Design of High Precision pH Meter Based on STM32

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Abstract: To solve the problems of large volume, low detection accuracy and high cost, we design a pH meter based on ultra-low power consumption MCU. In order to meet the measurement accuracy, the pH meter has three-point calibration, automatic temperature compensation and other functions. The measurement results show that the pH value of the solution can be accurately measured by the pH meter, and the measurement accuracy has reached ± 0.02.

1. Introduction

With the improvement of human living standards, pH value is usually used to judge whether drinking water meets standards or whether products are qualified. There are many ways to measure pH value including chemical analysis, test paper analysis and potential analysis. Since neither chemical analysis nor test paper analysis can measure pH automatically, the pH meter designed in this paper adopts potentiometric analysis.

The design uses the Cortex-M3 core ARM processor as the microprocessor. Through glass composite electrodes and thermistors, this pH meter can collect the pH and temperature of the measured solution [1]. In the acquisition process, the aging of the electrode, the temperature change of the aqueous solution and the stability of the measurement circuit will cause measurement errors of the pH value [2, 3]. In order to reduce errors, the composite glass electrode must be calibrated at three points after a period of use, i.e. the system calibrates three standard solutions with known pH values, and stores the calibrated parameters in the Flash of the microprocessor [4, 5]. In the subsequent measurement process, the pH value of the solution to be measured is calculated by this set of parameters.

2. Measuring Principle

2.1 Principle of Potentiometric Analysis

Water is chemically neutral. In a neutral solution, the concentration of hydrogen ions and hydroxide ions are both $10^{-7}$ mol/L. The pH value is the negative value of the base-10 logarithm to hydrogen ion concentration, so the pH value of the neutral solution is equal to 7. And the water molecules will spontaneously decompose in certain cases.

$$H_2O = H^+ + OH^-$$

(1)

where $H^+$ and $OH^-$ are hydrogen ions and hydroxide ions. The pH value is usually measured by a potentiometric method. Different pH, different potential. There is a one-to-one relationship between the voltage signal obtained from the sensor and the concentration of hydrogen ions, which is the theoretical basis of the Nernst equation.

$$E = E_0 + \left(2.30259RT/nF\right) \cdot \log {a_{H^+}}$$

(2)
where \( E \) is the output electromotive force of the galvanic cell, \( E_0 \) is the standard electric potential and a constant, \( R = 8.31447215 \text{ J/(K·mol)} \) is the gas constant, \( T = 273.15 + t \) is the absolute temperature of the measured solution, \( n = 1 \) is the valence of hydrogen ions, \( F = 96485 \text{ C/mol} \) is the Faraday constant, \( a_{H^+} \) is the hydrogen ion activity.

The pH value of the solution can be expressed as:

\[
pH = -\log a_{H^+},
\]

Therefore, equation (1) can be rewritten as:

\[
E = E_0 - 2.30259 \left( \frac{RT}{F} \right) \cdot pH = E_0 - KpH
\]

\[
K = 2.30259 \frac{RT}{F} = 1.9842 \times 10^{-4} T
\]

It can be seen from equation (4) the pH value of the measured solution is linearly related to the electromotive force output by the composite glass electrode.

2.2 Principle of Temperature Compensation

It can be seen from equation (4) that the electromotive force output by the composite glass electrode is also related to temperature, so the measured pH value must be related to temperature. At the same temperature \( T_1 \), the electrode was placed in two standard buffer solutions of \( pH_1 \) and \( pH_2 \), and the output electromotive forces of the electrode were measured as \( E_1 \) and \( E_2 \).

\[
\begin{align*}
E_1 &= E_0 - K_{T_1} pH_1 \\
E_2 &= E_0 - K_{T_1} pH_2
\end{align*}
\]

The slope at temperature \( T_1 \) and the zero potential of electrode can be obtained by solving equation (6).

\[
K_{T_1} = \frac{(E_1 - E_2)}{(pH_2 - pH_1)}
\]

\[
E_0 = \frac{(E_1 pH_2 - E_2 pH_1)}{(pH_2 - pH_1)}
\]

\[
K_{25} = K_{T_1} + (273 + 25 - T_{T_1}) \times \Delta K
\]

where \( \Delta K = 0.19842 \). When the temperature of the measured solution \( T \) and the output electromotive force of the electrode \( E \) are determined, the actual measured pH value can be obtained from the equation (10).

