

# Open-Source Low-Cost Wireless Potentiometric Instrument for pH Determination Experiments

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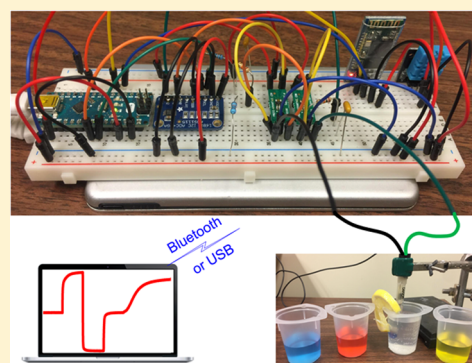
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## S Supporting Information

**ABSTRACT:** pH determination is an essential experiment in many chemistry laboratories. It requires a potentiometric instrument with extremely low input bias current to accurately measure the voltage between a pH sensing electrode and a reference electrode. In this technology report, we propose an open-source potentiometric instrument for pH determination experiments with Bluetooth wireless connectivity. The hardware is built on a solderless breadboard and mainly composed of an Arduino Nano microcontroller, a 16-bit analog-to-digital converter, two electronic buffer amplifiers, a temperature sensor, and a Bluetooth module with a total cost around \$50 (US dollars, including a portable power supply ~\$10). The software is written in Arduino Sketch and the cross-platform Python language, both of which the students can access and modify freely. The instrument was demonstrated with a traditional glass electrode and a custom palladium/palladium oxide pH sensing electrode, and compared with a commercial pH meter. Results showed that both the accuracy and precision of the developed instrument are adequate for teaching purposes. Understanding the workings of electronics of the pH meter can inform the students of the mechanism of pH determination.

**KEYWORDS:** Second-Year Undergraduate, Graduate Education/Research, Analytical Chemistry, Laboratory Instruction, Computer-Based Learning, Electrochemistry, pH, Potentiometry



## INTRODUCTION

Many chemical processes are highly dependent on the solution pH, and the experiment on pH determination is an essential part in teaching laboratories, such as understanding the potentiometric titration<sup>1</sup> and the nature of amphiprotic anions.<sup>2</sup> Potentiometry is one of the most common and accurate methods to measure the pH value of an aqueous solution. The pH value can be deduced from the voltage between a pH sensing electrode and a reference electrode (these two electrodes constitute a pH probe). Generally, the internal impedance between the two electrodes is very high (10 M $\Omega$  to 4 G $\Omega$ ).<sup>3</sup> Therefore, the potentiometric instrument requires extremely high input impedance ( $\sim 10^{12}$   $\Omega$ ) or extremely low input bias current ( $\sim$  pA). For example, in the worst case of 4 G $\Omega$  impedance, a 1 pA current results in a voltage of 4 mV and introduces  $\sim 0.07$  pH unit error at 25  $^{\circ}$ C (a pH sensitivity of  $\sim 60$  mV/pH is used here). Commercial pH sensing instruments always operate as black boxes, where little information on the hardware inside or the software algorithm is available to students, and the cost is generally high. The “open-source” instruments in scientific research, especially in analytical chemistry, are valuable for chemistry education owing to the disclosure of the hardware/software details and the freedom to

modify the instruments' configurations/functionalities.<sup>4</sup> Examples of open-source instruments for chemical laboratory experiments include pH instruments,<sup>5,6</sup> an epifluorescence microscope,<sup>7</sup> an automatic titrator,<sup>8</sup> a chromatography instrument,<sup>9</sup> and a potentiostat.<sup>10,11</sup> Particularly, for pH sensing instruments, Grinias et al.<sup>5</sup> proposed an Arduino-based data acquisition device that is suitable for general potentiometric applications. However, the device used an analog-to-digital converter (ADC) directly to measure the voltage, and it did not satisfy the requirement of low input bias current for pH sensing. Papadopoulos et al.<sup>6</sup> reported a microcontroller-based pH meter and used operational amplifiers for electronic buffering. Such a pH meter included several large-in-size and high-cost development boards. Therefore, it is not suitable for large-scale deployment in teaching laboratories. Additionally, both of the examples did not provide wireless connectivity, which will facilitate the usage as well as eliminate power line noise. There are some commercial wireless instruments in the market, such as the ones for water quality monitoring, but they

