Development of the portable device for the determination of nitrate-nitrogen contents in soil

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Abstract: Soil nitrate-nitrogen is a crucial source of plant nutrition, making the rapid, accurate, and cost-effective determination of its content highly significant for agricultural production and environmental protection. To address the limitations of traditional methods for soil nitrate-nitrogen determination, particularly the time-consuming and lab-based sample pretreatment and analysis procedures hindering on-site applications, we developed a portable soil nitrate-nitrogen determination device based on screen-printed electrodes modified with cadmium sulfide nanorods as the core components. This device incorporates mainstream embedded system technology and employs a peak-finding algorithm utilizing low-pass filtering and second-order derivatives to automatically analyze electrochemical data, enabling swift measurement of soil nitrate-nitrogen content. Performance and application tests demonstrated that this device exhibits several key features: a detection range of 0.1-3.0 mmol/L, a low detection limit of 0.03 mmol/L, repeatability error below 11.7%, and measurement error below 10% compared to UV spectrophotometry. The device is characterized by its rapidity, simplicity, affordability, efficiency, and adaptability, enabling swift and user-friendly on-site determination of nitrate-nitrogen content in various types and sources of soil samples, offering a practical alternative to traditional lab-based analysis.

Keywords: Nitrate-nitrogen, soil, electrochemical sensor, detection
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1 Introduction

Efficient nitrogen management is paramount for sustainable agricultural practices and global food security. In agricultural production, farmers often need to supplement soil nitrogen by applying chemical fertilizers to increase crop yields[1]. However, excessive use of nitrogen fertilizers wastes resources and causes economic losses and various environmental problems, such as eutrophication, soil acidification, and reduced quality of agricultural products[2-4]. For instance, statistics from Jiangsu, China, show that the overall consumption of chemical fertilizers has quadrupled over the past three decades[5], with nitrogen fertilizers accounting for a substantial proportion; however, their efficiency rate has dropped to about 30%[6]. This means that a considerable amount of nitrogen is not absorbed or used by crops but rather lost into the environment through leaching and volatilization[7-10]. Therefore, developing rapid, precise, and cost-effective methods for on-site soil nitrogen content assessment is of paramount importance for enabling precision fertilization practices, maintaining arable land quality, and ultimately promoting sustainable agroecological development.

To implement precision nitrogen management effectively, accurate assessment of plant-available nitrogen in soil is crucial. Soil nitrogen exists mainly in two forms: organic nitrogen and inorganic nitrogen. Organic nitrogen comprises high molecular weight compounds such as polyphenols and amino acids, making up over 90% of the total soil nitrogen content. However, plants can only directly use a limited amount of simple amino acids, amides, and other organic components[10], requiring the microbial conversion of most organic nitrogen into inorganic forms before it becomes plant-available[11]. Inorganic nitrogen includes nitric and ammoniacal forms, which are the primary sources of plant-absorbable nitrogen and crucial indicators for monitoring soil fertility and crop growth. Nitrate-nitrogen content is a key criterion for assessing potential nitrogen deficiency in upland crops because ammonium-nitrogen is unstable and prone to decomposition[12]. Consequently, accurate and rapid quantification of soil nitrate-nitrogen is of paramount importance for optimizing nitrogen fertilization, improving nitrogen use efficiency, and minimizing environmental pollution in modern agricultural systems.

Despite the recognized accuracy and reliability of laboratory-based methodologies, such as colorimetric and spectrophotometric methods[13-18], and the advancements in spectroscopic instruments[19-22], routine, high-throughput, on-site soil nitrate-nitrogen determination for precision agriculture remains fundamentally challenged. The inherent complexity of soil as a heterogeneous, multiphase system presents a significant obstacle to achieving both operational convenience and analytical accuracy in soil nitrate-nitrogen measurements[17,23]. Traditional laboratory methods, while highly accurate under controlled conditions[14,16,17], are unsuitable for rapid on-site deployment due to their procedural complexity, high equipment costs, and need for specialized personnel[15,16,24,25]. Colorimetric and spectrophotometric techniques, for instance, necessitate labor-intensive and time-consuming steps, including meticulous sample collection, transportation to the lab, extensive pretreatment involving extraction and filtration, and analysis using

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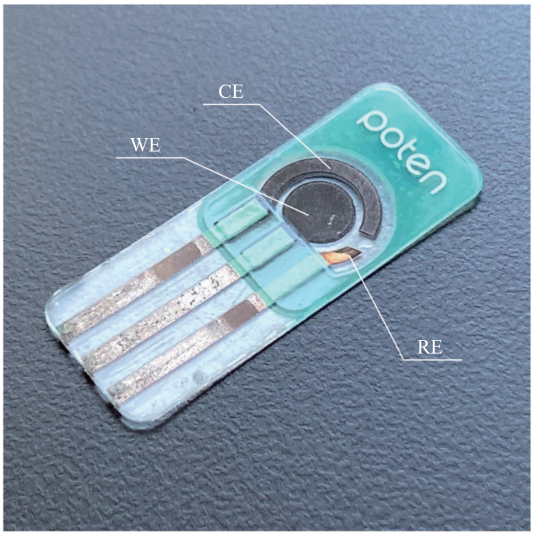
benchtop instruments[16,26]. This makes them impractical for the real-time, high-frequency field assessment demanded by precision agriculture. While portable spectroscopic techniques, such as near-infrared (NIR) and visible-near-infrared (Vis-NIR) spectroscopy, represent a partial solution to some of these limitations by offering miniaturization, speed, and reduced sample handling[15,20-24], their practical application for routine, high-throughput, on-site soil nitrate-nitrogen testing still faces remaining challenges in ensuring consistent accuracy and reliability in diverse field conditions.

Comparative evaluations and field validation studies have identified several key challenges hindering the widespread adoption of portable spectroscopic methods for routine on-site soil nitrate-nitrogen determination. Firstly, accuracy and reliability can be significantly compromised by the inherent complexity of soil matrices[23]. Heterogeneous soil samples and variable field conditions introduce substantial spectral interferences from organic matter, moisture content, and mineral composition[23], necessitating complex and often insufficient chemometric data processing to compensate for these confounding factors[27]. Secondly, achieving robust performance under diverse and uncontrolled field conditions remains a significant hurdle. Portable spectroscopic techniques are susceptible to fluctuations in humidity, temperature, and ambient light, which can significantly impact measurement consistency and reliability in real-world agricultural settings[21]. Thirdly, the cost of portable spectroscopic instrumentation, while decreasing, coupled with operational expenses, can still be substantial, often ranging into the thousands or tens of thousands of US dollars per unit. Widespread, routine deployment across large agricultural areas necessitates a large number of sensors, making instrument affordability a critical factor for broad adoption by agricultural practitioners. Fourthly, the effective operation and data interpretation of portable spectroscopic instruments still demand considerable user expertise and infrastructure, perhaps most critically. The complexity of spectroscopic data analysis, including spectral pre-processing and model calibration, and the nuances of soil spectral interpretation often require specialized experience in chemometrics, soil science, and data science[15,16,27], limiting accessibility for non-expert users in typical agricultural settings. Addressing these multifaceted challenges is essential. Overcoming these hurdles is crucial to bridge the persistent gap between the analytical promise of portable spectroscopic techniques and the practical demands of routine, high-throughput, on-site soil nitrate-nitrogen determination for precision agriculture. Electrochemical sensors, offering inherent advantages in cost-effectiveness, simplicity, and potential for robust field operation, present a promising alternative approach to overcome these limitations.

The electrochemical sensor is a device that utilizes an electrochemical instrument as a signal converter, enabling the sensing and detection of chemical quantities in a measured object by linking its electrochemical properties to an electrical signal[28]. Electrochemical sensors exhibit rapid response times, high accuracy, and cost-effectiveness, rendering them highly suitable for integration into diverse monitoring or automation systems[28,29]. In recent years, owing to advancements in screen-printed electrodes (SPE) and other complementary technologies, electrochemical sensors have witnessed remarkable progress in miniaturization and applicability[30]. Therefore, they have been widely used in various domains such as blood glucose detection[31,32] and pesticide residue analysis[33-35].

