficients can be determined by resolving a quadratic system of the Equations (4)–(7).

3.2. Performance Assessment

Performance evaluation of the developed device involved analyzing 546 soil samples collected from different locations within Dhanbad district in the state of Jharkhand, India. These samples underwent testing for nitrate, potassium, and chloride using the developed ISE-based soil nutrient analyzers. To assess the accuracy of the developed device, the same soil samples were also tested using other reference methods.

For potassium, the results of ISE were compared with those of flame photometric method, as well as a spectrophotometry-based digital soil testing kit (Make: Labtronics, India; Model: LT-671, Soil test fertilizer recommendation [STFR] meter). In the case of nitrate, the results of ISE method were compared with those obtained using an ultraviolet-visible (UV-Vis) spectrophotometer (Make: Systonic, India; Model: S-92). Lastly, for chloride, the results obtained through the ISE method were compared with those obtained using the UV-Vis spectrophotometer.

The developed ISE-based soil nutrient analyzers were utilized to analyse 46 soil samples in the agricultural fields where they were obtained (**Figure 6a**). On the other hand, the remaining soil samples (500), which were collected from different agricultural fields, underwent analysis using the ISE-based soil nutrient analyzers at the chemical test laboratory (**Figure 6b**) of the Central Institute of Mining and Fuel Research (CIMFR), India (23°49′03.08″ N and 86°25′40.17″ E).

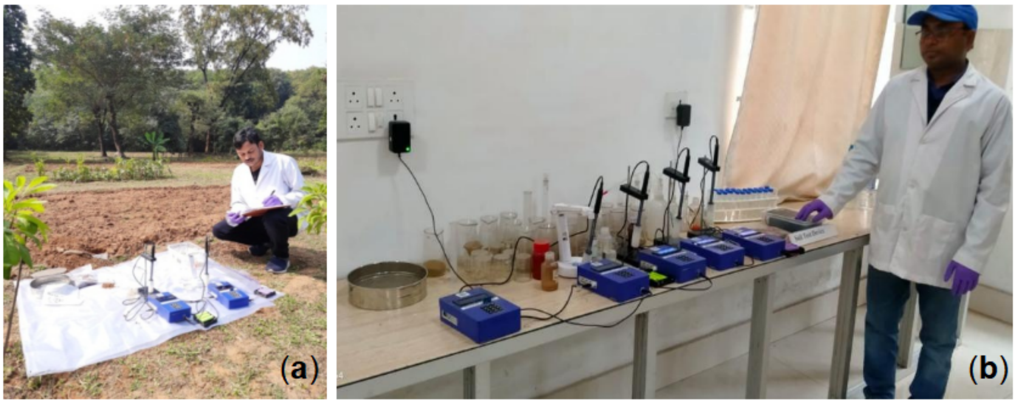


Figure 6. Soil nutrient analysis using ion-selective electrodes (ISE)-based soil nutrient analyzers (**a**) within agricultural fields and (**b**) in the laboratory at CIMFR, Dhanbad, India.

3.2.1. Soil Sampling

Figure 7 illustrates the initial level of soil preparation methods that are universally applicable to all nutrients.

3.2.2. Sample Preparation

The process of preparing the soil sample with the extracting solution was carried out according to the procedures outlined in **Table 4**.

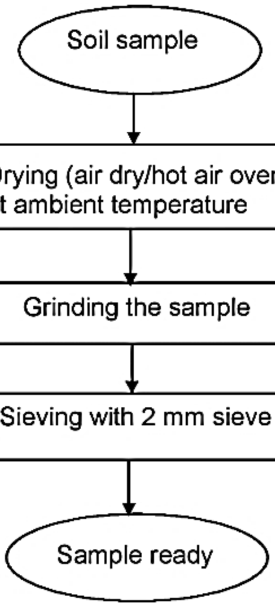


Figure 7. Soil sampling procedure.

Table 4. Steps for soil sample preparation with extracting solution.

