PH sensor design based on potentiometric analysis method

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Abstract

In order to accurately, continuously detect solution *pH* on line, regarding C8051F020 as the control centre, the output voltage of glass electrode is amplified through high input impedance circuit utilizing potentiometric method to obtain related voltage signal of *pH* value. Standard solution and temperature sensor ADT7301 are utilized for system calibration and moving average filter of the detected *pH* values, thereby achieving real-time online detection of *pH* value. Detection results are accurate and reliable; low power consumption and miniaturation also facilitate rapid collection and analysis of data under different environments.

Keywords: *pH* detection, C8051F020, glass electrode

1 Introduction

The *pH* value is a basic parameter for the acid concentrations of the solution, and an important standard determining the quality of a variety of water system such as industrial water, environmental water and domestic water. Common methods of detecting *pH* parameters are chemical analysis, paper strip analysis and potential analysis. Chemical analysis and paper strip analysis cannot achieve online real-time monitoring, so in this research, potentiometric method is utilized to design a portable sensor for rapidly detecting the *pH* value of water samples, which is suitable for operating personnel to duly analyse and estimate water quality on the spot. The sensor detects *pH* value by composite glass electrode, amplifies weak voltage signal through signal processing circuit and converts the signal into standard voltage signal. Temperature compensation is needed in *pH* detection, ADT7301 digital temperature sensor is utilized for temperature detection in this research, which can effectively improve the accuracy of detection.

2 Principle of *pH* detection

Detection of *pH* is to measure the concentration of hydrogen ions, and the definition of *pH* is the negative logarithm of hydrogen ion concentration, namely, $pH = -\log[H^+]$. The *pH* value 0 indicates strong acidic solution, while *pH* 14 indicates strong alkaline solution. At room temperature, the solution with $pH = 7$ is neutral solution. In this research, pH is measured through potentiometric method. Glass electrode and silver-chloride electrode are regarded as the indicating electrode and reference electrode, respectively, and the two electrodes are encapsulated together to form a composite glass electrode. After the sensor is inserted into the test solution, composite glass electrode and test solution can form a primary battery, and the positive pole and negative pole of primary cells are two output lead wires of composite glass electrode. In measuring the *pH* of the solution, the electrodynamic force between glass electrode and reference electrode will change with the change of hydrogen ion concentration in sample solution. If the electric potential difference between two electrodes is zero, then *pH* value of test solution is 7, and the potential of *pH* composite electrode is 0V. According to Nernst equation, the relationship between output electrodynamic force of primary battery, absolute temperature of test solution and pH value of test solution is as below [1].

$$E = E_0 + KT(pH_x - pH_s), \quad (1)$$

wherein, E is the output electrodynamic force of primary battery; constant E_0 is the potential difference determined by electrode material, internal reference solution, internal reference electrode and liquid junction potential; constant K is the Nernst factor; T is the absolute temperature of sample solution; pH_x is the pH value of the test solution; constant pH_s is the pH value of buffer solution in the composite glass electrode.

Through Equation (1), the output electromotive force of original battery is generated by pH value and temperature of test solution together, so after simultaneously measuring output electrodynamic force and solution temperature of primary battery, pH value of the test solution can be calculated according to Equation (1).

3 System hardware design

The overall system structure is shown in Figure 1. C8051F020 microcontroller is the control core of the system.

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Through signal processing circuit with high input impedance, weak electrical signals of *pH* detection electrode are sent into the built-in A/D module of microcontroller, conducting temperature compensation through thirteen-bit digital temperature sensor ADT7301. External advanced ferroelectric memory chip FM31256 is regarded as non-volatile memory to automatically save data when the system is powered down. Human-machine interface is composed of matrix keyboard and LCD dot matrix, which can communicate with the host computer through RS232 bus.

