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Design of High Precision and Low Drift PH Value Online Monitoring Instrument

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Abstract: The geological storage of carbon dioxide is a practical and effective method to reduce the greenhouse effect,In order to prevent the leakage of carbon dioxide bring about a serious impact on the environment, the need to carry out in situ online monitoring of pH value to determine the dynamics of underground carbon dioxide.In this paper,a high precision and low drift pH value online monitoring instrument based on temperature compensation is designed with MSP430F5438 as the core.The software flow chart and the relationship the pH value,the electrode signal and the temperature of the measured liquid,the hardware structure of the instrument and software process are introduced.By comparing pH standard solution and field water sample test, the measurement accuracy of the instrument is about 0.05pH,this instrument can meet the needs of online monitoring,have been used for engineering monitoring and have a wide range of application prospects.

Keywords: pH value; Aquifer; MSP430F5438; Dual-channel synchronous sampling; Digital filter

1 Introduction

When the carbon dioxide stored in the stratum is dissolved into the deep salt water layer, the acidity of the water environment will be enhanced, and the pH value is decreased obviously[1]-[4]. In order to grasp the dynamic information of carbon dioxide in detail, we need to carry out long-term online monitoring of pH value. At present, the software and hardware design of the pH field fast detection instrument is mature, the precision is high [5], but the fast detection instrument needs to be calibrated periodically.

This paper studies the pH value of the online monitoring instrument is often placed in a poor environment and sparsely populated, so there is a higher requirement for the hardware and software, both to ensure that the instrument is stable for a long time, reduce the number of rectification, but also has high anti-interference ability. Through many experiments, the simulation fitting calculation method of high precision temperature compensation based on quantitative analysis, grasp the characteristics of the pH electrode, and the impedance matching circuit[6], dual synchronous sampling circuit[9][10], and digital filter software algorithm[7][8], to ensure that the instrument with high precision and high stability. The experimental results meet the design requirements.

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2 PH value detection relation

Usually the pH value of the voltage measurement follows the Nernst equation [5], the Nernst equation with pH value as the output can be obtained:

$$pH=\frac{(E_0-E)F}{2.3RT}$$

In the formula: E is the electrode potential; R is the ideal gas constant, that is 8.314J/ (mol*K); T is the temperature; F is the Faraday constant, i.e. 96487C/mol; pH is the pH of the solution.

The measurement accuracy of pH is mainly affected by two factors, one is to measure the output voltage E, and the other is Liquid temperature is measured T.

In the instrument design, in order to achieve the purpose of temperature compensation, it is necessary to find out the mathematical relationship between the pH and the measured liquid temperature T, and the mathematical relationship between the electrode voltage E and the measured liquid temperature T. The temperature of 25℃ solution pH value of 4, 7 and 10.01, the different temperature of pH value and electrode voltage were measured by the hash measuring instrument with high precision, and then the measurement data were gotten by curve fitting the mathematical relationship between the pH value and temperature,the mathematical relationship between the electrode voltage and the temperature of the T, such as in Figure 1, shown in figure 2.

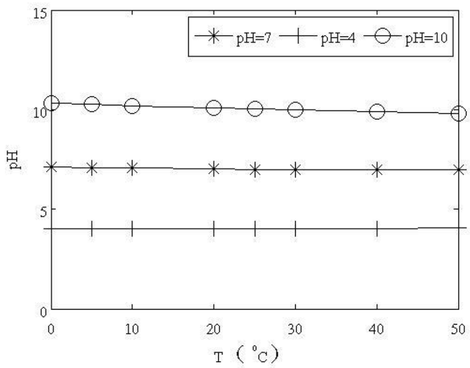

Fig.1 The fitting curve of pH and temperature

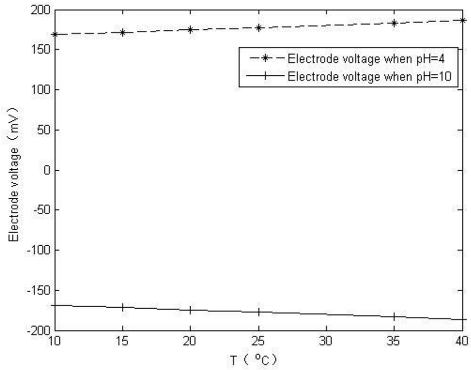

Fig.2 The fitting curve of the output voltage of the electrode and temperature

According to the fitting curve of Figure 1, the relationship between the pH value of 4.00、7.00 and 10.01 and the temperature T at the measured temperature is 25℃, the temperature of the liquid is, the value of which is pH, the value of which is:

$$pH_{41}=3.006\times 10^{-5}T^2-0.000366T+4 \qquad (1)$$

$$pH_{71}=6.754\times 10^{-5}T^2-0.00634T+7.116 \qquad (2)$$

$$pH_{101}=9.173\times 10^{-5}T^2-0.01469T+10.33 \qquad (3)$$

In the formula: pH_4 is measured as the pH value of the solution 4 in the measured temperature T; pH_7 is measured as the pH value of the standard solution 7 at the measured temperature T; pH_{10} is measured as the pH value of the standard solution 10.01 at the measured temperature; T is the measured temperature.