Step No.	Process	Potassium	Nitrate	Chloride
1	The soil sample is prepared as per the steps specified in **Figure 1**	Yes	Yes	Yes
2	*X* g of prepared soil sample is taken in *Y* ml of the Z extracting solution as mentioned in **Table 2**	*X* = 5 g *Y* = 100 mL *Z* = Potassium	*X* = 5 g *Y* = 25 mL *Z* = Nitrate	*X* = 10 g *Y* = 25 mL *Z* = Chloride
3	2.5 g charcoal powder is added to the prepared solution	Not applicable	Not applicable	Yes
4	Then, it is shaken for *X* minute on the mechanical shaker and filtered with Whatman No. 42 filter paper	*X* = 30 min	*X* = 10 min	*X* = 30 min
5	The clear supernatant obtained is ready for analysis in the *X* ion-selective electrode sensor	*X* = Potassium	*X* = Nitrate	*X* = Chloride

3.2.3. Sample Testing Procedure

The steps required for testing soil sample using the developed ISE-based device are summarized in **Table 5**.

Table 5. Sample testing procedure using the developed device.

Step	Action Required
1	After calibration, press 3 to select sample testing mode.
2	Enter sample ID followed by #.
3	Wait till the device calculates the nutrient's concentration and LCD displays 'Testing...'.
4	Sample value is displayed on LCD and stored in data logger.
5	Press 3 to test another sample and follow steps from 2 to 4.
6	Press 5 to exit test.

3.2.4. Reference Test Methods

The flame photometer method [38] and spectrophotometry using the STFR meter was used for Potassium determination.

For the determination of nitrate and chloride, a UV-Vis spectrophotometer was employed as the reference test method [38].

3.2.5. Dataset Description

The dataset used for validation consisted of 546 soil samples collected from multiple agricultural locations within Dhanbad district, Jharkhand, India. The samples represent a range of soil conditions, including variations in texture, moisture, and nutrient levels typical of the region. Out of these, 46 samples were tested directly in field conditions, while 500 samples were analyzed under controlled laboratory conditions.

Each soil sample was processed using standardized extraction procedures and tested using both the developed ISE-based analyzer and reference laboratory methods (flame photometry and UV-Vis spectrophotometry), ensuring reliable ground truth measurements.

3.2.6. Statistical Analysis

Statistical analysis was conducted to evaluate the performance of the fitting model on the soil test analysis data. Various tests were executed to demonstrate the efficacy of the fitting model on both calibration and sample tests, including F-test, T-test, and measurement uncertainty test. Additionally, descriptive analysis tests were carried out by computing parameters such as root coefficient of determination, coefficient of correlation (r), mean square error, and standard deviation [39]. These tests were performed with a 95% confidence level using the test data obtained. The null hypothesis and alternative hypothesis assumed for the above tests are as follows:

- The null hypothesis states that the polynomial fitting model is correct and fits the data as well.
- The alternative hypothesis states that the linear fitting model fits the data superior than the polynomial fitting model.

To ensure robustness, statistical validation was performed using multiple metrics including RMSE, coefficient of correlation (r), measurement uncertainty (MU), and hypothesis testing at a 95% confidence level. Although cross-validation is typically used in machine learning, the present study ensures generalization through:

- Large and diverse sample size (n = 546),
- Comparison with standard laboratory methods,
- Testing under both field and laboratory conditions.

The consistency of results across these conditions demonstrates strong generalization capability of the proposed system.

3.3. Data-Driven Modeling Approach

Although machine learning techniques are widely used in soil analysis, the present study employs a physics-guided statistical modeling approach rather than data-intensive machine learning models. Specifically, a second-order polynomial regression model is used for sensor calibration, derived from the electrochemical behavior of ion-selective electrodes.

This approach ensures interpretability, low computational complexity, and suitability for embedded systems, unlike black-box machine learning models that require large datasets and extensive training.

3.4. Integrated Modeling Framework

The study establishes following unified framework linking sensing, calibration, and validation:

- Sensor layer: Ion-selective electrodes generate voltage signals corresponding to ion activity.
- Calibration layer: Raw sensor outputs are processed using second-order polynomial regression to account for non-linearity and ion interference.
- Statistical validation layer: Model outputs are evaluated using R^2, RMSE, F-test, and T-test to ensure reliability.
- Comparative analysis layer: Calibrated outputs are benchmarked against standard laboratory methods (UV-Vis spectrophotometry and flame photometry).
- Application layer: Processed data is used for soil health assessment and fertilizer recommendation.