The performance of electrochemical sensors is closely linked to the composition and structure of electrode materials, making the exploration of novel materials and optimization of material composition and structure crucial in electrochemical sensor research[32,34,36]. In recent years, cadmium sulfide nanomaterials have garnered significant attention from the materials science community as an emerging functional material, finding applications in optoelectronic devices[37], photocatalysis[38,39], biosensors[40,41], and surface modification of SPEs[42]. Cadmium sulfide nanorods (CdS NRs) possess a rod-like morphology with diameters ranging from 1 to 100 nm and lengths varying from a few micrometers to several hundred micrometers. These CdS NRs exhibit high specific surface area and numerous active sites that enhance electrode-electrolyte contact area and charge transfer efficiency. They also demonstrate high electron mobility and carrier concentration, improving electrode conductivity and response speed.

Our research team[43] has previously demonstrated the successful synthesis of high-purity CdS NRs through a hydrothermal reaction utilizing $Cd(NO_3)_2{\cdot}4H_2O$, CH_4N_2S, and $C_2H_8N_2$ at 160°C for 48 h. The modification was achieved by depositing the suspension of CdS NRs onto NaOH-activated SPE and drying at room temperature. Experimental data confirmed that the CdS NRs-modified SPE (CdS NRs-SPE, shown in Figure 1) exhibited excellent sensitivity and selectivity towards nitrate-nitrogen components in samples. The peak current measured via cyclic voltammetry also displayed a strong linear correlation with nitrate-nitrogen concentration in the sample. The electrode can be prepared at approximately $3 and maintains its performance without significant degradation for over one month. These attributes, including compact size, affordability, ease of preparation, and superior performance, render it highly suitable for the on-site determination of nitrate-nitrogen in soil.



Note: WE: Working electrode; CE: Counter electrode; RE: Reference electrode.

Figure 1 Screen-printed carbon electrode modified with cadmium sulfide nanorods

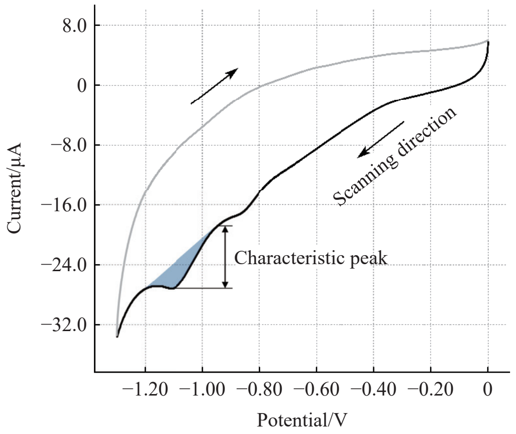
To address these persistent challenges in on-site nitrate-nitrogen determination, this study details the development and validation of a portable electrochemical device utilizing CdS NRs-SPEs and cyclic voltammetry. This innovative device is engineered to provide a unique and advantageous combination of field-portability, seamless system integration, high analytical performance, operational simplicity, and affordability, representing a significant departure from the limitations of existing portable spectroscopic and conventional laboratory techniques. Through rigorous performance evaluations and comprehensive application testing on diverse soil samples, this paper aims to demonstrate the analytical capabilities and practical utility of this novel electrochemical sensor technology for routine, high-throughput, on-site soil nitrate-nitrogen monitoring, and to highlight its potential to bridge the critical gap between laboratory precision and field-based practicality in sustainable agricultural practices.

2 Materials and methods

2.1 Operational principles

Cyclic voltammetry (CV) is a crucial technique for implementing electrochemical analysis, serving as a technical tool to investigate electrochemical reactions occurring at the electrode-electrolyte interface. Typically, researchers[44,45] conduct the CV experiment in a three-electrode configuration that comprises a working electrode (WE), a counter electrode (CE), and a reference electrode (RE), as shown in Figure 1. The WE is the site for oxidation and reduction reactions. The CE acts as the current supplier or consumer, necessitating good conductivity and stability without interfering with the working electrode's reaction. Lastly, the RE ensures a constant potential by exhibiting excellent stability and repeatability.

When determining nitrate-nitrogen content in the soil, researchers typically extract the nitrate-nitrogen content into solution by adding an extractant (e.g., potassium nitrate solution) to the soil sample[46-48]. The resulting extract is then diluted and employed as a sample for CV analysis. In this study, we initiated the WE voltage relative to RE at 0 V, gradually decreased it at a rate of 0.05 V/s until reaching −1.3 V, and subsequently reversed the direction of voltage change to return to the initial voltage using the same rate. Throughout this process, we continuously recorded both voltage and current values of the WE to obtain the CV curve, depicted in Figure 2. The primary focus of this study lies in the variation of current values during the first half of the cycle. Figure 2 shows a distinct negative peak on the curve at approximately −1.1 V, representing the characteristic peak associated with nitrate-nitrogen. The magnitude of this peak (i.e., peak current) exhibits a significant correlation with the concentration of nitrate-nitrogen present in the sample. By quantifying the height of this distinctive peak on CV curves, we can deduce the concentration of nitrate-nitrogen within test samples. In practical applications, using different electrodes may lead to variations in the curve shape. Before testing an actual soil sample, it is customary to construct a *standard curve* using a reference sample (e.g., sodium nitrate solution with known concentration) to establish the relationship between peak height and concentration for the specific electrode employed. This foundation makes determining nitrate-nitrogen content in soil samples readily achievable.



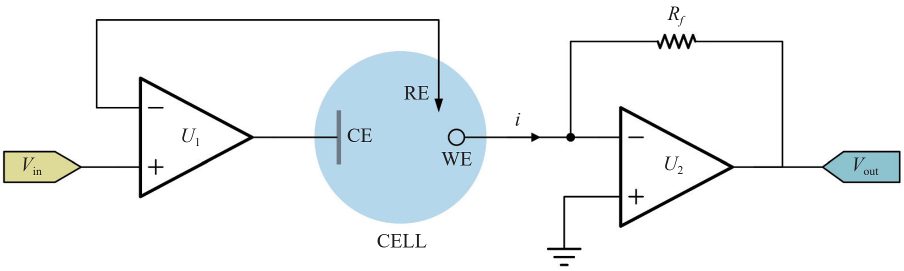
Note: Data was measured using self-developed CdS NRs-SPE and CHI660E electrochemical workstation.

Figure 2 A typical cyclic voltammetry curve from soil extract

2.2 Hardware design

The potentiostat is an indispensable measurement and control device in electrochemical analysis, serving as a fundamental component of modern electrochemical workstations. Its primary function is precisely regulating the voltage between WE and RE while measuring the current flowing through WE. In addition, ensuring that no substantial current passes through RE is imperative throughout this process, preventing any potential impact on the reaction[49].

The functional architecture of the potentiostat can be simplified to a primary circuit comprising two ideal operational amplifiers[49], as illustrated in Figure 3. The design ingeniously exploits the electrical characteristics of the op-amps. On the one hand, both inputs of the ideal op-amp maintain an identical voltage potential. Consequently, for U_1, RE should have a voltage equal to V_{in} at its input terminal. Similarly, for U_2, WE is considered as ground and thus maintains a constant actual voltage of 0 V. In this scenario, when RE serves as a reference point, WE exhibits a voltage of $-V_{in}$. On the other hand, due to its extremely high input impedance, an ideal op-amp can be approximated as having no current flowing into its inputs. This property ensures that no current flows through RE for U_1 and allows V_{out} (the output voltage) for U_2 to be directly proportional to the current i passing through WE. This configuration allows users to control the operating voltage and measure response currents easily.



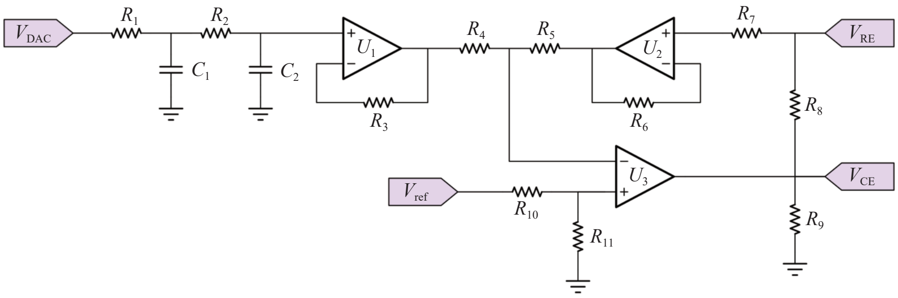
Note: V_{in}: Input control voltage; V_{out}: Output voltage proportional to the cell current; U_1, U_2: Operational amplifiers; R_f: Feedback resistor; RE: Reference electrode; CE: Counter electrode; WE: Working electrode. CELL represents the electrochemical cell containing the three-electrode system and the sample.