According to the fitting curve of Figure 2, pH value of 4.00、7.00 and 10.01 of the standard electrode voltage V_4, V_7, V_{10} in 25℃, pH and are calibrated to the measured temperature:

$$V_{41}=V_4+(T-T_4)\times 0.59 \qquad (4)$$

$$V_{101}=V_{10}+(T_{10}-T)\times 0.595 \qquad (5)$$

Type: V_{41} is the electrode voltage which is used to measure the temperature of the liquid, and the V_{101} is the electrode voltage of 10.01;V_4 is the electrode voltage to adjust the value of the temperature subscript

4; V_{10} is to adjust the electrode voltage of the temperature subscript 10.01, T_4 is the calibration temperature of the calibration liquid is 4; T_{10} is the calibration temperature of the calibration liquid is 10.01.

By type (1) ~ (3), the correction of temperature correction under the standard solution of 4, 7 and 10.01 of the pH value of the compensation to the measured temperature; the type (4), (5), the correction electrode voltage output 4 and 10.01 of the standard value of the compensation to the measured temperature temperature. Therefore, by type (1) ~ (5), were established in acidic and alkaline conditions in the temperature measuring linear equations for slope and intercept:

Acidic： $K_1 = (pH_{71}\text{-}pH_{41})/(V_7 - V_{41})$

$$b_1 = pH_{41} - K_1V_{41}$$

Alkaline: $K_2 = (pH_{71}\text{-}pH_{101})/(V_7 - V_{101})$

$$b_2 = pH_{101} - K_2V_{101}$$

First of all, the assumptions for the calculation of acidity, the measuring electrode voltage V into a linear formula under the condition of acid ： $pH = K_1 \times V + b_1$ .If the pH value of acid results, that is no longer used basic formula, the results are displayed directly. If the result is alkaline, the electrode voltage V under the measurement conditions is introduced into the basic linear formula $pH = K_2 \times V + b_2$, And show the results.

3 hardware circuit design

The overall framework of the system is shown in Figure 3, the system based on MSP430F5438 microcontroller [11], pH electrode collect weak signal through a high impedance amplifier circuit to enlarge, and then through the signal conditioning circuit, filtering, amplifying and shaping of the input signal, and then through the MSP430F5438 of pH signal, incentive reference electrode the voltage signal and 18B20[12] measured temperature signal for the synchronous data acquisition [13][14]. The results of the operation to send LCD display or CAN bus [15]-[18] communication.

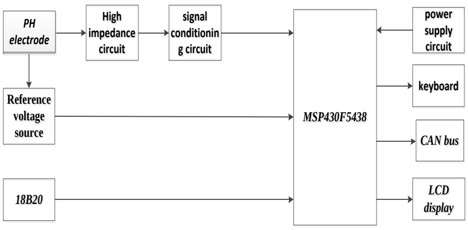

Fig.3 Hardware block diagram of pH value measuring instrument

3.1 high impedance matching circuit

The resistance of pH composite glass electrode is very high, about 10^8 ~ 10^{10}, so the measurement circuit must have a very high input impedance. In this paper, the input impedance is 10^{12} INA121. The gain of the instrument amplifier is $G = 1 + 50\text{K}\Omega / R_G$, Magnification set to 50. As shown in figure 4.

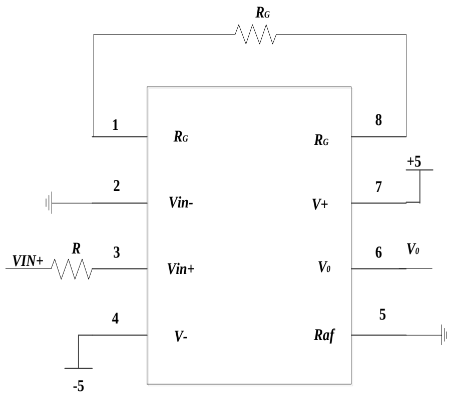

Fig.4 *INA121* connection circuit

3.2 signal acquisition circuit

The signal acquisition circuit is shown in figure 5. The circuit through the reference voltage source of 1.25V is applied on reference electrode , the output electrode is connected with a high impedance amplifier circuit, output voltage of V_0 measuring electrode, voltage V_0 into the analog-to-digital to 12 bit A/D conversion in MSP430F5438. Therefore, it can be seen that the actual output voltage of the pH electrode ,can effectively restrain the influence of the external environment.

