International Journal of Electronics Engineering (ISSN: 0973-7383)
Volume 10 • Issue 2 pp. 485-491 June 2018-Dec 2018 www.csjournals.com

Improved Accuracy pH meter: A Circuit Designers Approach

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Abstract: A novel electronic circuit has been designed for the accurate measurement of pH. A critical requirement of satisfying the principle of potentiometric sensor is fulfilled by optimum circuit design of buffer amplifier. It also includes design of data conversion and a power source. A required buffer amplifier is designed with the use of low input bias current MOS Op-Amp. The accuracy is improved by enhancing the S/N ratio, particularly due to EMI and Johnson's noise. Accuracy is further improved by high resolution type ADC with stable voltage reference. The error in the pH value due to computation of data conversion from integer potential value into real pH value is minimized by software technique. The developed circuit is successfully tested for some solutions and it shows remarkable improvement in the accuracy of pH measurement.

Keywords: accuracy, buffer amplifier, pH, S/N ratio.

- **Introduction**

Electronic instruments are used in variety of fields from the beginning of 20^{th} century. They are used for the accurate measurement of electrical and physical process parameters [1, 2] in the laboratory and industrial process control. The value of manufactured industrial products depends on the quality of measuring system. The quality is monitored by the performance parameters [3, 4] such as accuracy, precision, sensitivity, etc. The accuracy in the measurement of some parameters such as pH, conductivity, turbidity has great importance in the industries such as pharmaceutical and food processing.

Instrument manufacturing industry upgrades the instrument [5, 6] either by improving the parameters or simplifying the measurement techniques. Improvement is carried out by adopting the new technology and novel ideas. The automation in the measurement simplifies the handling of instrument. There are many industries as well as research laboratories working in the field of making of instruments. They improve the performance either by using a newly available electronic devices or by redesigning the schematic of instrument. The improved instrument is superior in quality and better in performance than its previous version. Such high performance instruments have good quality parameters, particularly accuracy and sensitivity. These instruments are expensive and usually required in scientific research laboratory.

Analytical instruments are widely used in medical [7] and pharmaceutical field [8, 9] for the diagnosis and quality control respectively. There is no analytical instrument which has perfect parameters whose values are near to the ideal one. The analyst always demands for the improved and upgraded instruments for his work. The circuit designer has a scope to improve the circuit design for the betterment of instrument parameters that will satisfy the demand of analyst. In the present work, a new circuit is designed for commonly used analytical instrument i.e. pH meter. The article includes following sections: Methods are discussed in section 2.Experimental work is presented in section 3. Results and discussions are discussed in section 4 and 5 respectively.

- **Methods**

The activity of H^+ ions in an aqueous solution generates electrostatic potential. It is sensed by potentiometric pH sensor [10] such as glass electrode or IGFET. This potential is basically due to contribution of some ions and it is weak in strength. When it is measured by pointing type PMMC meters then the meter shows zero deflection because of weak signal. The measurement of such signal requires a special type of meter which has following characteristics: very high input impedance, minimum loading effect and less parallax error. In the following section, two commonly used electronic circuit designs those satisfy above characteristics are presented. These circuits are essentially required for the increase in strength of signal and also used for the conversion of measured potential into pH value.

2.1. Linear Op-Amp based pH amplifier

The traditional pH amplifier [11] is designed using linear components like Op-Amp and discrete components. Such circuit design includes two or three Op-Amps and some resistors as shown in Fig.1.

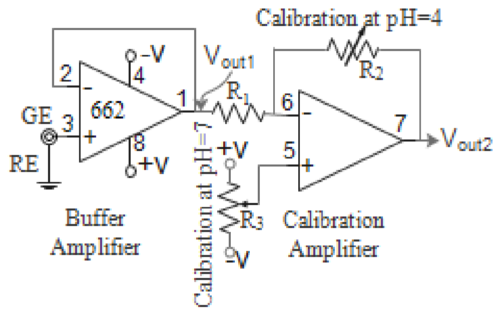

Figure 1. Op-Amp based pH amplifier

2.1.1. Buffer amplifier

It is required for increasing the strength of pH signal. A special type of non-inverting configuration of Op-Amp with unity gain can be used as buffer amplifier. Buffer amplifier shown in fig.1 has following two functions:

- To match the impedances of glass electrode and measurement circuit.
- To prohibit the current entering into the glass electrode.