Figure 3 Schematic diagram illustrating the working principle of a classic three-electrode potentiostat circuit

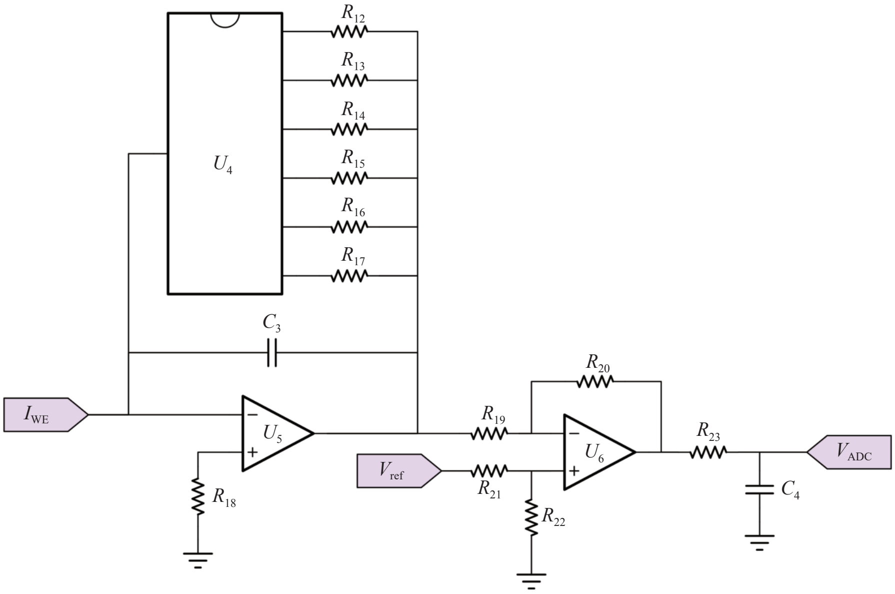
According to the abovementioned principle, the potentiostat circuits were devised as shown in Figure 4.

In Figure 4a, V_{ref} denotes the externally supplied stabilized reference voltage source with a fixed value of 2.5 V. By utilizing the characteristics of resistors and op-amps, this circuit can make the voltage at each location connected to it satisfy the relationship V_{RE}=V_{ref}−4×V_{DAC}. Therefore, by keeping the reference voltage constant at V_{ref}, researchers can achieve precise control over the potential of the RE through adjustments made to V_{DAC}.

In Figure 4b, the input current of the WE electrode (I_{WE}) exhibits a wide range of variation (10^{-7} A to 10^{-2} A) due to the diverse nitrate-nitrogen content in different soils. This study introduces a feedback resistor network based on the traditional trans-impedance amplifier circuit to enhance device applicability and sensitivity, utilizing a multiplexer TMUX1108 and six precision resistors ranging from 10 Ω to 1 MΩ.



a. Voltage output circuit (connected to RE and CE)



b. Current-voltage conversion and amplification circuit (connected to WE)

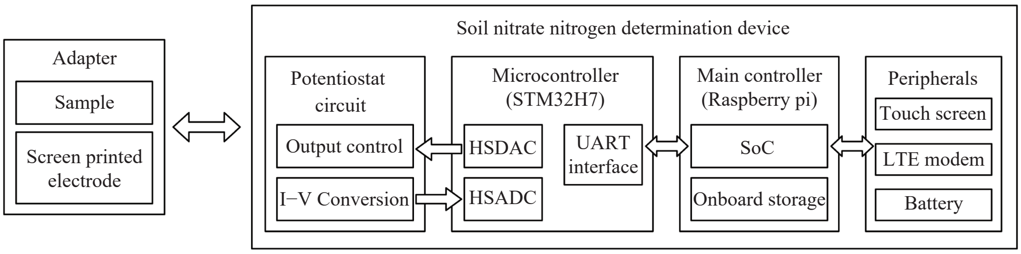
Note: U_1-U_3: Operational amplifiers; V_{DAC}: Digital-to-analog converter output voltage; V_{ref}: Stabilized reference voltage; V_{RE}: Voltage at the reference electrode; V_{CE}: Voltage at the counter electrode; U_4: Multiplexer; U_5, U_6: Operational amplifiers; I_{WE}: Current flowing through the working electrode; V_{ADC}: Analog-to-digital converter input voltage.

Figure 4 Schematic diagrams of the potentiostat circuit implemented in the portable device

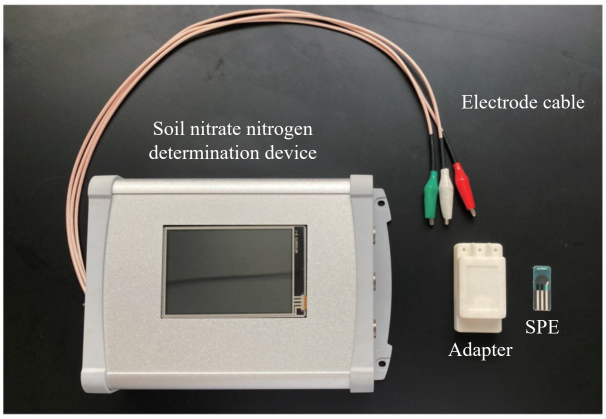
Conventional potentiostat circuits typically employ intricate components such as independent voltage sources, signal generators, DACs, and ADCs to generate voltage, control, and acquire signals for current measurements[50]. These components are expensive, large, and necessitate additional external circuitry and auxiliary elements, which hinder device integration and miniaturization. To address the requirements of soil nitrate-nitrogen determination that demand a narrow range and slow rate of voltage change, we chose the STM32H743VIT6 microcontroller in this study to accomplish voltage generation and current measurement functions. The performance of its analog peripherals adequately satisfies the demands for soil nitrate-nitrogen detection.

The op-amps are fundamental components of a potentiostat circuit, playing a crucial role in determining the quality of the electrochemical signal and the reliability of measurement results. During testing, the voltage output from the device takes the form of a delta waveform with a narrow range of variation (less than 3 V) and a slow rate of change (less than 1 V/s). Therefore, high bandwidth or slew rate is unnecessary for op-amps used for voltage output. However, op-amps must have low input bias current to ensure minimal current flow through RE. On the other hand, there is significant variation in the current flowing through WE during testing. Noise or other circuit disturbances can easily corrupt this small current signal when it encounters them. Therefore, op-amps used for current input should possess low noise and offset voltage. Additionally, since the entire device operates outdoors, the op-amps must exhibit minimal temperature drift. Considering these requirements, we select OPA392 for front-end circuitry. Its ultra-low input bias current and low temperature drift, in addition to built-in EMI and RFI filters, make it an ideal candidate for precise control and measurements.

In practice, the potentiostat circuit acquires voltage and current signals at a rate of up to 10 kHz. The resulting large volume of data presents challenges regarding reception, processing, storage, and display. To address this issue, we incorporated the Raspberry Pi Zero 2 W as the primary controller for the entire device. This controller is responsible for operational control, data analysis, and human-computer interaction (HCI), among other functions. We developed a multi-threaded data processing program and HCI using Python 3.11 and Qt 6.5, respectively. The data processing program primarily handles serial communication with the STM32 microcontroller by receiving transmitted data from it and performing tasks such as filtering, peak search, and peak height measurement on that data. On the other hand, HCI focuses on user interaction by displaying information, including parameter settings details and data visualization results, while also providing corresponding operation buttons and menu options to facilitate convenient initiation or termination of measurements. Furthermore, our design integrated a touchscreen, an LTE communication module, and a lithium-ion rechargeable battery. As depicted in Figure 5, we employed 3D printing to encapsulate these components, resulting in a portable soil nitrate-nitrogen content determination device.



a. The functional block diagram



b. The complete set of equipment assembled

Figure 5 Portable soil nitrate-nitrogen content determination device

2.3 Algorithm development

As previously mentioned, this study's primary data processing and analysis objective was to determine the position and measure the magnitude of the characteristic peak associated with nitrate-nitrogen on the CV curve. Due to the intricate morphology of these curves, conventional peak-finding algorithms based on absolute height or prominence are not applicable, necessitating manual intervention. Some researchers have proposed automated peak-finding methods utilizing polynomial fitting or second-order derivatives[51,52], which have partially streamlined CV curve analysis. However, compared to these studies, soil sample CV curves possess distinct characteristics that prevent the direct application of existing findings.

