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STUDY ON WATER CONTENT COMPENSATION METHOD AND EXPERIEMNTAL FOR SOIL PH DETECTION SENSOR

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ABSTRACT

Evidence suggests that soil pH is among the most important factors for soil fertility and nutrients. Precise regulation and detection of soil pH during crop growth is an urgent need for modern digital agriculture. This paper focuses on the online detection of soil pH is greatly affected by soil moisture, resulting in poor online detection accuracy. Based on the modified membrane all-solid antimony electrode pH sensor, design the water content compensation model by the binary regression analysis method, and experimentally study the influence of soil moisture on the online pH value detection. The research results show that the maximum absolute error of online soil pH detection before compensation reaches 1.88, and the minimum threshold of water content for online detection is 7%. After compensation for water content, the absolute error of online soil pH detection does not exceed 0.36, and the relative error does not exceed 4.3%. The water content coefficient sensitivity of online detection is reduced from 0.27 to 0.097, and the stability and accuracy of online detection are significantly improved.

Keywords: ***Online pH detection; water content compensation; binary regression analysis; all solid-state pH sensor; soil; water content threshold***

1. Introduction

The pH is one of the most important physical and chemical parameters of soil and directly affects the growth and quality of crops [1–2]. Research has shown that the effective nutrients in the soil have the best properties in the pH range of 6.5 to 7.5. The nutrient status of plants will be affected under too acid or too alkaline environments and cause the quality of crops to decline [3–5]. The reason for the pH test results is related to the soil moisture [6-8] is that the hydrogen ions in the soil are attached to the water molecules and combine with water molecules to form hydronium ions (H_3O^+). Therefore, it is great significance to compensate the water content of soil pH online detection, and effectively improve the accuracy of pH detection.

The research of pH detection mainly focuses on the environmental temperature compensation. In 2011, Bhadra, Sharmistha proposed a passive sensor with integrated coupling coil. The sensor consists of thermistor, varactor diode and pH electrode. Through thermistor detection to realize the temperature compensation of pH detection result. In the range of 25 ºC ~55 ºC, the detection accuracy of the sensor to the buffer solution reaches 0.1pH[9]. In 2012, Chen Yao established temperature compensation model by least square method and reduced the pH measurement error [10]. In 2020, Sinha S compensates the temperature and time drift of the ion-sensitive field effect tube (ISFET) pH sensor through machine learning. The results show that the random forest method has the best compensation effect. In the range of 15 ºC ~55 ºC, the pH of the buffer solution is in the range of

2~12, the minimum deviation of pH is less than 0.025[11]. In 2017, Xu Kun studied the relationship between the pH sensor's detection performance and water content in peat and vermiculite cultivation substrates, and established the substrate water content compensation model through the method of difference fitting.

In summary, the compensation methods commonly used for pH sensor online detection mainly include regression analysis method, hardware compensation method, machine learning and difference fitting method. The regression analysis method compares the interdependence between variables and to analyzes its changing law. Its advantages include simple principle, less data demand, and higher compensation accuracy. Through revise compensation model to improve the adaptability of online pH detection to the environment.

On the whole, the automatic temperature compensation method has the advantages of high accuracy, flexible application, and convenient operation. However, soil and other heterogeneous systems have different changes in water content and are insufficient to form a saturated solution. There is a lack of research on water content compensation for online pH detection and it is necessary to research on soil pH online detection and water content compensation. In this paper, based on the modified membrane all-solid antimony electrode pH sensor, use binary regression analysis method, study soil pH online detection water content compensation method, establish water content compensation mathematical model and test the application effect.