2.1.2. Calibration amplifier

It converts the potential ranging from -420 mV to +420 mV into pH value in the range 0-14. Fig. 1 shows the simplified diagram of calibration amplifier, which is a difference amplifier with facility for adjusting its output at values 4 and 7 for the input voltages at -180mV and zero respectively. It is possible by varying the resistors R_2 and R_1. The calibration amplifier shown in fig. 1 has voltage gain of R_2/R_1 for converting mV's into pH.

Where, V_{out1} and V_{out2} are the voltages at the outputs of buffer and calibration amplifiers respectively. Calibration amplifier also shifts the pH scale to the acidic or basic side for compensating the offset error. The readout device is generally centre zero pointer type PMMC meter, whose accuracy is limited by parallax error and loading effect.

2.2. Microcontroller based pH method

In modern pH meter the calibration amplifier is replaced by the microcontroller [12]. Fig.2 shows block diagram of microcontroller based pH meter.

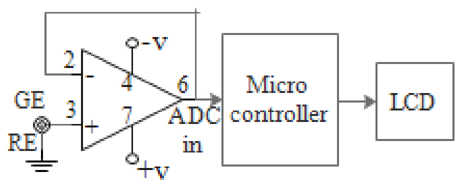

Figure 2. Microcontroller based pH meter

Microcontroller or microprocessor in pH meter are used for the data conversion, recording and data manipulation. They are prefer to use in instruments because the peripherals like alphanumeric liquid crystal display (LCD) and membrane keypad can be easily interfaced to them. The advantages of microcontroller based method over the linear method are shown in table1.

Table 1: Comparison between linear and microcontroller based methods

Parameter	Linear method	Microcontroller method
Recorder	No	Yes
Calibration	Tedious	Simple
Data analysis	No	Yes
Readout error	Parallax for Pointer type	No read out error
Loading effect	Yes	Relatively less
Data communication	No	Yes

- **Experimental section**

An experiment for improvement in the accuracy includes following two parts.

3.1 Design of electronic circuit

The circuit is designed using microcontroller as shown in fig.3. The precision microcontroller with 24-bit Δ ADC is the main component of design. The power supply requirement is fulfilled by use of linear IC regulator, which has minimum load regulation as well as maximum ripple rejection.