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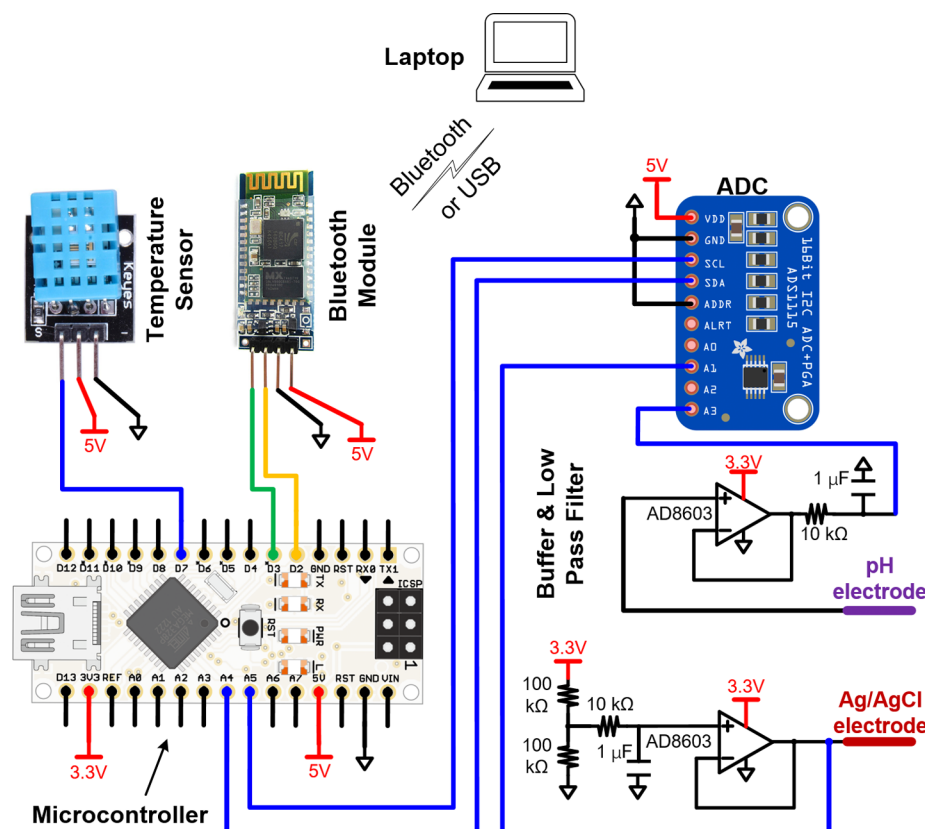


Figure 1. System schematic of proposed wireless potentiometric instrument for pH determination.

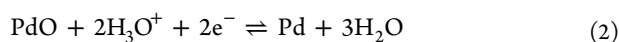
are very expensive and not suitable for education. In this technology report, we propose a compact low-cost wireless potentiometric instrument, especially suitable for pH determination experiments. It is composed of an open-source (the MIT License) cross-platform software and microcontroller-based hardware. The system provides a 200 fA low input bias current electronic buffer, a temperature sensor for the automatic temperature compensation for pH, and a Bluetooth module for wireless communication.

## DEVELOPMENT OF THE INSTRUMENT

pH is a numeric scale used to specify the acidity or alkalinity of an aqueous solution, and it is defined as  $\text{pH} = -\log_{10}(a_{\text{H}_3\text{O}^+})$ , where  $a_{\text{H}_3\text{O}^+}$  is the activity of hydronium ion. An ion-selective electrode (pH sensing electrode) can be used to measure the pH, and the electrical potential ( $E$ ) in solution is determined by the Nernst equation. For a traditional glass pH electrode<sup>12</sup> or a palladium/palladium oxide (Pd/PdO) electrode,<sup>13</sup> the Nernst equation is reduced to

$$E = E_{\text{pH}}^{\circ} + \frac{RT}{F} \ln(a_{\text{H}_3\text{O}^+}) \quad (1)$$

where  $E_{\text{pH}}^{\circ}$  is the standard electrode potential of pH electrode,  $R$  the gas constant,  $T$  the absolute temperature (Kelvin), and  $F$  the Faraday constant. This is because at the surface of a Pd/PdO electrode, the most commonly accepted mechanism depends on the following redox reaction between PdO and Pd<sup>13</sup>



where every involved hydronium ion leads to the transfer of one electron, which is the same case as that for a traditional glass electrode.