This integrated pipeline ensures consistency between sensing, modeling, and validation, overcoming limitations of fragmented approaches used in earlier studies.

4. Results and Discussions

4.1. Calibration Results

The accuracy of the calibration model and the ability to predict future values can be measured using the coefficient of determination (R^2) in polynomial regression [40]. The R^2 value of zero indicates that the sensor cannot be calibrated as it cannot predict the concentration of the nutrient based on raw readings. On the other hand, an R^2 value closer to 1 indicates a successful calibration, with the sensor accurately predicting the nutrient's concentration. In the case of chloride, potassium, and nitrate, the R^2 values obtained from polynomial fitting were 0.999, 0.988, and 0.991, respectively (**Figures 8–10**). These values being close to 1 suggest that polynomial fitting is the best choice for calibration. The calibration curves shown in **Figures 8–10** represent the standardization graphs obtained for each nutrient using one data set. To calibrate the respective sensor, the best fit curve for the specific nutrient must be used each time.

The ISE-based soil nutrient analyzer underwent testing using the standard solution, and the results were compared with the standard/reference methods. The linear regression graphs for chloride, potassium, and nitrate can be observed in **Figures 11–13**.

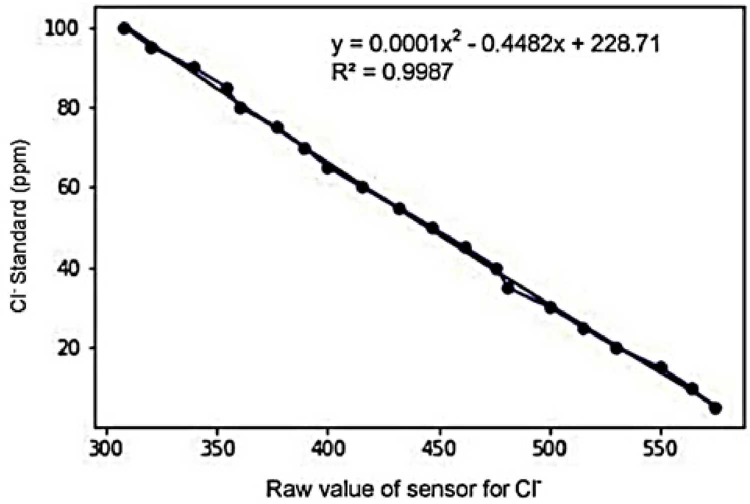


Figure 8. Chloride calibration graph.

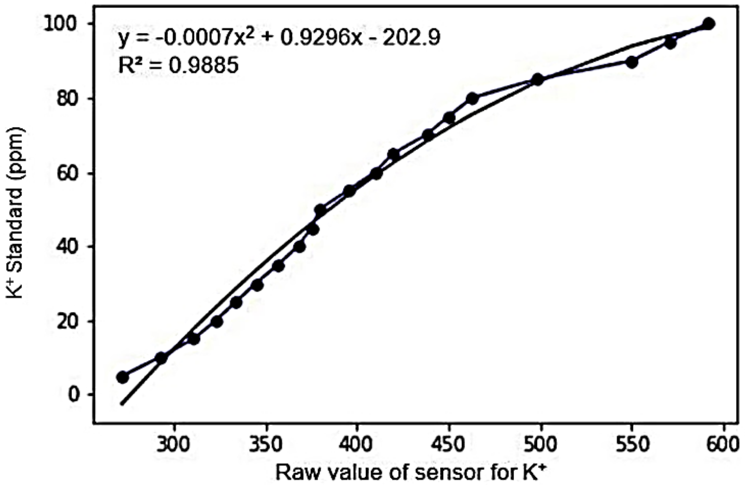


Figure 9. Potassium calibration graph.

