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THE ELECTRONIC DETAIL OF A DIGITAL PH-METER

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Abstract: This paperwork presents the complete circuitry used to build a microcontroller-based pH-meter. Key control software is also discussed. An industry-standard glass combination electrode has been employed for pH detection. Electrode parameter extraction procedure is presented. Good measurement results, with 1 % error, have been attained.

Keywords: pH measurement, pH-meter, pH electrodes.

1. INTRODUCTION

pH is a measure of hydrogen ions concentration, $[H^+]$, in an aqueous solution and it indicates not only the acidity of the solution, but also the degree of a reaction occurring in it. Because chemical properties and process data as a reaction's speed and a compound's solubility can be inferred through pH measurement, pH has become the most frequently measured electrochemical variable [1]. Today it is estimated that there exist millions of pH-meters under operation worldwide, in applications ranging from chemical, pharmaceutical and food industries to biological process monitoring [2].

Mathematically, pH is given by Eq. (1), where $[H^+]$ is the hydrogen ions' molar concentration.

$$pH = -\log\left[H^+\right]. \tag{1}$$

Despite steady effort to developing new pH sensors [3-4], H^+-permeable glass-membrane electrodes are ubiquitous and will likely continue to dominate the scene for years to come. The voltage difference, E_{pH}, that appears between such a special glass electrode, called sensing electrode, and a reference electrode, as illustrated in Fig. 1, is governed by the Nernst equation [5]:

$$E_{pH} = E_0 + \frac{2{,}3RT}{nF}\cdot\log\left[H^+\right] \tag{2}$$

where E_0 is the voltage difference in a solution with pH equal to 7, R is the general gas constant (8.3144 J/(K/mol)$^{-1}$), T is the temperature, in Kelvin, n is the number of valence electrons per mole (1 for H^+), and F is Faraday's constant (9.6485 x 10^4 C/mol). Since E_0 varies between individual electrodes and with temperature, and electrodes can slightly deviate from ideal Nernst equation, [1] has modified Eq. (2), by introducing the parameters E' and s, to give the practical Eq. (3), after substitution of constants and solving for the *pH*.

$$pH = \frac{E' \cdot T - E_{pH}}{sT\cdot 1.98158\cdot 10^{-4}}. \tag{3}$$

Accurate pH measurement can be made through Eq. (3), once E_{ph} and T are accurately measured and E' e s are known. Electrode calibration, i.e., determination of its (E' and s) parameters can be easily done by recording the E_{ph} readings for two distinct buffer solutions (known pH solutions, at a given temperature), and then solving the system of two linear equations given by Eq. (3).

The ever decreasing cost and increasing computing power of microcontrollers have favored the complete substitution of moving-coil display, analog pH-meters by digital models. Microcontroller-based pH-meters beyond reading pH electrode's voltage and solution temperature to calculate the solution's pH by means of Eq. (3), can readily display or print its value and yet carry out a number of useful and more complex functions, such as recording, monitoring, controlling and communications with a supervisory system, for instance. The following sections of

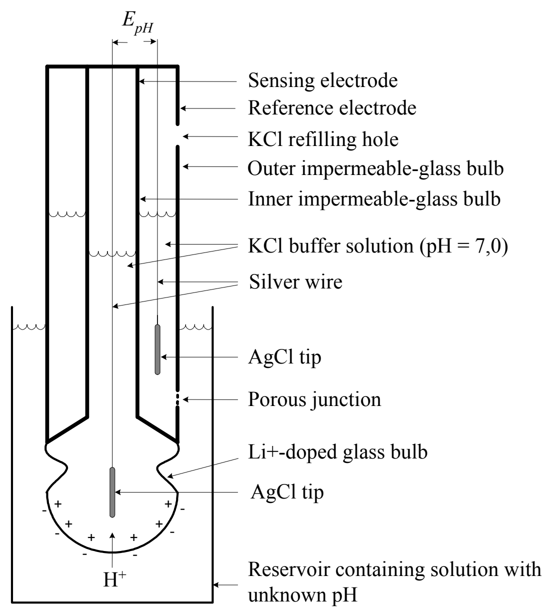

Fig. 1. Illustrative longitudinal section of pH combination electrode

this paperwork will present the analog and digital circuits used to design a digital pH-meter, as well as the pH-meter calibration and test procedure and results.