Lower data quality. Our portable device is specifically designed for determining nitrate-nitrogen content in soil for agricultural scenarios, such as farmland and greenhouses. The field environment poses more significant challenges than laboratory settings, with potential external influences and signal transmission interferences leading to occasional abnormal phenomena in the measured CV data, including duplication, missing values, and jitter, as depicted in Figure 6. Consequently, the data quality is inferior to that of traditional electrochemical workstations and cannot be directly analyzed.

Complex curve features. Due to numerous components other than nitrate-nitrogen, the soil constitutes a complex system, resulting in CV curves exhibiting multiple features such as peaks and troughs. The number and location of these features vary across different soil samples due to variations in chemical composition, posing challenges for processing the CV curves using simplistic methods like polynomial fitting.

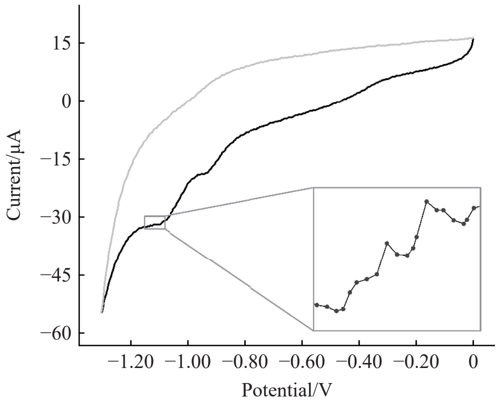
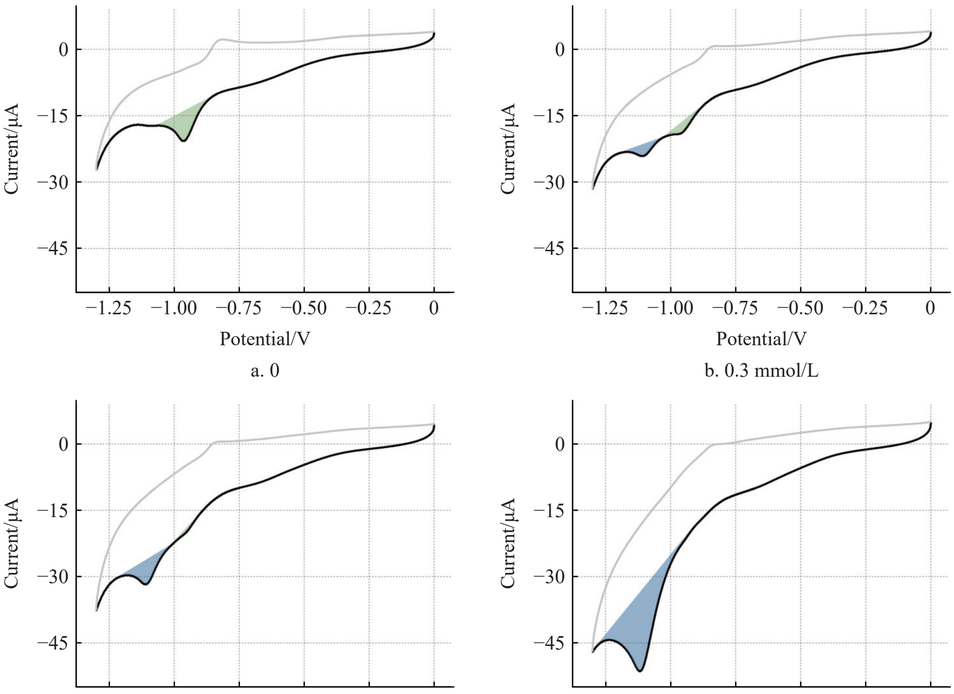


Figure 6 Typical data quality issues on cyclic voltammetry curves

Variable curve morphology. On the one hand, due to inter-individual variations in the performance of SPEs, CV curves obtained for the same sample using different electrodes may exhibit diverse patterns. On the other hand, when measuring samples with varying concentrations of nitrate-nitrogen using a single electrode, significant changes are observed in the CV curves (as depicted in Figure 7). In the absence of nitrate-nitrogen, the curve displays a characteristic peak around −0.9 V attributed to dissolved oxygen presence. However, even a tiny amount of nitrate-nitrogen introduces a new characteristic peak at −1.1 V in the curve. As nitrate-nitrogen concentration increases, this peak shifts towards more negative potentials while its width and height increase concurrently. Simultaneously, other features, including the dissolved oxygen peak, become less prominent and eventually vanish altogether. These complexities pose challenges for analyzing soil sample CV curves using conventional static algorithms.

The present study proposes a data processing and analysis method combining low-pass filtering with the second-order derivative approach to address the unique characteristics of CV curves in determining nitrate-nitrogen content in soil samples. The overall process is shown in Figure 8. This methodology effectively addresses issues related to poor data quality, complex curve features, and variable curve morphology, enabling precise identification of characteristic peaks and accurate measurement of peak height.



a. 0

b. 0.3 mmol/L

c. 0.5 mmol/L

d. 1.0 mmol/L

Note: Blue Area: the characteristic peak of nitrate-nitrogen; Green Area: the characteristic peak of dissolved oxygen.

Figure 7 Cyclic voltammograms obtained for KNO_3 solutions of different concentrations

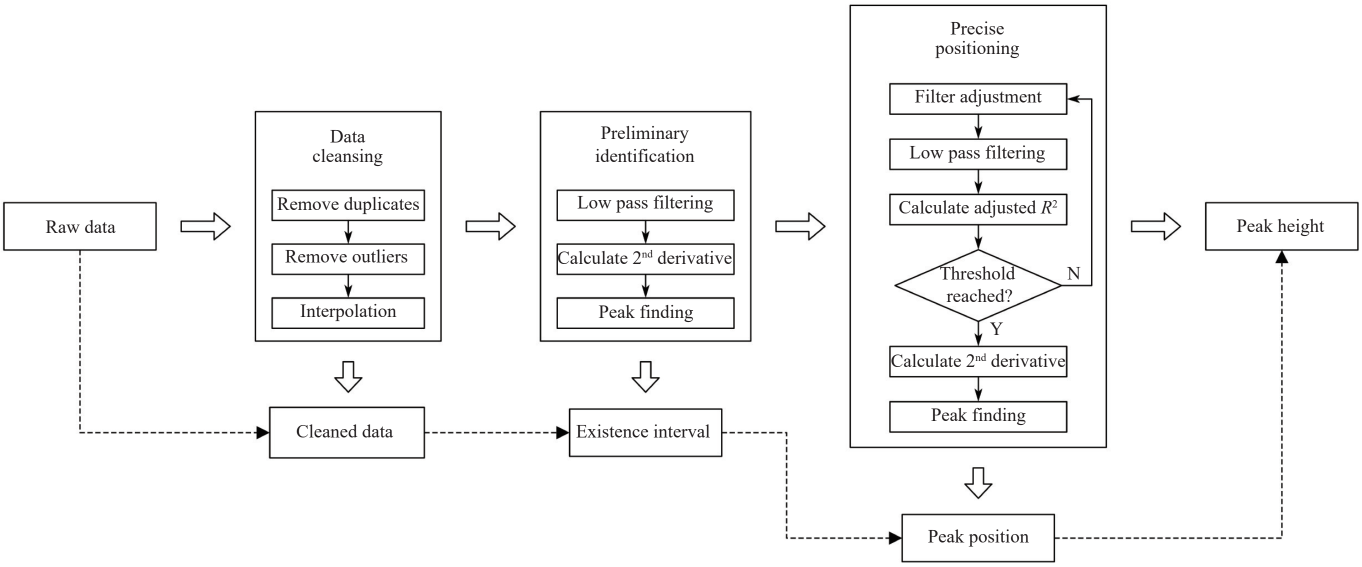


Figure 8 Process flow of cyclic voltammetry data processing and analysis

The initial part of the process involves data cleansing, which encompasses the removal of duplicates, outliers, and missing points. In this study, we can regard the CV curve as a simple signal with voltage as the independent variable and current as the dependent variable, exhibiting unidirectional changes.