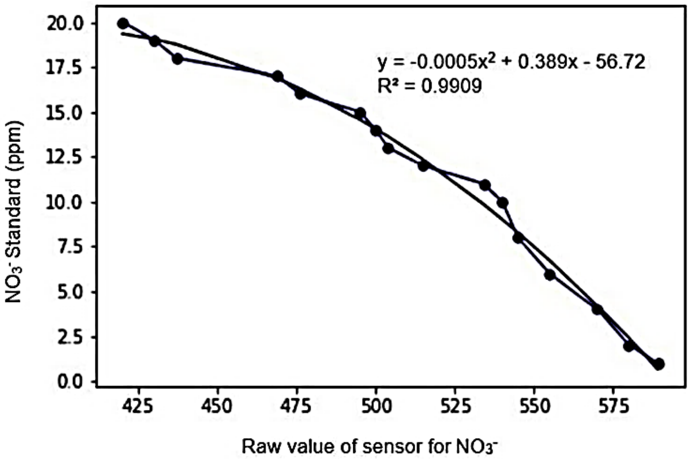


Figure 10. Nitrate calibration graph.

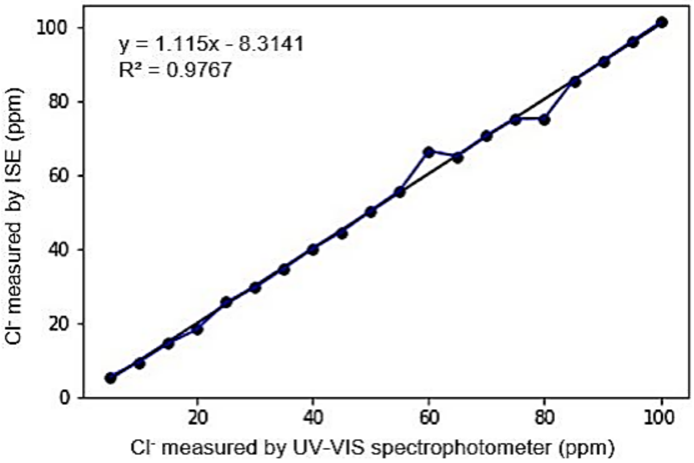


Figure 11. Linear regression graph for chloride test results by ion-selective electrodes (ISE) and ultraviolet-visible (UV-Vis) spectrophotometer.

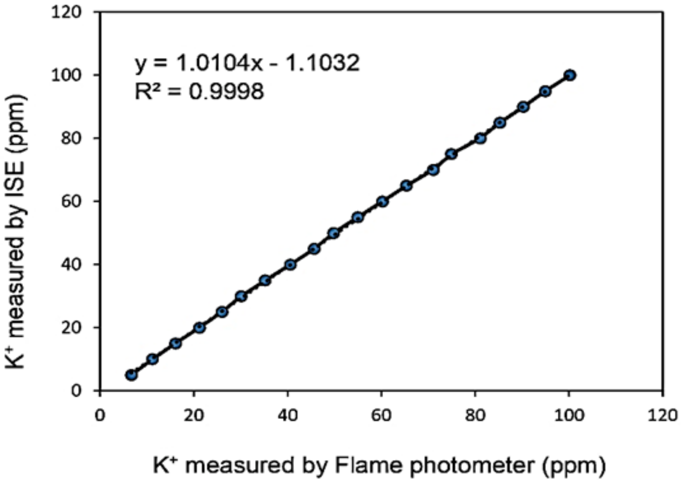


Figure 12. Linear regression graph for standard potassium test results by ion-selective electrodes (ISE) and flame photometer.