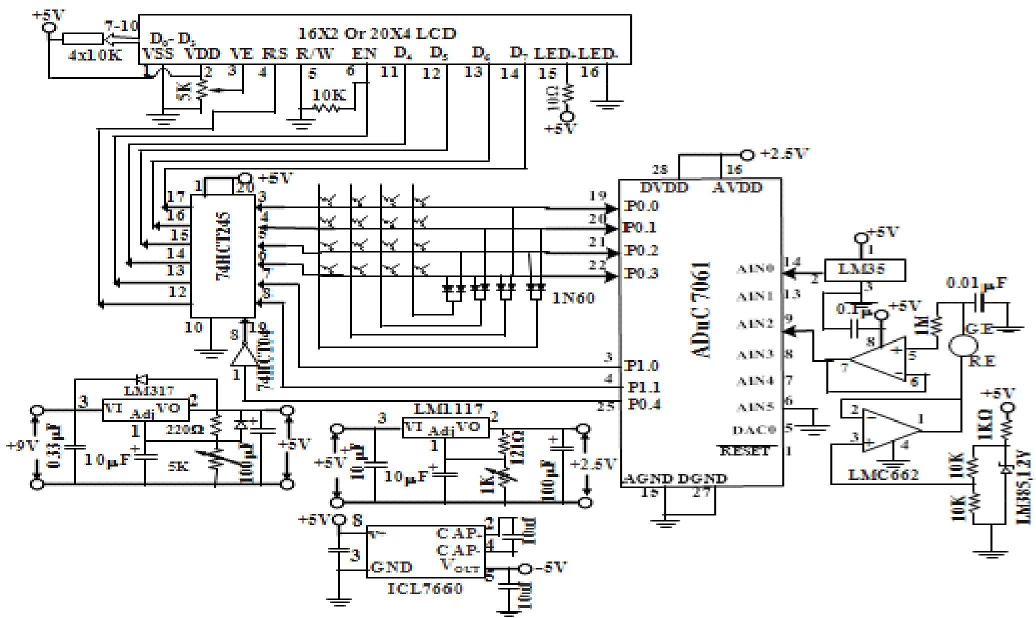

Figure 3. Microcontroller based pH meter

3.1.1. Circuit description

The glass and reference electrode are connected to the non-inverting terminal of buffer amplifier through a BNC connector and decoupling capacitors as well as resistor for limiting the bias current. The potential at reference electrode is shifted at 0.6V above the ground level with the help of a level shifter circuit, constructed with the help of stable reference source LM385 (1.2V). The analog output voltage of buffer amplifier is converted into digital by the 24-bit ADC section of microcontroller. The external sample and hold circuit is not required due to slow varying nature of pH signal. A software program is executed by the microcontroller for the conversion of digital value into pH. A keypad and LCD are multiplexed using diode gating logic and interfaced to the microcontroller GPIO pins. A bus driver IC 74HCT245 is used for conversion of voltage level from 2.5 V to 5V [13]. A DC power supply is constructed using three pin adjustable voltage regulators LM 317 and LM 337. The voltage regulation and ripple factor are improved with the use of filter capacitors.

3.1.2. Software description

A software program executed on microcontroller performs following functions:

- Data conversion: The analog pH data is converted into digital by use of high resolution 24-bit. ADC at the reference voltage of 1.2V. Converted digital value corresponds to analog voltage given by equation,
- Data manipulation: A digital value is manipulated into pH with the help of Nernst's equation.
- Determination of slope: The slope required for the calibration is calculated from the potentials measured at two known pH values. Where V_4 and V_7 are the measured potentials of pH=4 and pH=7 respectively.
- Multiplexed LCD and keypad: Look up table (LUT) method is used to obtained value of the pressed key. LUT is implemented using one dimensional array of values of keys and the index is the combination of scan and return code.

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The program is edited and compiled in keil-IDE Version 4 [14] and downloaded into microcontroller with the help of ARMWSD [15] downloading program. The program is successfully tested and gives acceptable result. Software program will be freely available from author on demand by reader.
It also provides facility for temperature measurement and display. The flow chart of developed program is shown in fig.4.

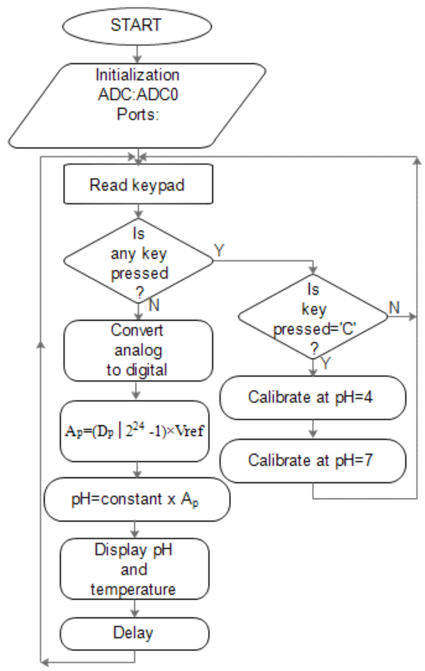

Figure 4. Flow chart of developed program

- **Results**

Measurement of pH for different combination of capacitors are taken and shown in Table 2. It also shows the observations for different accuracy levels. The improvement of accuracy in pH measurement is checked for different dilution level solution and shown in Table 3. Fig.5 shows the graphs for the study of accuracy.

Table 2. Effect of filter capacitor (C) on pH potential

Time in seconds	Value of pH Potential in milivolts		
	C=100nF Tantalum	C=3.3nF Polystereme	C=0.047nF Paper
0	821	824	826
30	821	824	824
60	821	828	826
90	821	830	825
120	821	838	826
150	821	836	826
180	821	836	826
210	821	834	826
240	821	834	827
270	821	836	828
300	822	835	831

Table 3. Accurately measured value of pH of some solutions

Solution	Accuracy	
	Expected pH Range	Measured pH
Surface Water	6.5-8.5	6.824
RO Water	5-5.5	5.456
Distilled Water	6.9-7.0	6.961

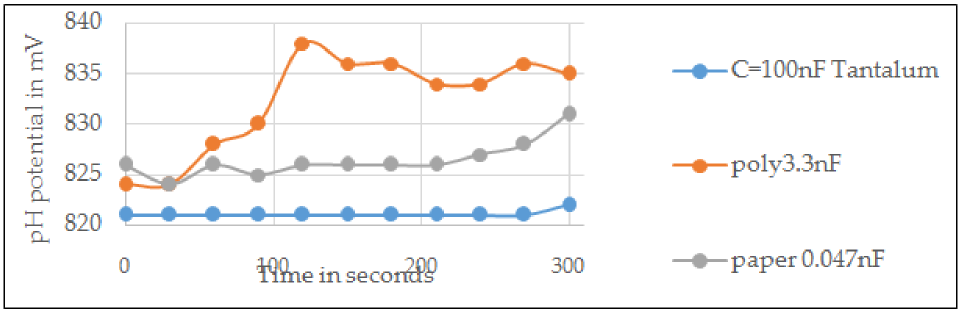

Figure 5. Graph showing change in pH value

5. Discussion

Accuracy in pH measurement depends on the quality of glass electrode and pH amplifier circuit. In the present work, accuracy is improved by applying some approaches which are discussed below:

5.1. Improvement in accuracy by fulfilment of Maximum Power Transfer Theorem (MPTT)

Accuracy depends on the amount of quantity measured by a meter. In pH meter, accuracy in measurement is improved by transferring maximum amount of potential to the voltmeter for the fulfilment of condition of maximum power transfer theorem. According to maximum power transfer theorem, power transferred by glass electrode to the meter is maximum if the impedances of them are equal. The transferred power (P) is given by,

$$P=I^2R_g,$$

Where R_g is the resistance of glass electrode and, I is the current due to developed potential. Accuracy in solution depends on the value of R_g. Fig.6 shows the variation in accuracy with Rg.

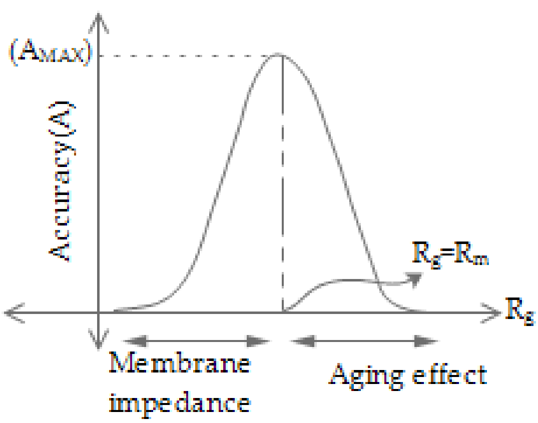

Figure 6.Graph shows variation in accuracy

Accuracy is maximum at $R_g = R_m$, where R_m is the meter resistance. Accuracy drops due to aging effect of electrode and increase in membrane impedance. In pH measurement system, pH amplifier is connected in parallel with the electrode. At some point, the power transferred to the meter is maximum

- Improving the accuracy by satisfying the condition of potentiometric sensor:

When the glass electrode is connected to the pH amplifier, then some reverse current flows through the electrode. The current is either added or subtracted from the current due to H^+ ions. It certainly introduces error in accuracy. The error can be minimized by selecting low input bias current OpAmp and external series resistor R_1.

- Improving the accuracy by enhancing the S/N ratio:

Accuracy depends on the noise level in the signal. Signal with noise is amplified and digitized by buffer amplifier and data converter respectively. It is necessary that noise should be removed from signal before applying to the buffer amplifier. In the present work, some noise filtering capacitors are used as shown in figure 3. There is need of different value capacitor C for removal of different types of noises. The capacitor of value 100nf, 3.3nf, 0.47nf are used for removal of EMI, hum, unknown and electrochemical noise respectively. The noise present in the power supply is removed by decoupling capacitor of value 0.1µf. Improvement in the S/N ratio is more important for measurement of pH of neutral solution. The numbers of ions contributing to the formation of potential are less for neutral region as compared to the number of ions contributing to formation of noise signal. The S/N ratio for these solutions is of the order of 10%. To improve it, there is a need of high resolution of ADC and some software techniques.
In present work, I have checked the S/N ratio by observing the pH of distilled and conductivity water. The S/N ratio for pH signal in distilled water is calculated by the formula,

Capacitors in fig. 3 are used for the removal of external noise and power supply noise. The internal noise i.e. produced by the components and PCB is also significantly contributes to S/N ratio. Each component of circuit is a source of Johnson's noise and it increases with the values of components. Johnson noise is a function of temperature and difficult to remove by capacitive filters. However, it can be minimized by appropriate design of power supply.

- Improving the accuracy by optimizing the parameters of data conversion:

  The accuracy is improved by use of high resolution ADC. It is necessary part of digital pH meter which is essentially required for converting the analog pH signal into digital. It improves the accuracy at three levels:
- Sampling rate:
  For better accuracy, the sampling rate should be high. But it is not very important for slowly varying pH signal.
- Minimizing quantization error:
  It increases with number of bits of ADC. However, it can be minimized with appropriate use of time delay required for controlling the sampling rate.
- Use of high resolution ADC with conversion time improves the accuracy. The delta sigma ADC is more suitable due to its high resolution and high speed sampling of applied signal.

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