The so-called *duplicate points* in this investigation refer to data points sharing identical horizontal coordinates (voltage) but differing vertical coordinates (current). Their presence disrupts the correspondence between these two sets of coordinates and hampers subsequent analysis. Eliminating duplicate points is a straightforward procedure: arrange all data points based on their horizontal coordinates, identify those with the same horizontal values, and eliminate them.

The term *outlier* in this study refers to individual data points that deviate from the original CV curve. In traditional signal analysis, researchers typically employ statistical methods to assess the abnormality of data, and sometimes they calculate the change rate of the value to detect anomalous changes. However, for CV curves, the occurrence and location of outliers do not follow a statistically regular pattern. In many cases, sudden changes in the data are common and reasonable. Through extensive analysis of the experimental data, we note that for an ideal CV curve, when we look at an arbitrarily chosen narrow interval (e.g., less than 0.05 V) on the curve, we can see that the vertical coordinates of all the points in that range vary monotonically. Leveraging this characteristic allows us to quickly identify and remove anomalous points by detecting inconsistencies in the direction of change among neighboring data points within each interval. Finally, cubic interpolation is applied to repair and complete missing data points resulting from transmission errors or outlier elimination processes, enhancing data density and continuity.

The second part of the process involves peak identification. Due to the non-linear baseline of the CV curve, traditional comparison methods that directly compare vertical coordinate values of data points are inadequate for peak detection. Therefore, this study adopts a widely used industry approach based on second-order derivative analysis for peak detection. By representing the concavity and convexity of the original data curve, the second-order derivative value enables the precise determination of extreme points, which correspond to peaks on the original curve. Additionally, these extreme points provide information about the prominence or intensity of each peak on the original curve, facilitating the accurate localization of characteristic peaks in CV curves.

Due to the high sensitivity of the second-order derivative method towards fluctuations in the original data, even a minor perturbation on the curve can lead to significant variations in the calculated second-order derivative value. Therefore, prior to peak identification, it is essential to smooth the original data. Researchers commonly employ polynomial piecewise fitting or Savitzky-Golay filtering for processing raw signals in conventional practice. However, given the intricate and diverse morphology exhibited by CV curves of soil samples, determining an appropriate number of segments and polynomial order for fitting becomes challenging when using polynomials. Similarly, selecting an optimal window length poses difficulties during Savitzky-Golay filtering. Considering these inherent characteristics of CV curves observed in soil samples, this study employs low-pass filtering for data smoothing.

In this study, a two-step filtering and peak-detection algorithm was developed to preserve the essential information for measurements while eliminating extraneous interferences that could impact the results. The premise of the algorithm is that the position and height of the characteristic peak of nitrate-nitrogen on the CV curve constitute the sole morphological features of interest, with no similar waveforms nearby. With this in mind, a low-pass filter was initially applied with a fixed, low cutoff frequency to smooth out noise in the raw curve. Although this may alter the shape of the filtered curve, particularly affecting its width and height at the characteristic peak, it does not significantly shift its position (horizontal coordinate). At this stage, both the presence and approximate range of existence (existence interval) can be determined by taking second-order derivatives of the filtered curve and identifying peaks on this derivative curve. Subsequently, we gradually increase the cutoff frequency so that within the existence interval, shape similarity between filtered and original curves improves until reaching a certain threshold, as quantified by the adjusted R^2 value. Once the value reaches this threshold, we again employ the second-order derivative method to detect peaks within the existence interval, accurately pinpointing the exact locations of characteristic peaks.

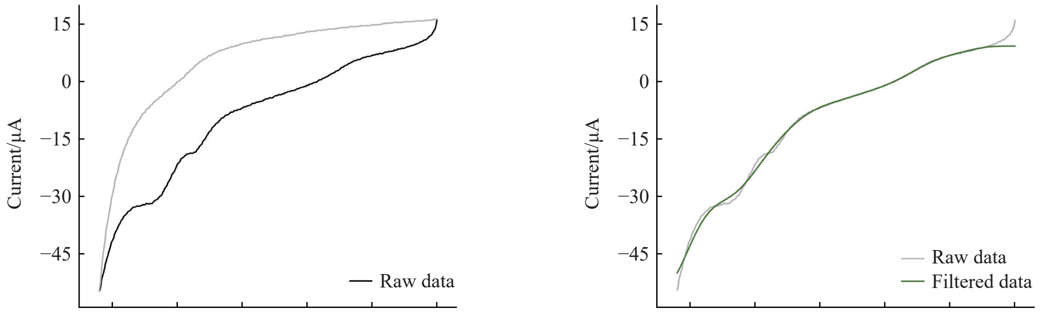
In the experimental procedure, we initially designed a 4th-order Butterworth filter with a normalized frequency of 0.8×10^{-4} using the SciPy library in Python. Subsequently, we applied this low-pass filter to the original curves and calculated the second-order derivative of the filtered data. As depicted in Figure 9, for samples containing nitrate-nitrogen components, we can observe a distinct peak in the second-order derivative curve at approximately −1.1 V. This specific region was defined (−1.2 V to −0.8 V, as shown in Figure 9) as the existence interval of the characteristic peak. To determine an accurate location for this characteristic peak, we incrementally increased the normalization frequency of the filter by steps of 1.0×10^{-6}. We recalculated adjusted R^2 values between each newly filtered curve and its corresponding original curve over this existence interval until surpassing a threshold value of 0.995. Finally, by taking a second-order derivative of these filtered curves again, we can identify the exact position of the characteristic peak associated with nitrate-nitrogen.

Based on the study above, we have devised a comprehensive procedure for determining the nitrate-nitrogen content in soil samples by referring to the manual measurement process, principles, and precautions. We initially conducted a CV scan on a blank sample devoid of nitrate-nitrogen content. This step aims to ascertain the proper functioning of the electrode and stabilize its performance. Subsequently, we individually scanned three or more standard samples with varying concentrations, calculating and averaging their peak heights. The device automatically constructs a standard curve using these samples' average peak height and concentration. Finally, actual soil samples are extracted and subjected to scanning; their peak heights are calculated and averaged to determine the nitrate-nitrogen content through conversion utilizing the standard curve. Considering the characteristics of SPEs, performing at least six scans for each sample is typically recommended.

2.4 Soil sample pretreatment

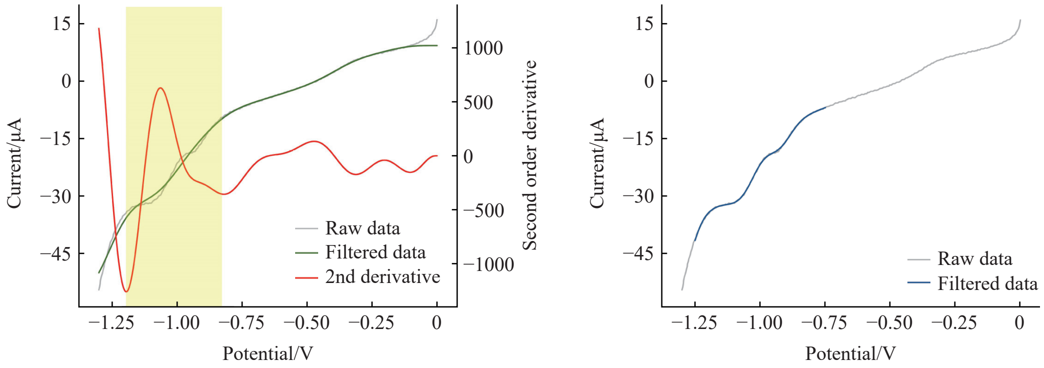
For efficient on-site nitrate-nitrogen determination, a rapid and easily implemented soil sample pretreatment method is crucial to overcome the limitations of traditional laboratory procedures. In this study, we employed an easily conducted extraction filter (ECET) as an essential external pretreatment component for our portable detection system. The ECET facilitates rapid extraction of nitrate from soil samples within a short timeframe, enabling efficient on-site analysis. This external pretreatment component is designed for seamless integration with our portable electrochemical detection device, forming a complete system for rapid field measurements.