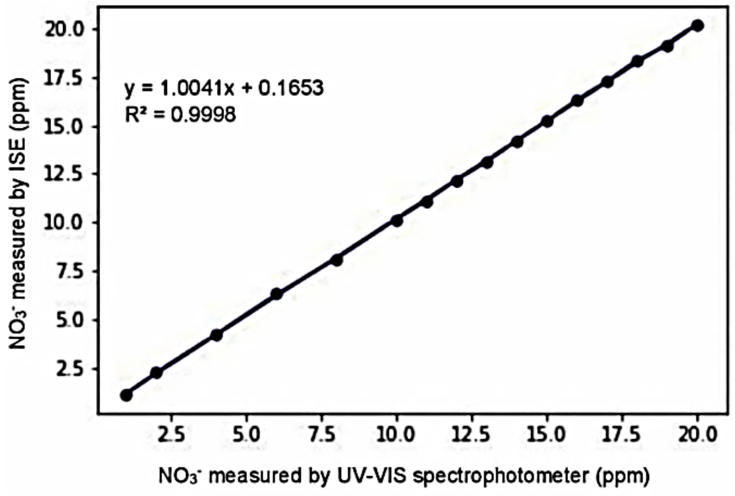


Figure 13. Linear regression graph for standard nitrate test results by ion-selective electrodes (ISE) and ultraviolet-visible (UV-Vis) spectrophotometer.

The statistical analysis data obtained from calibration test results have been summarised in **Table 6**. The results assure that the selection of polynomial fitting is a good choice for better calibration and analysis results by the ISEs. The *p*-value, *f*-value, and *t*-value support null hypothesis. The RMSE values are also very low for the calibration data.

Table 6. Statistical analysis of the polynomial regression fitting observations.

Nutrients	Polynomial Fitting Model	R^2	MU	*f*-Value	*p*-Value	*t*-Value	RMSE
Potassium	$y = -x^2 + 0.929x - 202.9$	0.9987	0.1216	1.0167	0.9532	2.0243	0.3801
Nitrate	$y = -x^2 + 0.389x - 56.72$	0.9909	0.1971	0.9946	0.9209	2.0243	0.0275
Chloride	$y = x^2 - 0.448x + 228.7$	0.9983	0.0732	1.0233	0.9632	2.0056	1.2700

Note: x = sensor's output, and y = nutrient concentration. MU, measurement uncertainty; R^2, determination coefficient; RMSE, root mean square error.

4.2. Performance Assessment Results

The potassium *r* values were determined to be 0.99 and 0.99 for the flame photometer and STFR meter, respectively, as illustrated in **Figures 14** and **15**. The ISE-based soil analyzer, developed in this study, recorded a lower potassium value of 5 kg/ha for the soil, because this value was taken as the lowest standard value for potassium ISE calibration (**Table 3**). It is evident that the standard curve of potassium obtained using the ISE-based analyzer closely aligns with the results from the flame photometer and STFR meter. The nitrate *r* value was calculated to be 0.93 using a spectrophotometer, as depicted in **Figure 16**. The ISE-based analyzer recorded a lower nitrate value of 1 kg/ha for the soil, because this value was taken as the lowest standard value for Nitrate ISE calibration (**Table 3**). There was no significant difference in nitrate test results between the spectrophotometer and ISE method. Similarly, the chloride *r* value was found to be 0.946 using a spectrophotometer, as shown in **Figure 17**. No significant difference was observed in chloride test results between the spectrophotometry and ISE method. The ISE-based chloride analyzer demonstrated reliable measurement of soil chloride content for agricultural diagnostics, with a lower detection value of 5 kg/ha, because this value was taken as the lowest standard value for Chloride ISE calibration (**Table 3**). The sample testing results have verified that this device can measure potassium up to 250 kg/ha (**Figure 14**), nitrate up to 40 kg/ha (**Figure 16**), and chloride up to 90 kg/ha (**Figure 17**) in soil. However, the measuring range can be extended by calibrating the system with standards of higher value.

The test results for potassium, nitrate, and chloride obtained by reference methods and ISE-based devices were compared and statistical analysis of measured data is presented in **Table 7**. The results indicate that the selection of polynomial fitting is a suitable choice. Furthermore, the *p*-value, which is more significant than the predetermined α value of 0.05, supports the null hypothesis.