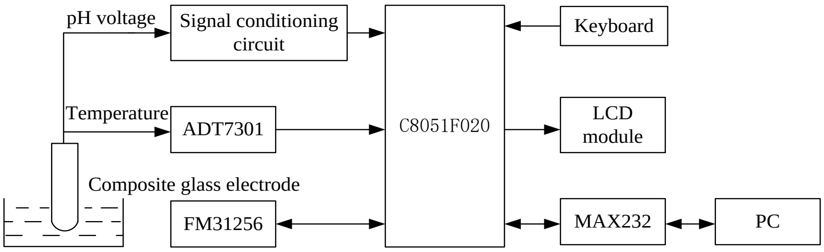

FIGURE 1 Block diagram of *pH* detection system

3.1 STRUCTURE AND PERFORMANCE CHARACTERISTICS OF C8051F020

C8051F020 is a mixed-signal system microcontroller produced by Cygnal Company [2], the instruction set of which is fully compatible with MCS-51. Compared with previous 51-series microcontrollers, C8051F020 has a lot of new features, but its reliability and speed should been improved. Generally, the change in the *pH* value of solution is a slow transition process, which does not need A/D converter with high sampling rate. C8051F020 microcontroller has twelve-bit successive approximation A/D converter and sampling holder, connecting with the outside world through an eight-port analog multiplexer. The A/D converter has a nonlinear accuracy of 0.25LSB and a sampling rate up to 100kbit/s at the highest resolution. Therefore, there is no need to configure an appropriative A/D converter if C8051F020 microcontroller has been chosen as system MCU. Meanwhile, C8051F020 microcontroller has built-in in-system programming Flash (64K bytes), RAM (4352 bytes) and E^{2}PROM (512 bytes), so we do not need to design additional extenders and data memories, and the on-chip E^{2}PROM is directly utilize to store system parameters. C8051F020 has six operating modes and automatically enters the sleep state when the system is not working, thus effectively lowering the power consumption of the system.

3.2 DETECTION MODULE OF *PH*

In detection module, *pH* composite electrode and amplification circuit constitute the detection unit. If the *pH* value of test solution is distributed in the range of 0-14, *pH* composite electrode will output bipolar analog signals. However, due to the high internal resistance of *pH* composite electrode $\left(10^{8}\Omega \sim 10^{10}\Omega\right)$, the output signals are relatively weak, usually hundreds of millivolts. Therefore, output signal needs amplification and translation to meet the input range of A/D analog-digital conversion circuit; composite *pH* electrode has high resistance, so the key of detection circuit is to achieve high input impedance and consider impedance matching, which requires input impedance of detection circuit to maintain in the range of $10^{12}\Omega \sim 10^{13}\Omega$, thus effecttively reducing detection errors. Detection circuit of *pH* value is shown in Figure 2.