Since the electrical potential cannot be measured by one electrode, a Ag/AgCl electrode is usually used as the reference electrode, and its electrical potential ( $E_{\text{ref}}$ ) is<sup>14</sup>

$$E_{\text{ref}} = E_{\text{Ag/AgCl}}^{\circ} - \frac{RT}{F} \ln(a_{\text{Cl}^-}) \quad (3)$$

where  $E_{\text{Ag/AgCl}}^{\circ}$  is the standard electrode potential of the Ag/AgCl electrode, and  $a_{\text{Cl}^-}$  is the activity of chloride ions. The difference of  $E$  and  $E_{\text{ref}}$  is the galvanic voltage ( $E_{\text{gal}}$ ), from which the pH of solution can be deduced. Subtracting eq 3 from eq 1, and using  $\log_{10}()$  instead of  $\ln()$ , we get

$$E_{\text{gal}} = E_{\text{pH}}^{\circ} - E_{\text{Ag/AgCl}}^{\circ} + \frac{2.303RT}{F} \log_{10}(a_{\text{Cl}^-}) - \frac{2.303RT}{F} \text{pH} \quad (4)$$

$E_{\text{pH}}^{\circ}$  and  $E_{\text{Ag/AgCl}}^{\circ}$  are dependent on the electrode materials, and are considered to be constants at room temperature. However, when the temperature changes, they are linearly dependent on the temperature.<sup>14</sup> pH 7 is usually used as the calibration buffer, and the  $E_{\text{gal}}$  at pH 7 is called the offset voltage, which is considered to be a temperature independent constant in many literature reports,<sup>13,15,16</sup> although we found it was necessary to express it as a temperature dependent variable according to eq 4. Then, the following equation is used to calculate the pH from measured galvanic voltage:

$$E_{\text{mea}} = k_1 T - k_2 T (\text{pH} - \text{pH } 7) \quad (5)$$

where  $E_{\text{mea}}$  is the measured galvanic voltage between a pH electrode and a Ag/AgCl reference electrode.  $k_1$  and  $k_2$  are coefficients that can be extracted from the measured data at standard pH buffers, and they are used as calibrated values to measure the pH of an unknown solution.  $k_2T$  is the sensitivity of the pH sensor with an ideal value of 59.16 mV/pH at 25 °C.<sup>13</sup> However, in reality,  $k_2T$  will deviate from the ideal value and is different in acid and alkaline solutions. In the calibration procedure, we use standard pH 7 buffer solution to calibrate  $k_1$ , and then pH 4 and pH 10 buffer solutions to calibrate  $k_2$  in the acid and alkaline regions, respectively.

For the accurate monitoring of the pH values, a temperature sensor is needed to automatically compensate the pH at different temperatures, because both the offset voltage and sensitivity are temperature dependent variables. Also, an electronic buffer stage with extremely low input bias current is required in the electronics to accurately acquire the galvanic voltage between electrodes. The schematic of the proposed system is shown in Figure 1. The hardware is composed of a microcontroller (Arduino Nano), a unity gain electronic buffer with a 200 fA input bias current for measuring the potential at pH sensing electrode, an electronic buffer for setting the potential of the Ag/AgCl reference electrode to 1.65 V (half of 3.3 V, for maximum the measurement range of instrument), two low-pass filters with cutoff frequency of 16 Hz, an ADC module to convert the analog voltage signal to a digital signal, and a Bluetooth module to provide wireless connectivity to a laptop or mobile phone. The 16-bit ADC is Texas Instruments' ADS1115, which has 15-bit resolution for effective magnitude conversion and 1-bit for sign. Its default least significant bit (LSB) is 0.1875 mV, corresponding to 0.003 pH resolution (a pH sensitivity of  $\sim 60$  mV/pH is used here), which is better than the requirement of most pH determination applications. The Bluetooth wireless interface provides two main advantages over a USB connection: (1) If the instrument is powered by a battery, then accessing data by wireless interface can eliminate power line noise, which will affect the precision of measured voltage data. (2) It provides for the possibility of using a smart phone to control the instrument. Other detailed information about the hardware can be found in the Supporting Information. Figure 2 shows the photograph of the hardware system on a solderless breadboard.

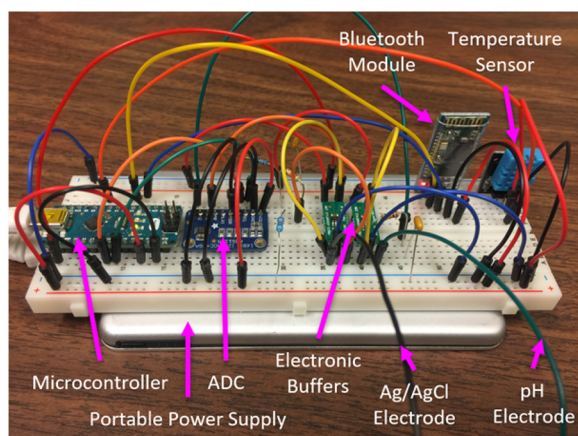
The open-source software used to control the instrument and display the data was developed in Python, a cross-platform