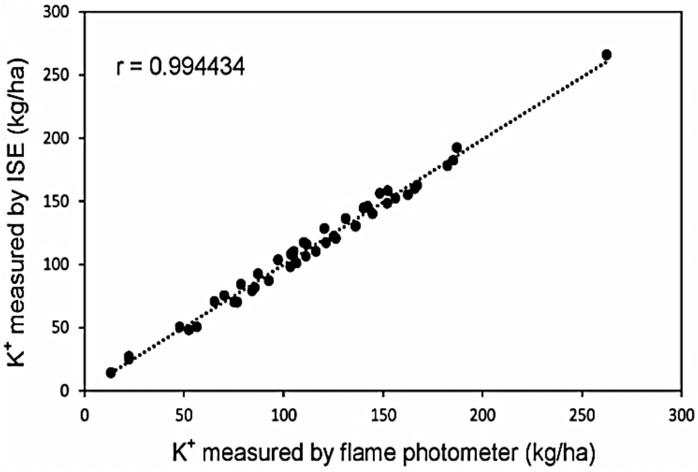


Figure 14. Comparison of soil K^+ test results with ion-selective electrodes (ISE) and flame photometer.

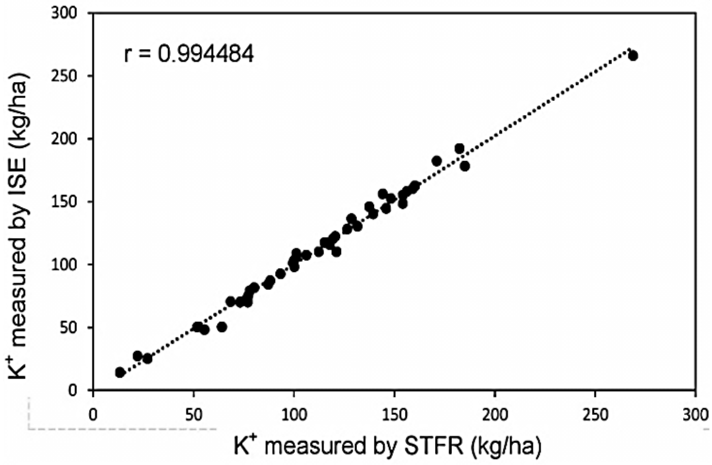


Figure 15. Comparison of soil K^+ test results with ion-selective electrodes (ISE) and soil test fertilizer recommendation (STFR) meter.

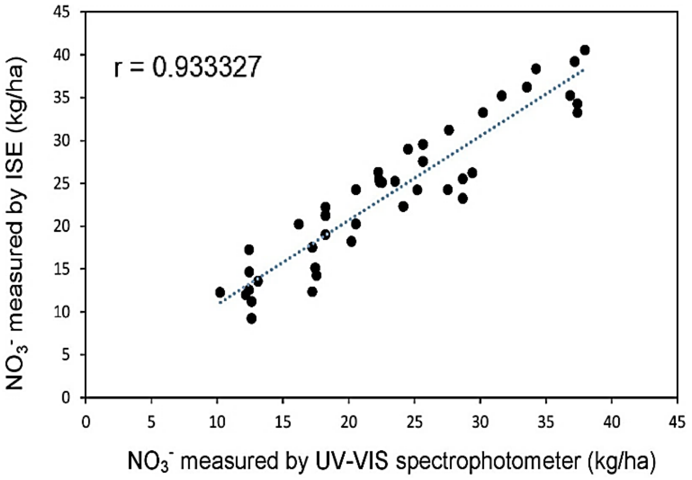


Figure 16. Comparison of soil NO_3^- test results with ion-selective electrodes (ISE) and ultraviolet-visible (UV-Vis) spectrophotometer.