2. THE DIGITAL PH-METER

Figure 2 shows the block diagram for the digital pH-meter, and Fig. 3 presents a photograph of the prototype. A microcontroller (Atmel AT89S52) samples the combination electrode's voltage (Analion V-620, Brazil), E_{ph}, and the solution temperature, in order to calculate the unknown pH, using Eq. 3, and then presents the pH and temperature values on an LCD display. The control program has been written in C language, and it repeatedly routes the output of both pH and temperature signal conditioners, one at a time, through the suitable channel of the analog multiplexer (Texas Instruments CD4051), to the 8-bit half-flash A/D converter (National Semiconductor ADC0820). Figure 5 presents the complete prototype schematic.

2.1. Signal conditioning for the pH electrode

Within the 0-14 pH range, glass pH electrodes generate a signal, E_{ph}, that ranges approximately from +200 mV to -200 mV, at circa 50 mV/pH, with a source impedance of circa 400 MΩ. Therefore, an ultra high-impedance buffer (Intersil CA3130) is mandatory to lower the signal source impedance (Fig. 5). A summer and dc-amplifier (National Semiconductor LM324: A, B, C) have been utilized to translate the pH signal to the +2.5-V input dynamic range of the A/D converter. Some low-pass filtering has been provided together with the amplification stage. An LM336-2.5 (National Semiconductor) generates a precise 2.5-V voltage reference for the A/D converter.

2.2. Signal conditioning for the temperature sensor

Solution temperature, T, is measured by means of a semiconductor temperature sensor (National Semiconductor LM335), which generates a low source impedance, 10 mV/K output signal. Therefore, some translation and amplification (LM323: E, F, G) are needed, before the A/D can sample the temperature signal. As in the pH case, some low-pass filtering has also been implemented. Since temperature calibration in not an easy task, a precision voltage reference (Analog Devices AD589) has been used in the temperature signal translation stage. Due to the fact that pH sensitivity to temperature is not strong (e.g., H_2O pH is 7.46 at 0 ºC, 7.0 at 25 ºC, and 6.15 at 100 ºC), a temperature sensor (LM335) of 1-ºC resolution is good enough.

2.3. Control firmware

Keil's µVision IDE (Keil Software Inc.) has been used during software development and debugging. Program has been written entirely in C and machine language program has almost fully occupied the 8-kByte flash memory space of the microcontroller. This was due to the many HMI facilities, to ease the prototype operation, not showed here and also due to some control function also omitted. Flow diagram shown in Fig. 4 is only to illustrate the main program control loop. Bigger program may be burnt either in external EPROM-like program memory, or in the internal flash memory of an 8051 member with a larger memory.