2. Experiment on the Influence of Soil Moisture Content on Antimony Electrode pH Sensor Detection

Take a soil sample about 10 cm below the ground surface and process the soil sample, use soil particles with a particle diameter of less than 2 mm as the test sample. Dry the soil samples and divided it six parts evenly and each part of the soil was soaked and use PBS buffer with pH of 3.75, 4.26, 5.85, 7.04, 8.33, 9.72 for each soil to soak and stir. Divide the soil samples with different pH values into two evenly, one as the pH sensor test sample, and the other one as the reference sample measured by the extraction method. Take out 100g from the test sample and put it into different beakers. Add 15g, 25g, 35g, 45g, 55g, 65g of water to different beakers to obtain soil samples with mass water content of 15%, 25%, 35%, 45%, 55% and 65% respectively, insert the pH sensor into the sample, and use electrochemical workstation to measure output voltage. The relationship between the voltage and the soil moisture is shown in Figure 1.

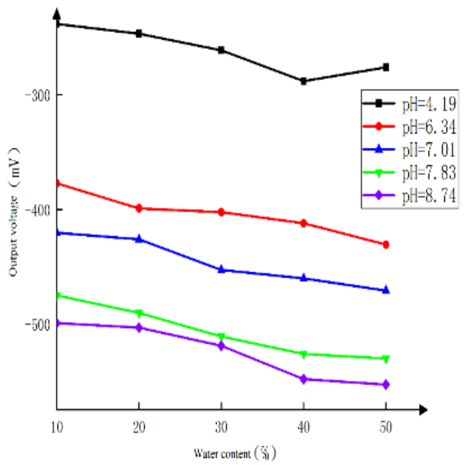

Figure 1. Output voltage of pH sensor under .different soil moisture

It can be seen from Figure 1 that the soil moisture has a significant effect on the output potential of the antimony electrode pH sensor. With the water content increase, the output voltage of the pH sensor continues to decrease and gradually slow down. After conversion, the pH measurement is getting closer and closer to the reference true value. In the range of 15%~65% soil moisture, the absolute deviation of pH is between 0.64~1.85.

3. On-line detection of soil pH and water content threshold experiment

When the soil moisture is too low, the soil cannot resolve hydrogen ions, and it is difficult to detect pH. At this time, even if through model compensation, the desired effect cannot be reached. Therefore, this section determines the appropriate soil moisture threshold for online pH detection by control the soil moisture.

Take out the dried soil samples, divide them into 8 evenly, configure soil samples with soil moisture of 1%,3%, 5%, 7%, 10%, 14%, 17% and 20% respectively. Insert the pH sensor into the sample, repeat the measurement three times, use electrochemical workstation to measure the output voltage, calculate the pH measurement value according to the sensor sensitivity relationship, and calculate the change in the average pH value and the relative standard deviation within the group.

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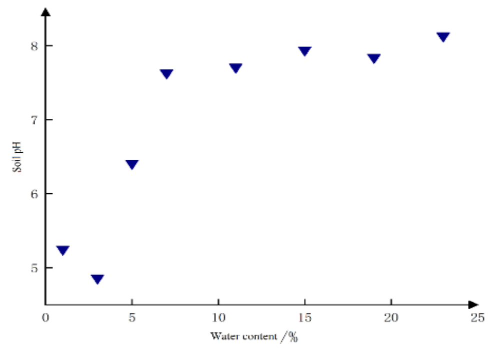
The measurement results of soil moisture and pH are shown in Table 1 and Figure 2.

Table 1. Water content threshold analysis.

Parameter	Soil moisture content /%							
	1%	3%	5%	7%	11%	15%	19%	23%
Average pH	5.25	4.86	6.41	7.63	7.71	7.94	7.84	8.13
Relative standard deviation /%	7.82	6.35	1.04	0.77	0.43	0.89	0.66	0.52



.Figure 2. Water content threshold analysis

Comprehensive Table 1 and Figure 2 show that with the increase of soil moisture, the average value of pH measurement show an overall upward trend, and the relative standard deviation within the group continues to decrease. Comparing the relative standard deviation within the group show that when the soil moisture is 5%, the relative standard deviation is 1.04%, which is much less than the relative standard deviation of 3%; however, when the soil moisture increases from 5% to 7%, the measured average pH value increases by 1.22, which is greater than the maximum deviation of the average pH value of soil moisture from 7% to 23%.When the soil moisture is greater than 7%, the relative standard deviation within the group becomes significantly smaller, and the average pH value changes smoothly, so it is believed that the appropriate water content threshold for the antimony electrode pH sensor online detection is about 7%.