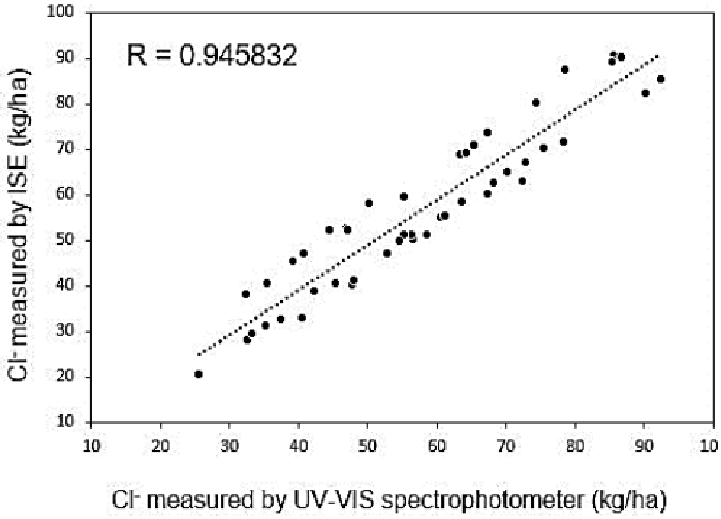


Figure 17. Comparison of soil Cl^- test results with ion-selective electrodes (ISE) and ultraviolet-visible (UV-Vis) spectrophotometer.

Table 7. Statistical analysis of the sample test observations.

Comparison of Test Results of ISE and Other Methods	*r*	MU	*f*-Value	*p*-Value	*t*-Value	RMSE
Potassium:						
• ISE vs. Flame photometer	0.994	0.110	1.009	0.979	0.027	5.046
• ISE vs. STFR meter	0.994	0.110	1.054	0.967	0.042	5.116
Nitrate (ISE vs. UV-Vis spectrophotometer)	0.933	0.042	1.104	0.710	0.372	3.025
Chloride (ISE vs. UV-Vis spectrophotometer)	0.946	0.089	1.004	0.902	0.123	5.923

Note: ISE, ion-selective electrodes; MU, measurement uncertainty; *r*, coefficient of correlation; RMSE, root mean square error; STFR, soil test fertilizer recommendation; UV-Vis, ultraviolet-visible.

The ISE-based analyzer closely matched the flame photometer in potassium level measurement. Compared to the findings reported by Cieśla et al. [22], the present ISE demonstrated slightly steeper slopes in calibration curves for potassium, indicating improved accuracy in assessing soil potassium content. Nitrate test results obtained from the UV-Vis spectrophotometer and ISE methods showed no significant differences, and consistent with the findings of Fayose et al. [25], Li et al. [15], and Kim et al. [41].

The *r* value for chloride, measured using the UV-Vis spectrophotometer, closely resembled the results reported by Cangea et al. [36]. Additionally, there were no significant differences in chloride test results obtained from spectrophotometry and the ISE method. The soil analysis conducted using the developed ISE demonstrated excellent agreement with laboratory-based techniques, highlighting improvements in precision and sensitivity analysis.

Table 7 presents the statistical analysis results of sample tests for Potassium, Nitrate, and Chloride conducted using the developed ISE-based device, spectrophotometer, and flame photometric method. The *r* and MU values ranged from 0.933 to 0.994 and 0.042 to 0.110, respectively, indicating comparable performance between the ISE-based sensors and standard methods (**Table 7**).

The strong agreement between ISE-based measurements and standard laboratory methods (r = 0.933–0.994) demonstrates the robustness of the integrated sensing–calibration framework. The use of polynomial regression significantly improved prediction accuracy by capturing non-linear electrode behavior, which is not adequately addressed by conventional linear models.

Unlike previous studies that report standalone sensor performance, the present work validates a complete analytical pipeline, thereby enhancing both reliability and applicability in real-world agricultural settings.

Moreover, the *p*-value, which holds greater significance than the predetermined α value of 0.05, supports the null hypothesis, ranging from 0 to 1 and measuring the likelihood of observing a test statistic under the null hypothesis. The inverse relationship of the *p*-value is crucial, indicating substantial evidence against the null hypothesis. *F*-test outcomes ranging from 0 to positive infinity, with higher *f*-values suggesting potential differences in group means, confirmed the suitability of the polynomial regression model's overall fit, with obtained F-test results approaching 1.

The α value, serving as a threshold against which the p-value is assessed, is determined based on a confidence level of 95% in ISE testing. The t-value, ranging from negative to positive infinity, indicates a more significant deviation from the null hypothesis mean, with higher absolute t-values suggesting greater deviations. Our analysis revealed a lower t-value.