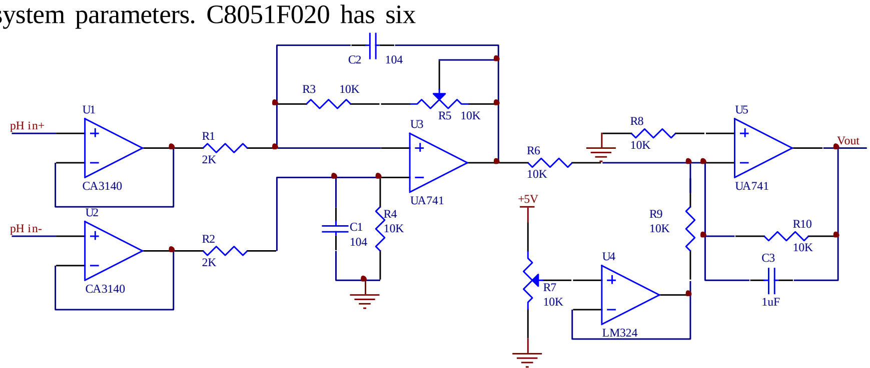

FIGURE 2 *pH* detection circuit

In order to reduce detection noise and improve system stability, an operational amplifier CA3140 is utilized in this research, which is a BIMOS operational amplifier developed by the Radio Corporation of America. On the integrated chip, piezoelectric PMOS transistor technology, the advantages of high-voltage bipolar transistor, MOS/FET input and the technology of bipolar output are utilized by combining the excellent performance of COS/MOS op amp for the first time. COS/MOS op amp is characterized by high input impedance, low bias current, low noise and high gain, and mainly utilized to complete impedance matching, reduce detection noise and improve system stability. In order to improve input impedance of the whole transmitter, transforming part of input impedance is made up of CA3140 with input impedance up to $10^{14}\Omega$. Each CA3140 is connected to a voltage follower, constituting the first stage circuit to improve input impedance. Besides, due to the symmetrical structure, CMRR can be effectively improved if two devices have the same parameters, and the common-mode signal and offset error signals can also offset.

Generic op amp UA741 is chosen as the second-stage differential amplifier, and amplification can be deduced by Equation (2).

$$Vout = (\frac{R_1 + R_3 + R_5}{R_2 + R_4})V_+ - \frac{R_3 + R_5}{R_1}V_-, \quad (2)$$

where $Vout$ is output of U_3 in Figure 2; V_+ and V_- are the output voltages of two voltage followers. Amplification can be set by changing the resistance value of variable resistor. Through the addition operation between the amplified signal and output of LM324 follower circuit, the output signal of second-stage differential amplifier is added to a fixed voltage, thus realizing level conversion and finally achieving the output of 0.5V-4.8V signal through the reverse amplifier circuit composed of UA741.

3.3 TEMPERATURE DETECTION

In this design, 13-bit digital temperature sensor ADT7301 is utilized to detect temperature. The sensor, with no other external circuitry, does not need to convert analog signal to digital signal, and it can directly output digital quantity. ADT7301 makes the system structure more simple and reliable. ADT7301 and microcontroller C8051F020 utilize SPI communication mode; the serial interface consists of four wires-C/S, SCLK, DIN and DOUT. Temperature detection circuit is shown in Figure 3.

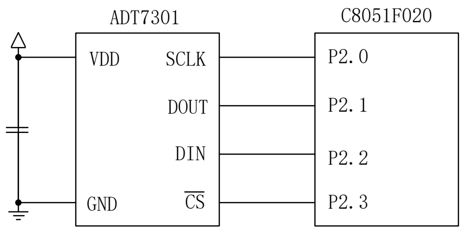

FIGURE 3 The temperature detection circuit

A bandgap temperature sensor for temperature detection and a thirteen-bit A/D converter [3] are integrated in ADT7301 chip, which has a low supply current, high temperature conversion precision, low power and flexible, convenient serial interface. Crystal oscillator is also integrated in AD7301, so clocks can be directly connected to serial port at work, with no need of A/D conversion. The chip has two modes-normal operating mode and power-saving mode. In normal operating mode, the internal clock oscillator will drive automatic conversion timing, so that the chip electrifies the analog circuitry once per second for a temperature conversion, which generally takes 800us. After the conversion, chip analog circuit will automatically power off, and then automatically power on after one second. Therefore, the latest temperature conversion value can always be obtained in temperature value register. Temperature value register is a fourteen-bit read-only register utilized to store temperature conversion result of ADC, and the result is composed of thirteen-bit binary complement code and one-bit sign bit, the top digit. This sensor has a detection accuracy of ± 0.5℃, temperature resolution of 0.03125℃ and detection range of -40℃~+150℃.

By setting control register ADT7301, the chip can be set to power-saving mode. In power-saving mode, the on-chip oscillator is turned off without temperature conversion in ADT7301 until the normal operating mode. By writing zero to the control register, the chip will restore to normal operating mode. Power-saving mode of C8051F02 microcontroller can effectively reduce the power consumption of the system.