4. Construction of Compensation Model for Online Soil pH Detection and Water Content

Ideally, the pH sensor is a single-input-single-output system, but because the pH sensor is affected by soil moisture and other factors in the soil detection process, therefore, in reality, the pH sensor becomes multiple-input-single-output system. This paper only considers the influence of soil moisture on the online detection of pH sensors, so binary regression analysis is used to study the compensation of soil moisture to online pH detection. Suppose the output voltage of the antimony electrode pH sensor is U_p and the soil moisture is ω, then the pH of the soil is composed of a binary function of voltage U_p and water content ω:

$$pH = f(U_p, \omega) \quad (1)$$

Hypothesis: pHi in a plane is determined by two-dimensional coordinates (U_{pi}, ω_i), which can be described by a quadratic curve fitting equation:

$$pH = \alpha_0 + \alpha_1 U_p + \alpha_2 \omega + \alpha_3 U_p^2 + \alpha_4 U_p \omega + \alpha_5 \omega^2 + \varepsilon_1 \quad (2)$$

In the formula, α_0~α_5 are constant coefficients of the regression equation, and $\varepsilon_1$is a high-order infinitesimal.

In the range of pH sensor 3~10, determine N pH calibration points, and determine M water content calibration points when the soil water content exceeds the threshold range. The standard input of each calibration point is as follows:

pH_i: $pH_1, pH_2, pH_3 \ldots pH_n$

ω_i: $\omega_1, \omega_2, \omega_3 \ldots \omega_n$

If each constant coefficient of the previous formula is known, when collect the output U_p of the pH sensor and the soil moisture ω, can calculate the pH by replacing U_p and ω with the formula. The pH value calculated by the antimony electrode sensor after the i-th water content compensation is pH_i (U_{pi}, ω_i), according to formula (3):

$$pH_i = \alpha_0 + \alpha_1 U_{pi} + \alpha_2 \omega_i + \alpha_3 \omega_i^2 + \alpha_4 U_{pi} \omega_i + \alpha_5 \omega_i^2 \quad 3)$$

Among them, i=1, 2...m×n. According to the principle of least squares, the coefficient value obtained should meet the minimum mean square error condition, and there is an error e_i between the actual pH of the i-th soil sample and the calculated pH_i value pH_i (U_{pi}, ω_i), the variance is ei_2:

$$e_i = pH_i(U_{pi}, \omega_i) - pH_i \quad (4)$$

$$e_i^2 = [pH_i(U_{pi}, \omega_i) - pH_i]^2 \quad (5)$$

which is:

$$e_i^2 = [(\alpha_0 + \alpha_1 U_{pi} + \alpha_2 \omega_i + \alpha_3 \omega_i^2 + \alpha_4 U_{pi} \omega_i + \alpha_5 \omega_i^2) - pH_i]^2 \quad (6)$$

There is a total of $m \times n$ calibration points, and the mean square error R_1 should be the smallest, that is:

$$R_1 = \frac{1}{m \times n} \sum_{i=1}^{m \times n} [(\alpha_0 + \alpha_1 U_{pi} + \alpha_2 \omega_i + \alpha_3 U_{pi}^2 + \alpha_4 U_{pi} \omega_i + \alpha_5 \omega_i^2) - pH_i]^2 \quad (7)$$

It can be seen that the mean square error R_1 is a multivariate function of the parameters α_0, α_1, α_2, α_3, α_4, α_5, that is:

$$R_1 = R_1(\alpha_0, \alpha_1, \alpha_2, \alpha_3, \alpha_4, \alpha_5)$$

According to the extreme condition of multi-water content, calculate the partial derivatives of α_0, α_1