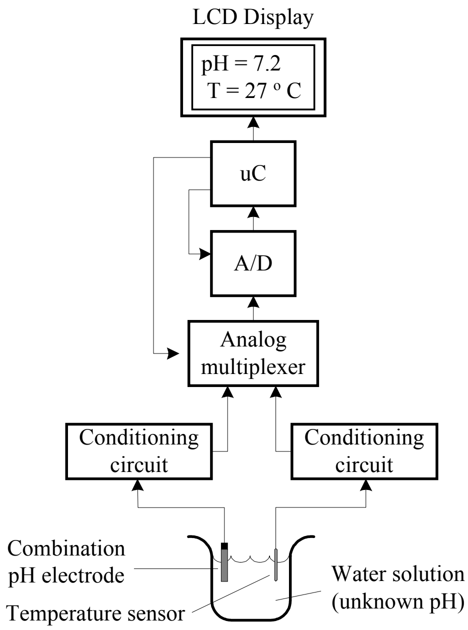

Fig. 2. Block diagram of the pH-meter

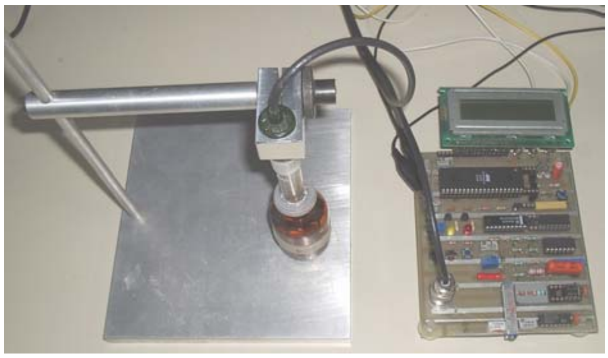

Fig. 3. Picture of prototype

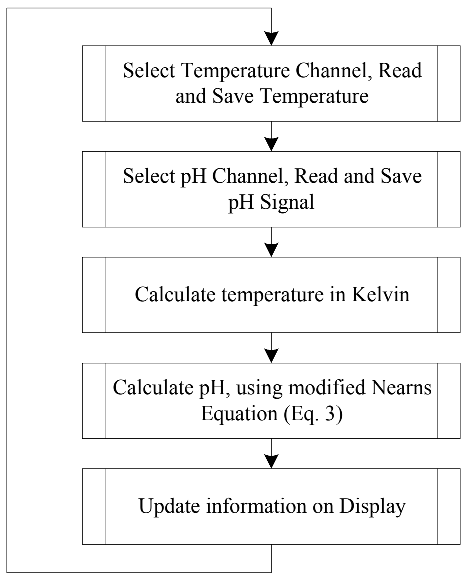

Fig. 4. Main program flow graph

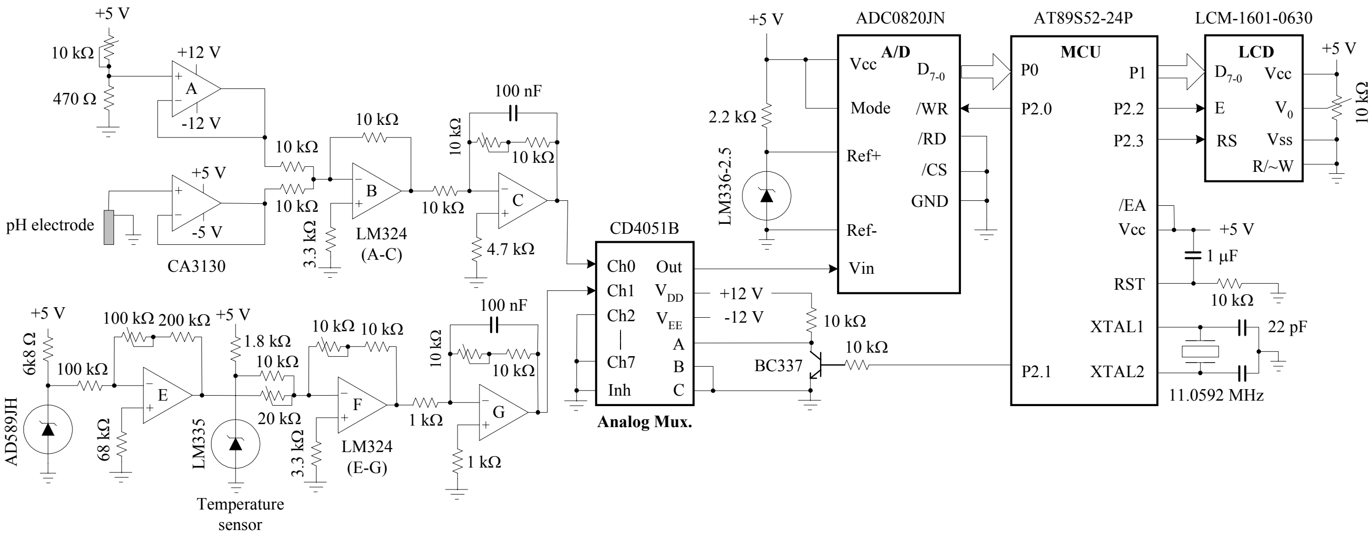

Fig. 5. Prototype schematic

3. EXPERIMENTAL RESULTS AND DISCUSSION

This section presents the pH combination electrode calibration data and the pH-meter assessment.