As shown in Figure 10, the ECET is a simple syringe-based filtration device, primarily composed of a standard syringe, a 0.45 μm polyethersulfone (PES) membrane filter placed at the syringe tip, and the syringe plunger. In operation, a small amount of soil sample (approximately 1.78 g) is introduced into the syringe



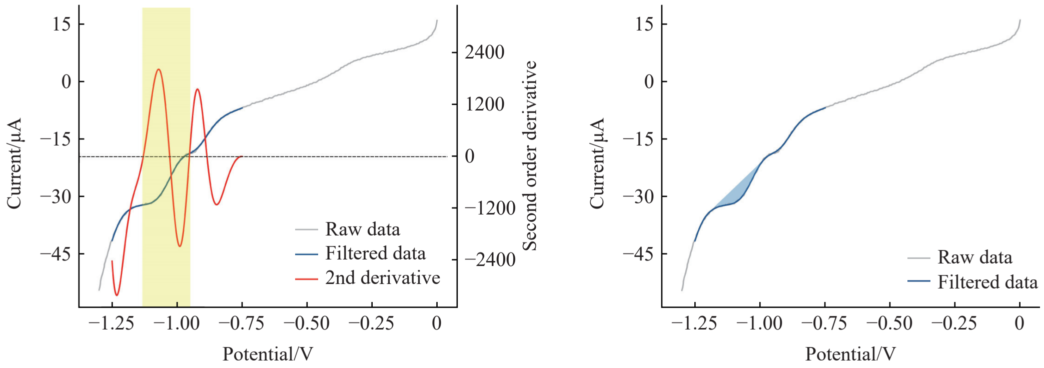
a. Raw data

b. Perform data cleaning and preliminary low-pass filtering



c. Calculate the second derivative and determine the existence interval

d. Perform more accurate low-pass filtering on the data at the existence interval



e. Calculate the second derivative again to find the range of the characteristic peak

f. Determine the precise location

Figure 9 Step-by-step illustration of the algorithm for locating the characteristic peak of nitrate-nitrogen on cyclic voltammograms of soil samples

Figure 10 Obtaining soil extracts using an easily conducted extraction filter (ECET)

barrel, followed by 9 mL of a 1 mol/L potassium chloride (KCl) solution in 0.04 mol/L phosphate-buffered saline (PBS) at pH 8.0. The KCl solution effectively extracts nitrate from the soil matrix, while the PBS buffer optimizes electrochemical detection. The syringe is then briefly shaken to ensure thorough mixing and extraction. Finally, the plunger is pressed to force the soil extract through the PES filter, yielding a clear filtrate ready for nitrate-nitrogen measurement with our portable electrochemical device.

ECET provides a rapid, efficient, and reproducible method for soil nitrate extraction, requiring significantly reduced extraction time and sample/reagent volumes compared to traditional methods. The use of ECET as an external pretreatment component is therefore instrumental in enabling the portable device for practical and rapid on-site soil nitrate-nitrogen determination.

2.5 Performance tests

To rigorously evaluate the performance of our portable device for on-site soil nitrate-nitrogen determination, particularly in addressing the limitations of existing portable methods, we conducted a series of laboratory tests focused on key performance parameters crucial for field applicability: accuracy, repeatability, and selectivity. The following subsections detail the experimental design and rationale for each test.

2.5.1 Accuracy test

To validate accuracy, a critical parameter for reliable on-site nitrate determination and superior to current portable spectroscopy limitations in complex soil matrices, we performed an accuracy test using standard KNO_3 solutions. Accuracy was defined as the proximity of measured values to the accepted reference values, aiming to quantify device accuracy across its operational range and generate a calibration curve for nitrate-nitrogen quantification.

A freshly prepared CdS NRs-SPE was used with the portable device. The electrochemical performance of the electrode was stabilized by six CV scans in distilled water (blank solution). Potassium nitrate (KNO_3) standard solutions (0.1, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 mmol/L) were sequentially analyzed to construct a calibration curve based on the correlation between voltammetric peak heights and known concentrations. For validation, a separate set of KNO_3 solutions (0.6, 1.2, 1.8, and 2.4 mmol/L) was measured, and the determined nitrate-nitrogen concentrations were compared to true values to evaluate device accuracy and calibration curve reliability.

The detection limit (LOD) was estimated using the 3S/N method: $LOD=3\times N/S$, where N is the standard deviation of the blank signal (distilled water CV scans), and S is the average peak height for the 0.1 mmol/L KNO_3 standard solution. This method provides a practical measure of device sensitivity.

2.5.2 Repeatability test

To characterize the robustness and short-term operational stability of our portable nitrate-nitrogen determination device, essential for reliable field deployment in variable conditions, we conducted a Repeatability Test to assess the consistency of measurements under identical conditions. Characterizing repeatability, the degree of agreement between independent measurements obtained with the same device on the same sample within a short timeframe, is crucial for ensuring data reliability in dynamic field environments.

In this experiment, we employed the portable device, using the same CdS NRs-SPE electrode, to repeatedly examine potassium nitrate (KNO_3) solution samples at four different concentrations: 0.6 mmol/L, 1.2 mmol/L, 1.8 mmol/L, and 2.4 mmol/L. Each sample was measured in replicates, with each replicate measurement performed eight times sequentially at intervals of 5 min, maintaining identical experimental conditions throughout. Subsequently, for each concentration level, we calculated the relative deviation for the set of eight replicate measurements to quantitatively evaluate the device's measurement repeatability.

2.5.3 Selectivity and interference test

To evaluate the selectivity of the CdS NRs-SPE for nitrate-nitrogen detection, and to ensure accurate measurements in complex soil matrices containing potential interferents, we conducted interference studies focusing on common soil interferents. Representative anionic (carbonate, sulfate, perchlorate, bromide) and cationic (zinc, chromium (Ⅲ), lead (Ⅱ), copper (Ⅱ), mercury (Ⅱ)) interferents, selected based on their potential co-existence with nitrate in soil, were assessed for their influence on electrochemical performance.

For each interferent, a test solution was prepared by spiking a 1 mmol/L nitrate-nitrogen standard with the specific interferent. Anion interference was tested at 10 mmol/L, and cation interference at environmentally relevant concentrations (0.5 μmol/L for Cd^{2+} and Hg^{2+}, 1.2 mmol/L for Cr^{3+}, 0.3 mmol/L for Pb^{2+} and Cu^{2+}, and 0.8 mmol/L for Zn^{2+}). CV curves were recorded for each interference solution and a control solution (1 mmol/L nitrate-nitrogen standard). All CV measurements were performed in triplicate under identical parameters. Peak currents were quantitatively compared to determine the extent of interference for each ion, using the peak-finding algorithm from Section 2.3.

2.6 Application test

To rigorously validate the practical applicability and real-world performance of our portable device for on-site soil nitrate-nitrogen determination in complex and variable soil matrices, and to demonstrate its effectiveness beyond controlled laboratory settings, we conducted an Application Test using authentic soil samples collected from agricultural fields. Validating performance with real-world samples is crucial to ensure effectiveness and reliability in practical application scenarios, moving beyond controlled laboratory conditions.