\[
\begin{align*}
K_T &= K_{25} + (T - 298) \times \Delta K \\
pH_T &= \frac{(E_0 - E)}{K_T}
\end{align*}
\]

3. System Hardware Design

The whole system is composed of several modules, including the master control part, the sensor part, the signal processing part, the storage part, the keyboard part and the display part. Using STM32F103 of ST company as microprocessor in the master control part, the system can realize the acquisition and processing of pH signal. Figure 1 shows the overall function block diagram of the system.
3.1 Signal Processing

According to the principle of potentiometric analysis, the potential of the composite glass electrode is required to obtain the pH value. However, due to the very high internal resistance of the composite glass electrode, an amplifier with high input impedance is required to match it when amplifying the signal [6]. Therefore, a dual-channel operational amplifier with high input impedance (TLC27L2) is selected in this design.

![Fig. 1 Structure diagram of system](image)

As shown in Figure 2, to ensure that the reference electrode voltage is always positive, we use a channel of the operational amplifier to track the reference electrode signal. The other three channels make up a differential amplifier circuit to amplify the sensor signal.

3.2 Button control

According to the functional requirements, the key part of the pH meter is composed of three freestanding buttons, including ON-OFF button, CAL button and HOLD button. Through the ON-OFF button, the pH meter can realize the function of switch on and off. The pH meter can be calibrated in three standard buffer solutions through the CAL button. Any time the HOLD button is pushed, the measured value that appeared on the LCD screen at that moment will be locked until the HOLD button is pressed again.

4. Software Design

The software design of the whole system is written in C language and adopts modular programming method. The system software flow chart is shown in the figure.
Firstly, the system conducts the watchdog initialization, timer initialization, interrupt initialization and A/D conversion initialization. Then, it turns on the A/D conversion, pH signal processing and temperature compensation. Next, the LCD screen displays the measured value. Finally, we compare the measured value with the standard value and judge whether the data is accurate. If not, it carries out the three-point calibration subroutine processing until the measured value on the LCD screen is accurate.

5. Measure and Discuss

The sensor signal must be affected by the temperature change of the solution and the stability of the circuit. Therefore, in order to ensure the accuracy of the measurement results, it is necessary to conduct three-point calibration on the collected pH sensor data in the software.

Table 1 Measured values before and after calibration

<table>
<thead>
<tr>
<th>t/℃</th>
<th>Measured solution</th>
<th>Measured value before calibration</th>
<th>Error before calibration</th>
<th>Measured value after calibration</th>
<th>Error after calibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>4.01</td>
<td>4.05</td>
<td>0.04</td>
<td>4.02</td>
<td>0.01</td>
</tr>
<tr>
<td>25</td>
<td>4.01</td>
<td>4.02</td>
<td>0.01</td>
<td>4.01</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>4.01</td>
<td>4.09</td>
<td>0.08</td>
<td>4.01</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>6.86</td>
<td>6.88</td>
<td>0.02</td>
<td>6.88</td>
<td>0.02</td>
</tr>
<tr>
<td>25</td>
<td>6.86</td>
<td>6.86</td>
<td>0</td>
<td>6.87</td>
<td>0.01</td>
</tr>
<tr>
<td>30</td>
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<td>6.95</td>
<td>0.09</td>
<td>6.86</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>9.18</td>
<td>9.24</td>
<td>0.06</td>
<td>9.17</td>
<td>-0.01</td>
</tr>
<tr>
<td>25</td>
<td>9.18</td>
<td>9.20</td>
<td>0.02</td>
<td>9.18</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>9.18</td>
<td>9.24</td>
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<td>9.18</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 1 shows the measured data of the pH meter before and after calibration at different temperatures and different standard buffer solutions. The measured data show that after three-point calibration, the measurement error of the three standard buffer solutions in the range of 20 ~ 30℃ is less than ±0.02.

6. Summary

We propose a design of high precision pH meter, which focuses on solving the problems of high internal resistance, calibration and temperature compensation of glass electrode. From the measurement results, we can conclude that the pH meter can measure the pH value accurately, and
the error is not more than ± 0.02. Due to the good stability and simple operation of the pH meter, it has a broad application prospect.

References