, α_2, α_3, α_4 and α_5 respectively, and set the derivatives to 0. The calculation equation is as follows:

$$\left.\begin{aligned}
\frac{\partial R_1}{\partial \alpha_0} &= \frac{2}{m\times n}\sum_{i=1}^{m\times n}[\sum_{k=0}^{5}\alpha_k h_{ik} - pH_i]\times c_{i0} = 0, c_{i0} = 1\\
\frac{\partial R_1}{\partial \alpha_1} &= \frac{2}{m\times n}\sum_{i=1}^{m\times n}[\sum_{k=0}^{5}\alpha_k h_{ik} - pH_i]\times c_{i1} = 0, c_{i0} = u_i\\
\frac{\partial R_1}{\partial \alpha 2} &= \frac{2}{m\times n}\sum_{i=1}^{m\times n}[\sum_{k=0}^{5}\alpha_k h_{ik} - pH_i]\times c_{i2} = 0, c_{i2} = \omega_i\\
\frac{\partial R_1}{\partial \alpha_3} &= \frac{2}{m\times n}\sum_{i=1}^{m\times n}[\sum_{k=0}^{5}\alpha_k h_{ik} - pH_i]\times c_{i3} = 0, c_{i3} = u_i^2\\
\frac{\partial R_1}{\partial \alpha_4} &= \frac{2}{m\times n}\sum_{i=1}^{m\times n}[\sum_{k=0}^{5}\alpha_k h_{ik} - pH_i]\times c_{i4} = 0, c_{i4} = u_i\omega_i\\
\frac{\partial R_1}{\partial \alpha_5} &= \frac{2}{m\times n}\sum_{i=1}^{m\times n}[\sum_{k=0}^{5}\alpha_k h_{ik} - pH_i]\times c_{i5} = 0, c_{i5} = \omega_i^2
\end{aligned}\right\} \quad (8)$$

From the above equation:

$$\sum_{i=1}^{m\times n}[\sum_{k=0}^{5}\alpha_k c_{ik}]\times h_{ik} = \sum_{i=1}^{m\times n} pH_i \times c_{ik} \quad (9)$$

According to the nature of the matrix, simplify further to get:

$$\alpha \times C \times C^T = pH \times C^T \quad (10)$$

Where:

$$\alpha \times C = \sum_{k=0}^{5}\alpha_k c_{ik} \quad (11)$$

$$pH \times C^T = \sum_{i=1}^{m\times n} pH_i \times c_{ik} \quad (12)$$

Then the optimal solution of the undetermined coefficients α_0, α_1, α_2, α_3, α_4, α_5 of the regression equation is:

$$\alpha = pH \times C^T \times (C \times C^T)^{-1} \quad (13)$$

Using the data in figure 1 as sample data, according to the optimal solution of the matrix equation (13), use MATLAB to calculate regression coefficients, and the result is:

α_0=-1.4187, α_1=-26.7016, α_2=-1.9669, α_3=-9.8452, α_4=1.4814, α_5=1.2006.

The compensation equation obtained according to the binary regression analysis is:

$$pH = -1.4187 - 26.7016U_p - 1.9669\omega - 9.8452U_p^2 + 1.4814U_p\omega + 1.2006\omega^2 \quad (14)$$

4. Soil pH online detection of water content compensation effect experiment and result analysis

Compensate according to the compensation model. The statistical results of the pH detection data before and after compensation are shown in Table 2, and the data curve comparison is shown in Figure 3. The three curves represent the actual pH, the pH before and after compensation. The absolute error of the compensated pH value online detection does not exceed 0.36, and the average absolute error $\bar{e}$ = 0.09.