For this test, soil samples were collected from three distinct rice and wheat fields in Nanjing, China (32°01′59′′N, 118°52′11′′E), resulting in a diverse set of nine soil samples representing typical agricultural soils (Figure 11). Each soil sample was thoroughly mixed and then divided into two equal portions to enable parallel analysis using both our portable device and a reference method. One portion of each soil sample underwent nitrate-nitrogen extraction utilizing the ECET, followed by nitrate-nitrogen content measurement using our portable device. Concurrently, the other portion of each soil sample was subjected to nitrate-nitrogen content analysis employing UV spectrophotometry, following China's national standard GB/T 32737-2016 and utilizing a SHIMADZU UV-3600 Plus spectrophotometer as a reference method. Finally, we quantitatively compared the nitrate-nitrogen content measurements obtained by our portable device with those obtained by the UV spectrophotometry reference method to evaluate the practical applicability and accuracy of our device for real-world soil sample analysis.

a.Sampling areas of farmland soil

b. Part of the soil samples

c. SHIMADZU UV-3600 Plus

Figure 11 Application test setup for the portable soil nitrate-nitrogen determination device

3 Results and discussion

3.1 Results of performance tests

3.1.1 Results of the accuracy test

As detailed in Section 2.5.1, the accuracy of our portable device, a critical requirement for reliable on-site nitrate determination, was quantitatively evaluated using validation samples. Results, presented in Table 1, Table 2, and Figure 12, consistently demonstrate high accuracy, with measurement errors tightly constrained within 5% across the tested 0.1-3.0 mmol/L range. This unequivocally validates the device's accuracy throughout its operational range, fulfilling a fundamental prerequisite for practical soil nutrient assessment in agricultural and environmental contexts. The high correlation coefficient (R^2) of 0.9859 further substantiates the calibration curve's reliability, confirming its suitability for quantitative nitrate-nitrogen analysis using our portable device. The estimated LOD of 0.03 mmol/L indicates sufficient sensitivity for practical agricultural applications. While laboratory methods like UV spectrophotometry may offer slightly lower detection limits[14,53,54] and Vis-NIR spectroscopy comparable accuracy in controlled settings[24,55,56], the portable device achieves comparable accuracy and a sufficiently low LOD, while uniquely providing the key advantage of rapid, on-site measurement, unattainable with traditional laboratory or portable spectroscopic techniques.

Table 1 Measurement results of the calibration set

Concentration/mmol·L^{-1}	Peak height/μA
0.10	9.063
0.50	29.376
1.00	52.044
1.50	57.628
2.00	88.878
2.50	114.796
3.00	130.111

Note: Calibration Set: data points used to build the standard curve.

Table 2 Measurement results of the validation set

Concentration (True value)/ mmol·L^{-1}	Peak height/ μA	Concentration (Measured)/ mmol·L^{-1}	Absolute error/ mmol·L^{-1}	Relative error/ %
0.60	30.247	0.588	−0.012	−2.05
1.20	55.877	1.203	0.003	0.25
1.80	83.293	1.861	0.061	3.40
2.40	108.134	2.458	0.058	2.40

Note: Validation Set: data points used to evaluate the accuracy.

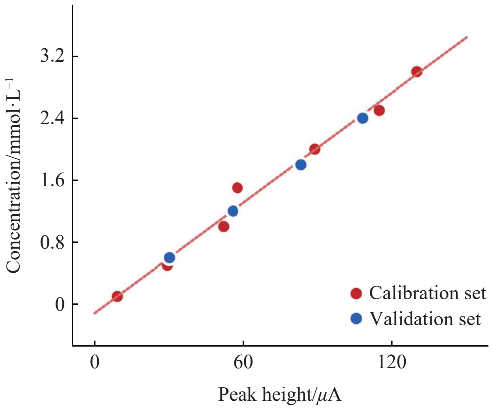


Figure 12 Data points obtained during the accuracy test

3.1.2 Results of the repeatability test

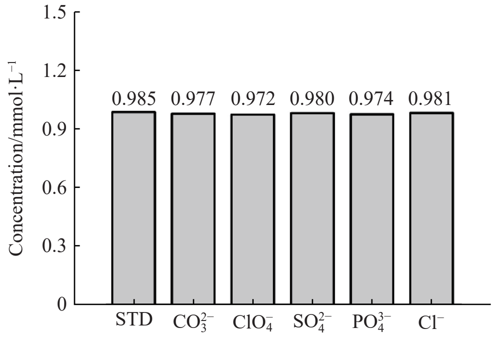
As outlined in Section 2.5.2, the Repeatability Test results, detailed in Table 3, characterize the device's robustness and short-term operational stability, essential for consistent on-site measurements. Table 3 demonstrates that the deviation between mean replicate measurements and known concentrations consistently remained within 5%, indicating high measurement precision even under repeated operation. Furthermore, a low standard deviation (SD<0.21 mmol/L) and relative deviations (RSD<11.7%) strongly highlight the device's excellent stability, minimal signal drift, and remarkable repeatability, crucial for reliable data acquisition in variable field conditions. This level of repeatability, with RSD values generally below 11.7%, is comparable to or even surpasses the typical repeatability of conventional UV spectrophotometry[14,53,54], and significantly outperforms some portable Vis-NIR spectroscopy devices that exhibit higher RSDs due to spectral noise and matrix effects[24,55,56].

Table 3 Results of the repeatability test

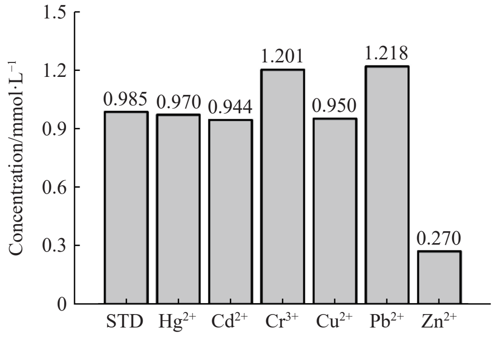
Concentration (true value)/ mmol·L^{-1}	Maximum measured value/ mmol·L^{-1}	Minimum measured value/ mmol·L^{-1}	Average measured value/ mmol·L^{-1}	Standard deviation/ mmol·L^{-1}	Absolute error/ mmol·L^{-1}	Relative error/ %
0.60	0.658	0.569	0.614	0.031	0.014	2.32
1.20	1.219	1.188	1.205	0.012	0.005	0.39
1.80	1.901	1.594	1.733	0.107	−0.067	−3.71
2.40	2.682	2.131	2.344	0.210	−0.056	−2.34

3.1.3 Results of the selectivity and interference test

As outlined in Section 2.5.3, the selectivity of the CdS NRs-SPE for nitrate-nitrogen, paramount for accurate measurements in complex soil matrices, and its resilience to interferences were evaluated via CV measurements (Figure 13). Results reveal the NRs-SPE's inherent selectivity, exhibiting negligible interference from common soil anions (carbonate, sulfate, perchlorate, bromide). For heavy metal cations, while zinc (Ⅱ) ions caused inhibition, and



a. Anion interferences



b. Cation interferences

Note: STD: Standard solution (1 mmol/L nitrate-nitrogen).

Figure 13 Results of the selectivity and interference test chromium (Ⅲ) and lead (Ⅱ) ions increased reduction currents, these interferences are effectively mitigated via appropriate pretreatment[43]. Overall, the selectivity and interference test underscores the CdS NRs-SPE's strong selectivity for nitrate-nitrogen detection, demonstrating superior selectivity to colorimetric methods (minimal anion interference) and a compelling balance of selectivity and simplicity compared to complex ion chromatography (IC) systems. This validates the device's capability for accurate and reliable measurements in complex environmental samples with minimal pretreatment, highly advantageous for portable and cost-effective on-site applications.

3.2 Results of the application test

As detailed in Section 2.6, the Application Test, employing authentic soil samples, was conducted to rigorously validate the device's practical applicability and real-world performance for on-site nitrate-nitrogen determination in complex soil matrices. Results (Table 4) show close agreement between nitrate-nitrogen content measurements from our portable device and laboratory UV spectrophotometry across diverse soil samples, with slight deviations consistently within 10%. This strongly validates the practical applicability of our device for soil nitrate-nitrogen determination in real-world agricultural samples, demonstrating its capability to provide laboratory-comparable accuracy in complex soil matrices directly in the field. This further suggests promising applicability and adaptability to diverse soil types and sources, indicating strong potential for widespread use in agricultural and environmental monitoring for routine on-site analysis. The high correlation coefficient (R^2) of 0.9969 further confirms the strong agreement and comparability, solidifying the device's validity for practical soil sample analysis and its ability to bridge the gap between laboratory precision and field-based practicality.