language popular in scientific computing<sup>17</sup> and widely used in open-source instruments for chemistry education.<sup>5,18</sup> PyQt5, pySerial, NumPy, and Matplotlib packages were used to build the graphical user interface (GUI), communicate with the serial port, manipulate data, and display figures, respectively. On the software GUI, students can choose to use USB or Bluetooth as the preferred communication method. Both the full temporal data and latest 10 s samples are plotted in different canvas regions. The configuration file (calibration data) and measured data are saved as JSON (JavaScript Object Notation) and delimited plaintext file, respectively. The firmware inside the microcontroller was developed in Arduino's official integrated development environment with Sketch, which will undergo some Arduino-specific preprocessing before being passed to a standard C++ compiler. The instrument gathers the galvanic voltage between electrodes and the environment temperature every 1 s (the maximum sample rate of temperature sensor), and updates the data display at the same frequency. All the hardware schematic and software code are free to students as open-source, and the details of software implementation are described in the Supporting Information. Open-source programs and hardware can help students to understand the measured data better because they can delve into the details of implementations, and motivated or inspired students can continue more in-depth research after the course. Therefore, the effect of teaching will be improved.

## RESULTS AND USING THE INSTRUMENT

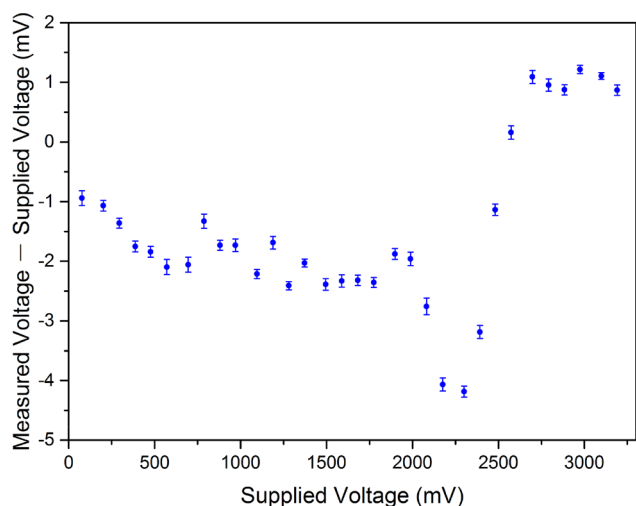
A dc power supply (Agilent 6655A, voltage accuracy of 0.06% + 51 mV, resolution of 10 mV) was used to simulate the output voltage of the pH electrode (connect Agilent 6655A's ground and positive output to the ground and pH electrode wire of the proposed instrument, respectively). A multimeter (Fluke 115, voltage accuracy of  $\pm 0.5\%$  + 2 mV, resolution of 1 mV) was used as a more accurate reader for the supplied voltage. The output of the dc power supply was swept from 100 to 3200 mV with the step of 100 mV, and the voltages shown at the multimeter and the proposed instrument were recorded, respectively. At every specified voltage, 20 data points (in 20 s) were recorded for the evaluation of the diversity of the measured voltages. As shown in Figure 3, the statistical mean and standard deviation of difference of the measured and supplied voltage is  $-1.45$  and  $1.45$  mV, respectively, within the accuracy range of Fluke 115. This means that the accuracy of the proposed potentiometric instrument is at the same level of the commercial Fluke 115. Additionally, the repeatability of every specified voltage is within  $\pm 1$  LSB (0.1875 mV), corresponding to  $\pm 0.003$  pH in pH determination application, demonstrating an excellent precision.

Two groups of electrodes were used to demonstrate the usage of the instrument. One is a traditional glass electrode (OKATON, WD-35805-04, lab grade) integrated with a Ag/AgCl reference electrode; another is a custom Pd/PdO electrode<sup>13</sup> with a separated Ag/AgCl electrode (CHI111, CH Instruments). Standard pH buffer solutions from VWR Analytical, BDH5018 (pH 4.00  $\pm$  0.01 at 25 °C), BDH5046 (pH 7.00  $\pm$  0.01 at 25 °C), and BDH5072 (pH 10.00  $\pm$  0.01 at 25 °C), were used for the verification and calibration of the proposed instrument. The electrodes were tested in each pH buffer solution for about 300 s and immediately transferred into the next pH buffer solution without rinsing or drying. To investigate the reversibility of the pH electrodes, two repeat cycles were conducted, and the environment temperature was