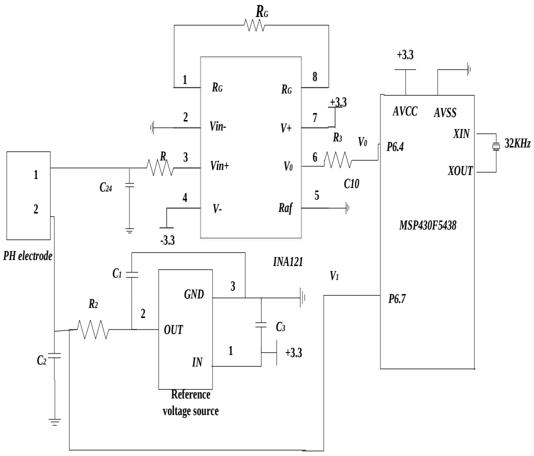

Fig.5 Signal acquisition circuit

4 software design

In order to reduce the influence of various interference factors in field environment and improve the accuracy and accuracy of the acquisition system. Software digital filtering using Pauta criterion and median average filter.

4.1 software flow chart

The software flow chart of pH measurement instrument is shown in figure 6.

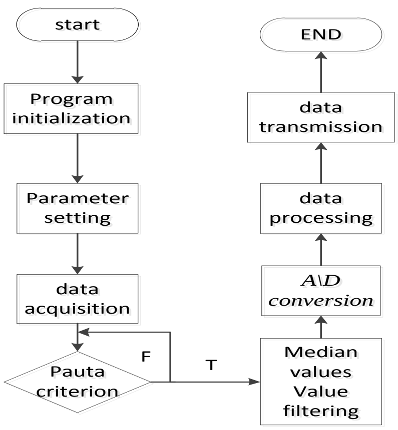

Fig.6 pH value measuring instrument software flow chart

4.2 gross error judgment method

Pauta criterion[20] is assumes a set of pH value detection data only contains random error, this set of data processing to calculate the standard deviation, according to a certain probability determine distribution of interval value. Where more than the error of the interval, that is the gross error, the gross error data will be removed.

Set to be measured for equal precision measurement, independent of X_1, X_2,...... X_{40}, calculate the residual error $V_i = X_i - X$ and the arithmetic mean value X_i (i=1,2,..., 40), and according to the Bessel formula of standard error. If the residual error V_b (1<=b<=n) of a measured value is X_b, it is considered that the X_b is a bad value with a large error value, which should be removed.

4.3 median value filtering

Software design of the median filtering algorithm, this algorithm is equivalent to the median value filtering method and combining the arithmetic mean filtering method, combining the advantages of two kinds of filtering methods, which can eliminate the error caused by sampling pulse interference.

After the removal of gross errors using Pauta rule, the filtering method will be obtained N data, remove a maximum value and a minimum value, and then calculate the arithmetic mean value of N-2 data. The pH of the measured temperature can be obtained by the software filtering is completed into the above detection method.

By comparing the measured data before and after the voltage measurement of the pH electrode,by median filtering and Pauta criterion comprehensive treatment, eliminating gross error, the test results of a small error, reached the requirements of high precision.

5 test verification

The accurate measurement and ease of use of the pH measuring instrument are based on the full test of the laboratory. In this paper, the pH standard value solution with 9.18 was used to compare the pH value of the pH solution at different temperature with the paper pH instrument and the instrument of Hach. The standard solution is placed in a constant temperature water tank with hot water. It can be seen from table 1 that the instrument has a good effect of temperature compensation and achieves high precision. As shown in table 1.

Table 1 Experimental measured data

Serial number	1	2	3	4	5	6
temperature/℃	20	20	30	30	40	40
Instrument pH value	9.20	9.19	9.18	9.17	9.05	9.04
Hach pH measurements	9.23	9.23	9.14	9.14	9.07	9.07
error	0.03	0.04	-0.04	-0.03	0.02	0.03

The above tests are based on laboratory. The equipment has been used in field operations, table 2 samples for field measurement data, test results and measurement data and Hach pH meter are compared. The data show that the device can accurately measure the pH value of water quality.

Table 2 Field measurement data

Serial number	1	2	3	4	5	6
Hach pH measurements	6.85	7.26	7.11	6.81	7.61	7.34
Instrument pH value	6.84	7.30	7.08	6.85	7.58	7.30
error	0.01	-0.04	0.03	-0.04	0.03	0.04

The test shows that the instrument has the function of temperature compensation and measurement precision is about 0.05, with high accuracy; through the dual synchronous sampling has good filtering and anti jamming effect, can meet the needs of application.

5 Conclusion

Due to the need of long-term in situ monitoring, the temperature compensation method is used to fit the relationship between pH value and electrode voltage and liquid temperature. The high precision measurement of pH value is realized, and the instrument is used for field test. The utility model has the advantages of compact structure, high precision, high reliability, etc., and has a positive effect on protecting the environment and water pollution, and has wide application prospect.

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