4 Electrode calibration and temperature correction

4.1 ELECTRODE CALIBRATION

Before use, pH sensor should be set to zero. The specific way is to insert pH composite electrode into the solution with temperature of 25℃ and pH value of 7, and adjust the zeroing end of pH detection circuit until output voltage signal of amplifying circuit is 0V. Then the glass electrode needs calibration. Due to reasons including the manufacturing process of glass electrode, the actual values of parameter E_0 and K in Equation (1) are different from their theoretical values, changing with the aging of electrodes. Therefore, in order to accurately detect pH value of the solution, standard buffer solution with the known pH value should be utilized for the correction of above-mentioned parameters. The calibration method is to select standard buffer solution $pH = 4.01$ and $pH = 9.18$ [4]. Specific means are as follows: the pH values of two standard buffer solutions are supposed as pH_1 and pH_2, respectively, and the output electrodynamic forces are E_1 and E_2; two solutions are calibrated under the same temperature, thereby obtaining relationship between output electrodynamic force E and pH value through Equation (1), shown in Equation (3).

$$\begin{aligned} E_1 &= E_0 + KT(pH_1 - pH_s) \\ E_2 &= E_0 + KT(pH_2 - pH_s) \end{aligned}, \quad (3)$$

$$K = \frac{E_2 - E_1}{T(pH_2 - pH_1)}. \quad (4)$$

For the test solution,

$$E_x = E_0 + KT(pH_x - pH_s). \quad (5)$$

Therefore, the pH value of test solution can be obtained.

$$pH_x = pH_1 + \frac{E_x - E_1}{KT} . \quad (6)$$

The pH value of two standard buffer solutions pH_1, pH_2, the corresponding electrodynamic force E_1, E_2 and the calculated parameter K are stored in E^2PROM. And pH of the test solution can be obtained through Equation (6). During the process of pH detection, the temperature of standard solution and test solution should be kept close and constant to prevent sudden changes in temperature.

4.2 TEMPERATURE CORRECTION

Based on Equation (1) and Equation (6), pH electrode output voltage changes with the change in the temperature of test solution, while pH value of the solution has no correlation with the temperature. Therefore, the temperature should be accurately detected to ensure the accuracy of instruments. In this research, a software method is utilized to correct thirteen-bit output of ADT7301. Theoretically, the digital quantity of ADT7301 has a corresponding relationship with temperature, shown in Equation (7).

$$T = N \cdot \frac{190}{2^{13}} + (-40) . \quad (7)$$

At temperature *t*, the actual digital quantity of ADC will change from the ideal value N to N' due to errors. If N' is substituted into Equation (7) for calculation without correction, there will be errors in the detection results. In this research, the actual digital quantity N' of ADT7301 is corrected into ideal value N. Then N is substituted into Equation (7), thus eliminating detection errors. Equation (8) is the correction equation.

$$N = \frac{N_{150} - N_{-40}}{N'_{150} - N'_{-40}} (N' - N'_{-40}) + N_{-40} , \quad (8)$$

wherein, N_{150} and N_{-40} are the ideal digital quantity of ADT7301 at 150℃ and -40℃, the values of which are 2^{13}-1 and 0, respectively; N'_{150} and N'_{-40} are the actual digital quantity of ADT7301 at 150℃ and -40℃, the values of which are measured and stored in E^2PROM. In actual detection, the digital quantity needs correction through Equation (8) before being substituted into the Equation (7), thus calculating the final temperature value [5].

5 System workflow and software filtering

According to requirements and characteristics of portable pH detection, system software can complete self-diagnostic of hardware and system initialization, handle keyboard commands and interface tasks, and conduct data acquisition and processing, temperature compensation and alarm. Figure 4 is the flow chart of main program. To reduce errors in detection data and ensure the stability and reproducibility of detection, using the method [6], the combination of moving arithmetic average filter and anti-pulse interference average value is utilized in the detection subroutine.