3.1. pH combination electrode calibration

The pH electrode has been immersed into three buffer solutions whose pH are 4.01, 6.86, and 9.18, respectively, at 25 ºC, and the resulting E_{ph} have been recorded with a precision multimeter (HP 34401A). A plot of E_{ph} as a function of the buffer solution pH is shown in Fig. 6. As the plot shows, electrode behaves as expected. Two measurement results (first and second, and then the second and the third measurement pairs) have been replaced in Eq. 3. The resulting linear equation system have been solved twice and the mean value for *E'* and *s* have been found as 1.35373×10^{-3} and 0.96497, respectively. These values have been entered the program for subsequent use.

3.2. pH-evaluation

Following electrode calibration, several buffer solutions have been prepared whose pH values have been tracked by a calibrated commercial pH-meter (Digimed, Brazil). These values appear in Table 1 and Fig. 7 as *rated pH*, whereas those measured by the prototype are named *measured pH*. In general, the results are quite good, with relative errors limited to less than 1%. The 5% error obtained when tests with 5.01-pH solution were done might be due to solution contamination or solution interaction with local atmosphere (in particular, this test solution was not as stable as desired). In any case, except for the 5.01-pH solution, tests have been repeated many times and the measurement results agreed well. In other words, the repeatability of the pH-meter prototype has appeared quite satisfactory.

4. CONCLUSION

Nowadays extremely high input impedance operational amplifiers can easily manage the amazingly high source impedance of glass pH-electrodes (~ 400 MΩ), thus lessen-

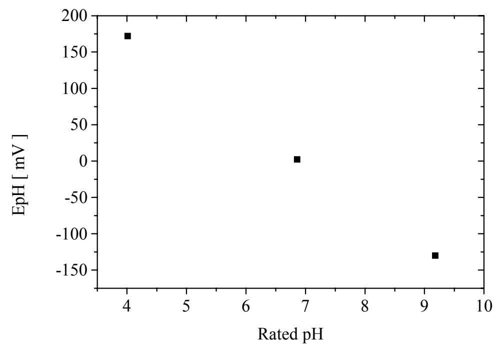

Fig. 6. E_{pH} versus pH

Table 1. pH-meter assessment data.

Measured pH	Rated pH	Error (%)
1.03	1.03	0
2.08	2.07	0.48
3.97	4.01	0.99
5.27	5.01	5.19
6.88	6.86	0.29
9.15	9.18	0.33
11.92	12.02	0.83

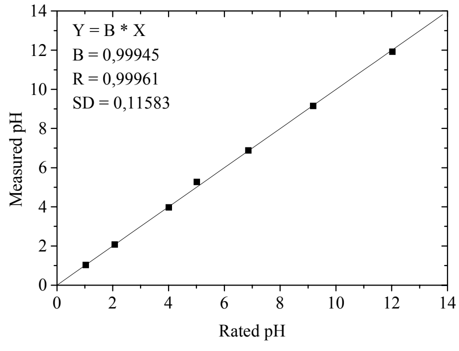

Fig. 7. Measured versus rated pH

ning the effort during the electrode's signal conditioning circuit design. Furthermore, microcontroller firmware enables easy electrode characterization, by enabling the incorporation of a modified Nernst equation to model the glass electrode behavior.

This paper has thoroughly presented the circuit for a digital pH-meter capable of realizing pH measurements within 1 % error. Electrode calibration has also been presented and discussed. The prototype can be further improved to increase its accuracy and incorporate closed loop pH-control function based on fuzzy or traditional control techniques.

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