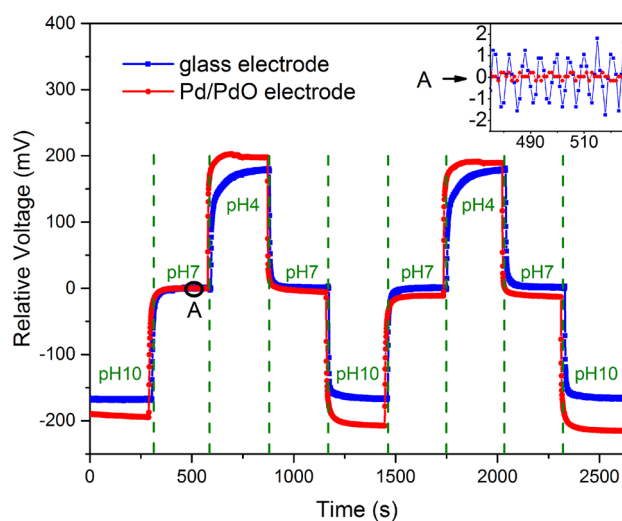
**Figure 2.** Photograph of hardware system on a solderless breadboard and powered by a portable power supply.





**Figure 3.** Difference of measured voltage and supplied voltage when pH electrode wire connects to a dc power supply, which simulates the output voltage of the pH electrode (from 100 to 3200 mV with the step of 100 mV, 20 data points were recorded at each specified voltage).

$21 \pm 2$  °C. As shown in Figure 4, the Pd/PdO electrode demonstrates a higher sensitivity ( $65.3 \pm 0.2$  mV/pH over 57.8



**Figure 4.** Comparison of temporal response of a traditional glass electrode and a custom Pd/PdO electrode at standard pH 4, pH 7, and pH 10 buffer solutions. Both the offset voltages at first for the pH 7 buffer solution are shifted to 0 mV for a more clear comparison. Inset is the zoom of temporal response centered at 500 s with span of 50 s (label A).

$\pm 0.9$  mV/pH), faster response (15 s over 75 s, defined as the time required for 90% change of the measured voltage from pH 7 to pH 4), and higher precision ( $\pm 0.003$  pH over  $\pm 0.015$  pH, statistical standard deviation of voltage at pH 7), while the glass electrode shows a better reversibility ( $0.6 \pm 0.9$  mV over  $9.6 \pm 0.2$  mV, shift of voltage at pH 7). The details of the Pd/PdO electrodes can be found in our previous papers.<sup>13,19,20</sup> Using this platform, students can conveniently study the sensitivity, response time, repeatability, and reliability of their own pH electrodes.

Before using the proposed instrument for pH measurements in other solutions, calibration is needed. A three-point

calibration function (pH 7, pH 4, and pH 10) is provided in the Python software. After the calibration, students can use the instrument and electrodes to measure the pH of unknown aqueous solutions. Examples of the measurement of tap water in McMaster University and lemon water can be found in the Supporting Information. A commercial pH meter (HANNA HI98100, with accuracy of  $\pm 0.2$  pH and resolution of 0.01 pH) was used as a comparison, and results showed a good consistency (7.29 and 4.53 by proposed instrument; 7.26 and 4.55 by HI98100).

The proposed instrument can be used for undergraduate or graduate teaching in chemistry and chemical engineering, to help students understand the basics of the pH concept or to assist their research work, respectively. It is suggested for a course where the instrumentation and the actual building of the instruments are the key objectives. We asked six graduate students in chemical engineering to build and use the instrument. The experiments were all successfully conducted, and their main consideration is why the electronic buffers are needed. To show the effect of the high internal impedance of the pH probe and demonstrate the necessity of electronic buffers, we used a general voltage data logger (Go!Link and voltage probe, Vernier) to measure the voltages of a glass pH probe at different standard pH buffer solutions, and results showed that it is not suitable for pH determination. The details were described in Supporting Information.

## FUTURE OUTLOOK

To make full use of Bluetooth wireless connectivity, in the future, a mobile app can be developed to control the instrument, and it is especially valuable for a pH determination in field applications. Java and Swift languages can be used to develop the app for Android and iOS, respectively. Also, the algorithm of evaluating the pH is the same as the Python code in this report.

Furthermore, the proposed instrument is also prospective for a general wireless data acquisition application that requires precise voltage measurement.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.7b00479.

Instruction on how to build the hardware, develop the software, and use the instrument (PDF, DOCX)

Copy of the described Python and Sketch code (with the most recent version available at <https://github.com/bc0403/wireless-pH-sensor>) (ZIP)

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### Notes

The authors declare no competing financial interest.

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