Assuming that $u(n)$ is the pH detection result at the n-th time, and L is the length of the moving average filter window, the filter output $x(n)$ at the n th time can be calculated through Equation (9).

$$x(n) = \frac{1}{L-2} \left\{ \sum_{i=1}^{L} u(n+i) - \max_{1 \le i \le L} u(n+i) - \min_{1 \le i \le L} u(n+i) \right\} , \quad (9)$$

wherein, $\max_{1 \le i \le L} u(n+i)$ is the maximum value; $\min_{1 \le i \le L} u(n+i)$ is the minimum value.

According to Equation (9), we need to sample L times in detecting a pH value, obtain L pH values with little differences and form the basic sequence, $u(n+1), u(n+2), \ldots, u(n+L)$. Then the first value of the sequence is removed after every sampling; the remaining values sequentially move forward by one bit; the sampled new value will be inserted at the last bit of the sequence, thereby obtaining a new sequence. After deleting the maximum and minimum value of new sequence, the average of remaining $L-2$ values is calculated as $x(n)$, the final result of detection. The value of L is determined by A/D conversion rate and the required stability time of detection. Based on actual tests and references [6], the value is $L = 9$ in this research.

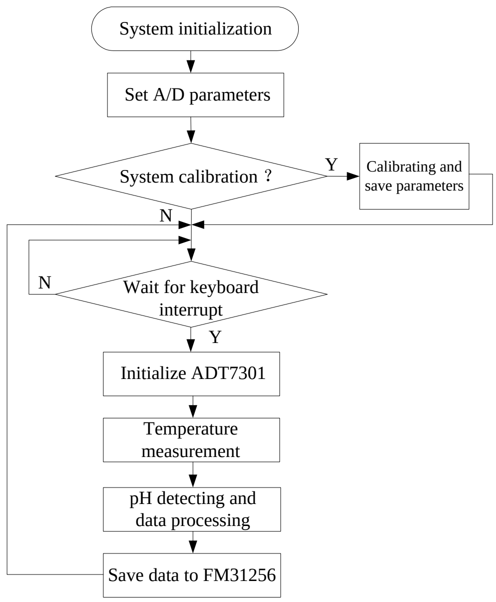

FIGURE 4 Flowchart of pH detection sensor

6 Experiment results and analysis

The standard buffer solution with the pH of 4.01 (Hach Company) was selected in this research. The experiment was carried out at about 25℃. The standard solution was put in a container with ice water or hot water to change the temperature of buffer standard and verify the accuracy of temperature compensation. In order to verify the reproducibility of sensor probe and the entire system, each standard solution was measured six times; the probe was put in the solution for 5 minutes each time; *pH* values were determined after the readings of *pH* sensor is stable. Table 1 is a part of the experimental results. According to Table 1, the difference between the detected six *pH* values is less than 0.008, showing good reproducibility of the sensor; the difference between detected value at different temperatures and theoretical value is less than 0.006, indicating that temperature has little influence on the detection results.

TABLE *pH* value of experimental data detection sensors

Standard solution		**Times**						**Theoretical value**
pH	*Temperature /℃*	*1*	*2*	*3*	*4*	*5*	*6*	
	5	4.002	4.006	3.999	4.002	3.998	4.003	4.00
4.01	25	4.014	4.011	4.009	4.013	4.015	4.014	4.01
	35	4.035	4.033	4.029	4.031	4.032	4.034	4.03

7 Conclusions

A method for online *pH* detection is proposed in this research with complete design of hardware and software programs. Impedance matching method is utilized to eliminate the influence of high resistance in glass electrode, and electrodes are calibrated through standard buffer solution, thus eliminating zero drift and electrode deviations. Besides, the output of temperature sensor is calibrated by software to effectively improve the accuracy of temperature detection. The accuracy and repeatability of sensors are effectively improved by establishing *pH* value sequence and utilizing moving average filter to process the *pH* values, realizing long-term, on-line and high-precision detection at the range of -40℃~+150℃ in the *pH* detection system.

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