Additionally, RMSE evaluates the average prediction error in regression analysis, with non-negative values indicating model accuracy. Lower RMSE values, observed for potassium, nitrate, and chloride values, demonstrate superior performance, although with slightly higher RMSE values for potassium and chloride.

5. Practical Applicability and Limitations

The developed device is suitable for real-time, on-site soil nutrient assessment and can significantly reduce dependency on laboratory-based testing. However, several practical challenges remain:

- Sensor performance may be affected by temperature variations and long-term drift,
- Soil heterogeneity and moisture content can influence extraction efficiency,
- Interfering ions may impact measurement accuracy despite calibration,
- Regular calibration is required for reliable operation.

Compared to image-based approaches, the proposed method is less sensitive to lighting and environmental conditions but requires physical sample preparation. Therefore, the system is best suited for quantitative nutrient estimation rather than rapid qualitative screening.

6. Conclusions

This study presents a portable and integrated soil nutrient assessment system based on ion-selective electrodes with advanced polynomial calibration. The system demonstrates high accuracy in measuring potassium, nitrate, and chloride, with strong agreement with standard laboratory methods. Key contributions include development of a field-deployable sensing device, implementation of a robust non-linear calibration model, and integration of sensing and validation into a unified framework. The proposed system effectively bridges the gap between laboratory precision and field usability, making it suitable for precision agriculture applications.

Furthermore, the device's automated calibration process augments its intelligence and correlation efficiency when assessing soil nutrients, leading to higher levels of accuracy. The achieved accuracy rates are noteworthy, standing at 0.994 for potassium, 0.934 for nitrate, and 0.946 for chloride, in comparison to other standard testing methods. The calibration process typically consumes about 15 min, while sample testing requires approximately 5 min. Consequently, the total time required for sample testing with calibration is approximately 20 min. Leveraging its automated nature, the device can identify and compute nutrient concentrations through its advanced data acquisition system and ISE sensors. Consequently, it finds applicability in soil testing laboratories and is well-suited for on-site soil monitoring in agricultural fields, particularly for precision farming applications.

Nevertheless, it is crucial to acknowledge the limitations of this device. It remains semi-automatic, requiring manual soil sampling. Furthermore, it lacks functionalities for crop forecasting and fertilizer recommendations. Future research should focus on automating the soil sampling process and expanding to multi-nutrient sensing platforms. Additionally, integrating machine learning techniques could empower the device to forecast soil nutrient levels and offer tailored fertilizer recommendations for individual agricultural plots.

Author Contributions

Conceptualization, data curation, investigation, methodology, validation, writing—original draft, P.M.; conceptualization, funding acquisition, investigation, project administration, resources, supervision, writing—review and editing, S.K.C.; formal analysis, investigation, methodology, validation, writing—review and editing, A.K.; system fabrication; investigation, methodology, resources, validation, writing—review and editing, N.K.; methodology, software, validation, writing—review and editing, V.K.; data curation, formal analysis, methodology, resources, V.K.R. All authors have read and agreed to the published version of the manuscript.

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Institutional Review Board Statement

This study does not involve human participants, human data, or personal information. Therefore, Institutional Review Board approval was not required.

Informed Consent Statement

Not applicable.

Data Availability Statement

The data that support the findings of this study are available from the authors upon reasonable request.

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Conflicts of interest

The authors declare no conflict of interest.

AI Use Statement

During the preparation of this work the author used the AI Sentence Rewriter Tool (https://ahrefs.com/writing-tools/sentence-rewriter) in order to enhance the quality and clarity of sentences, improve their construction, and grammar correction. AI was solely used for language editing. After using this tool/service, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

Abbreviations

Abbreviation	**Full Name**
A/D	Analog-to-digital
ISE	Ion-selective electrodes
LCD	Liquid crystal display
LED	Light-emitting diodes
MU	Measurement uncertainty
PVC	Polyvinyl chloride
RMSE	Root mean square error
STFR	Soil test fertilizer recommendation
UV-Vis	Ultraviolet-visible
Wi-Fi	Wireless fidelity

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