According to the compensation result, further calculate the sensitivity water content coefficient of the pH sensor before and after compensation. Before and after compensation, the sensitivity water content coefficient can be calculated by the following formula (15):

$$\alpha_s' = \left|\frac{pH_{\omega 1} - pH_{\omega 2}}{pH_{\omega 1}\Delta\omega}\right| \quad (15)$$

Among them, $pH_{\omega 1}$- $pH_{\omega 2}$ is the maximum difference of pH measurement when the soil water content is between ω_1 and ω_2. $\Delta\omega$ is the variation range of soil water content. In this experiment, $\Delta\omega$=50%. According to the data in table 2, the pH value with the largest deviation before compensation is soil sample 2 (reference pH value is 8.74), which is calculated with the formula, the sensitivity water content coefficient is α_s=0.27.

In the same way, according to the data in Figure 3 and Table 2, the maximum difference in pH after compensation is soil sample 2, which can be calculated as α_s'=0.097. It can be seen that after water content compensation, the sensitivity water content coefficient of online pH detection decreases.

In summary, the pH deviation after compensation is reduced, which is closer to the actual pH of the soil.

5. Discussion

In this paper, we configure different soil moisture samples, experiment study on the influence of soil moisture on pH online detection, explore appropriate soil moisture threshold and establish a water content compensation model based on binary regression analysis. The results show that soil moisture has a significant impact on online pH detection. For soil samples with the same pH, as the water content increases, the output electric potential of the sensor keeps decrease; the pH online detection appropriate water content threshold is 7%. After model compensation, the stability of pH detection is greatly improved, the absolute error does not exceed 0.36, the relative error does not exceed 4.3%, the pH online detection sensitivity water content coefficient is reduced from 0.27 to 0.097, the stability and accuracy of online pH detection are significantly improved (Liu et al., 2017; Wang et al., 2021; Zhang et al., 2019; Zuo et al., 2015; Zuo et al., 2017; Xiong et al., 2021; Chen et al., 2021; Zhou et al., 2019; Chaghakaboodi et al., 2021; Zeidali et al., 2021a; Haghshenas and Ghanbari Malidarreh, 2021; Farokhian, et al., 2021; Bakhshi et al., 2021; Zeidali et al., 2021b).

Supplementary Materials

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The following are available online at www.mdpi.com/xxx/s1, Figure S1: Output voltage of pH sensor under different soil moisture, Figure S2: Water content threshold analysis, Figure S3: pH sensor compensation effect diagram, Table S1: Water content threshold analysis, Table S2: Output value of pH sensor after compensation.

Table 2. Output value of pH sensor after compensation.

Soil sample	Water content ω	Reference pH	pH before compensation	Deviation before compensation	pH after compensation	Deviation after compensation
Soil sample 1	15%	4.50	3.22	-1.28	4.54	0.04
	25%	4.50	3.15	-1.35	4.27	-0.23
	35%	4.50	3.46	-1.04	4.48	-0.02
	45%	4.50	3.52	-0.98	4.43	-0.07
	55%	4.50	3.78	-0.72	4.55	0.05
	65%	4.50	3.69	-0.81	4.38	-0.12
Soil sample 2	15%	8.40	6.52	-1.88	8.30	-0.10
	25%	8.40	6.97	-1.43	8.45	0.05
	35%	8.40	7.16	-1.24	8.40	0.00
	45%	8.40	6.89	-1.51	8.04	-0.36
	55%	8.40	7.52	-0.88	8.43	0.03
	65%	8.40	7.43	-0.97	8.28	-0.12

.Figure 2. pH sensor compensation effect diagram: (a) pH=4.50; (b) pH=8.40

Author Contributions

Conceptualization, ZONG SHENGKANG, ZHANG XILIANG, LU CHENGXUAN and NI MENGYAO; methodology, ZONG SHENGKANG and LU CHENGXUAN; formal analysis, ZONG SHENGKANG; writing—original draft preparation, ZONG SHENGKANG and LU CHENGXUAN; writing—review and editing, ZONG SHENGKANG, ZHANG XILIANG, LU CHENGXUAN, MAO TIANYU, SU XIAOQING and NI MENGYAO; supervision, ZHANG XILIANG; project administration, ZHANG XILIANG. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement

Not applicable.

Acknowledgments

Not applicable.

Conflicts of Interest

The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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