Table 4 Results of the application test

Sample site	Sample No.	Concentration (based on CV)/ $\text{mmol}\cdot\text{L}^{-1}$	Concentration (based on UV)/ $\text{mmol}\cdot\text{L}^{-1}$	Absolute error/ $\text{mmol}\cdot\text{L}^{-1}$	Relative error/ %
Area1	1	0.723	0.7294	−0.0064	−0.88
	2	0.823	0.7740	0.0490	6.33
	3	1.291	1.2500	0.0410	3.28
Area2	4	0.413	0.4090	0.0040	0.98
	5	0.240	0.2190	0.0210	9.59
	6	0.102	0.1120	−0.0100	−8.93
Area3	7	0.381	0.3867	−0.0057	−1.47
	8	0.462	0.4694	−0.0074	−1.58
	9	0.614	0.6292	−0.0152	−2.42

3.3 Discussions

3.3.1 Research summaries

Comprehensive performance evaluations and application tests underscore the portable device's key attributes for on-site soil nitrate-nitrogen determination. Selectivity and interference studies demonstrate the inherent selectivity of the CdS NRs-SPE sensor, exhibiting minimal interference from common soil anions and manageable interference from heavy metal cations through potential pretreatment strategies. Accuracy evaluations demonstrate high accuracy (measurement error<5%, R^2=0.9859, Tables 2 and 4; Figure 12), satisfactory repeatability (RSD<11.7%, Table 3), and a detection limit of 0.03 mmol/L. Application testing on authentic soil samples (Table 4) further validates its practical applicability, showing close agreement with UV spectrophotometry (deviation< 10%, R^2=0.9969). These findings collectively highlight the successful development of a high-performance portable device capable of bridging the gap between laboratory-level analytical performance and field-based practicality for soil nitrate-nitrogen determination.

3.3.2 Novelty and value for on-site application

To comprehensively contextualize the performance and advantages of our portable device, Table 5 presents a comparative analysis against established methods for soil nitrate-nitrogen determination, encompassing key analytical features and practical considerations.

Table 5 Comparison of different methods for soil nitrate-nitrogen determination

Feature	Portable device (CdS NRs-SPE)	UV spectrophotometry[14,26,53,54]	Vis-NIR spectroscopy[21,24,55,56]	Ion chromatography (IC)[57,58]	Colorimetric methods[48,59,60]
Accuracy (error)	<5%	<5%	~10%-15%	High (≪5%)	~10%-20%
LOD (mmol/L)	~0.03	~0.01	~0.05	Very low (≪0.01)	~0.05
Repeatability (RSD)	<11.7%	5%-15%	Higher, variable	Very low (≪5%)	5%-15%
Selectivity	High (CdS NRs-SPE)	Good	Moderate	Very high	Lower, matrix-dependent
Analysis time (per sample)	<5 min (incl. extraction)	>1 h (per batch)	<1 min	>30 min	>30 min
Cost	Low	Medium	Medium	High	Low to medium
Portability	Excellent	Poor	Good	Poor	Poor to fair
On-site usability	Excellent	Poor	Good	Poor	Poor to fair
Sample pretreatment	Simple (ECET)	Moderate	Simple	Moderate to complex	Moderate
Operator skill	Minimal	Moderate	Minimal	Expert required	Moderate

The novelty and value of our portable device for on-site application are evident across multiple critical aspects, as clearly illustrated by the comparative data in Table 5.

Innovative principles and materials. The portable CV system leveraging CdS NRs-SPEs represents a novel approach, offering a compelling advantage in selectivity and practicality compared to existing methods (Table 5). Selectivity and interference tests (Figure 13) demonstrate the inherent selectivity of CdS NRs-SPEs, which translates to minimized matrix effects and simplified sample analysis, a clear advantage over less selective colorimetric methods and even some electrochemical sensors (Table 5: Selectivity). Furthermore, the simplified electrode fabrication, avoiding complex procedures and costly materials, directly contributes to the device's low cost and enhanced practicality, making it a more accessible and field-deployable solution compared to methods requiring complex or expensive sensors (Table 5: Cost, Sample Pretreatment).

Advanced system design and automation. A key innovation lies in the integrated system design, combining a high-performance CdS NRs-SPE sensor with miniaturized electronics and automated data processing. Accuracy assessments (Table 2 and Figure 12) demonstrate performance comparable to laboratory-based UV spectrophotometry (Table 5: Accuracy), while repeatability tests (Table 3) show RSDs on par with or exceeding typical UV methods (Table 5: Repeatability). This integrated design overcomes limitations of bulky laboratory workstations, enabling rapid on-site measurements with analysis times under 5 min per sample (Table 5:

Analysis Time), a significant improvement over time-consuming laboratory procedures. Moreover, the automated peak-finding algorithm ensures user-independent operation and robust data analysis even under variable field conditions, requiring minimal operator skill compared to methods demanding expert personnel (Table 5: Operator Skill).

Streamlined practical application and workflow. The integration of the portable device with the ECET provides a novel and efficient workflow, optimized for practical on-site application (Table 5: On-site Usability, Portability). Application testing using real-world soil samples (Table 4) further validates accuracy comparable to UV spectrophotometry in complex matrices, while significantly simplifying the analytical workflow. The ECET facilitates rapid soil sample pretreatment within just 2 min, dramatically reducing overall analysis time compared to conventional extraction methods and enabling high-frequency on-site assessment (Table 5: Analysis Time). This streamlined workflow, coupled with the projected measurement cost of less than $1 per sample (Table 5: Cost), positions our device as a highly cost-effective and field-deployable solution, offering significant advantages over laboratory-bound or complex portable techniques. This combination of features establishes a foundation for high-density, high-frequency soil condition monitoring, crucial for sustainable agriculture and environmental stewardship.

3.3.3 Limitations and shortcomings

Despite its performance and practical advantages, the portable device has limitations. Firstly, while CdS NRs-SPEs demonstrate high selectivity, complete elimination of matrix effects in diverse soil samples is not achieved. Interference from heavy metal cations, particularly Zn^{2+} (Figure 13b), necessitates consideration of pretreatment for certain soil types. Secondly, while ECET enhances portability, its extraction efficiency and robustness may be influenced by soil sample variability. Standardization of extraction protocols across diverse soil conditions warrants further investigation to ensure consistent and reliable performance.

3.3.4 Prospects and expectations

Future research should prioritize refining the CV methodology and optimizing soil extraction for broader applicability. Systematic investigation of CV parameters (scan rate, potential window) is crucial to further enhance specificity and reliability. Rigorous evaluation of ECET extraction parameters (extractant type, volume) across diverse soil matrices is essential to expand device applicability. Integrating the extraction component directly into the device for a fully self-contained system and expanding analytical scope to multi-nutrient detection represent significant avenues for future development. Furthermore, assessing device performance under diverse real-world environmental conditions (temperature, humidity) and exploring data integration with agricultural equipment and data platforms are vital steps towards realizing its full potential for sustainable agricultural practices.

4 Conclusions

This study has successfully detailed the development and rigorous validation of an innovative portable electrochemical device utilizing CdS NRs-SPEs and cyclic voltammetry for rapid on-site soil nitrate-nitrogen determination. Through comprehensive performance evaluations, we have demonstrably shown that this device achieves high accuracy (measurement error consistently< 5%) and excellent repeatability (RSD<11.7%) across a relevant nitrate concentration range (0.1-3.0 mmol/L). Application testing on authentic soil samples further validated its practical applicability, demonstrating close agreement with laboratory UV spectrophotometry (deviation<10%, R^2=0.9969) and robust performance in complex soil matrices. Critically, selectivity and interference studies confirmed the inherent specificity of the CdS NRs-SPE sensor, minimizing matrix effects and enabling simplified sample pretreatment with our ECET system. Compared to existing portable spectroscopic methods, our electrochemical device offers a distinct advantage in operational simplicity, affordability (projected cost < $1 per test), and robust field performance, while maintaining comparable analytical accuracy to laboratory standards. Consequently, this portable electrochemical device represents a significant and practical advancement in soil nutrient sensing technology, offering a rapid, cost-effective, user-friendly, and field-deployable solution that effectively bridges the critical gap between laboratory precision and on-site needs. This innovation holds substantial transformative potential for enabling routine, high-throughput soil nitrate-nitrogen monitoring, facilitating data-driven precision agriculture, and promoting sustainable environmental stewardship in agricultural practices.

Acknowledgements

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