

Integrating Chemistry Laboratory Instrumentation into the Industrial Internet: Building, Programming, and Experimenting with an Automatic Titrator

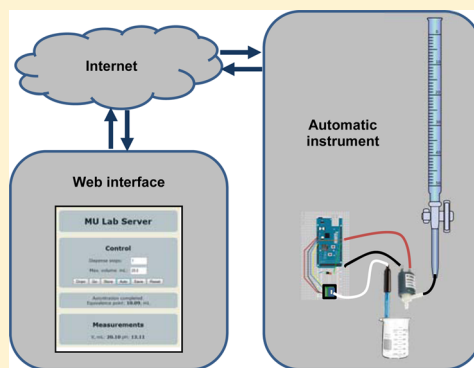
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S Supporting Information

ABSTRACT: This project is designed to improve physical chemistry and instrumental analysis laboratory courses for undergraduate students by employing as teaching tools novel technologies in electronics and data integration using the industrial Internet. The project carried out by upper-division undergraduates is described. Students are exposed to a complete process of building, calibrating, and programming an automatic titrator using an open-source microcontroller platform and standard pH probes, and integrating the instrument into the Internet. The approach is flexible and can be used to enable integration of various laboratory instruments (e.g., temperature, pressure, salinity probes, etc.) into the industrial Internet. The hardware and software are open-source, which makes further modification and development by the academic community possible.

KEYWORDS: Upper-Division Undergraduate, Analytical Chemistry, Physical Chemistry, Laboratory Instruction, Internet/Web-Based Learning, Laboratory Equipment/Apparatus, Laboratory Computing/Interfacing, Aqueous Solution Chemistry, Titration/Volumetric Analysis, Equilibrium



INTRODUCTION

There has been growing interest in integrating machinery into the industrial Internet, which is essentially the coalescence of physical hardware with networks and software. The industrial Internet takes advantage of machine learning, big data, and machine-to-machine communication to link hardware sensors to the Internet.^{1,2} This gives instrumentation and computers the ability to receive and process data and then act on the data by carrying out various protocols. Data collection via the industrial Internet is being implemented in a variety of fields^{1,2} and presents promising opportunities for the enhancement of chemical education.

It is customary to cover the physical and chemical principles of operation of commonly used instrumentation in classes such as instrumental analysis and physical chemistry.^{3,4} Recent improvements in technology have led to the development of inexpensive miniature electronic instruments suitable for use in chemistry teaching and research laboratories. These instruments include basic chemistry measurement tools for temperature, conductivity, salinity, pH, pK_a , etc.^{5–7} Many of these instruments, sensors, and probes can be interfaced to computers and networks through vendor's hardware adapters and proprietary software. Similarly, recent advances in computational chemistry,⁸ computer science, and electronics have provided a wide range of tools enabling simplification of the control of laboratory equipment, for example, portable computers, smartphones, and other technologies. Clearly, such

technological advancements provide an opportunity to improve the quality of laboratory measurements and bring experiments available for college and even K–12 education curricula to a new level of sophistication and relevance.⁹ However, new instructional challenges arise as a side effect of this technological progress. Many students experience certain difficulties grasping the relation between observed results (numbers and graphs) on the computer screen with actual physical and chemical phenomena occurring in a sample under study. Many laboratory experiments are drifting toward overly simplified “button pushing” exercises. Too often, the actual chemical processes are hidden, and instruments seem to operate “magically”.^{10,11} In this highly technological era, it is crucial that students understand the electronic components required for the instrumentation to work as well as the chemical explanations. Excellent examples of novel laboratory experiments designed to address this problem have been published in this *Journal*.^{11,12}

In the present experiment, students use state-of-the-art microcontroller hardware and an open-source software platform to build and operate chemistry laboratory equipment. Additionally, the integration of laboratory instrumentation into the Internet opens many opportunities for remote control of the instrumentation and further developments of new laboratory units.

The proposed laboratory experiment was introduced in our physical chemistry laboratory course taken by juniors and seniors majoring in chemistry. Students enrolled in this course completed two semesters of quantitative analysis and two semesters of physics (lecture and lab). A titration experiment has been chosen to capitalize on students' background knowledge and skills acquired in quantitative analysis and general chemistry courses.

LEARNING OUTCOMES

The experiment prelab assignments and postlab questions are designed to integrate concepts in chemistry and physics. The proposed project-based laboratory unit resembles real-life situations, such as when the students enter a research laboratory in graduate school or industry; for example, a problem has to be formulated by a student before it can be solved. Furthermore, the students learn to assess their data (e.g., using error analysis techniques) at each step to complete the project and make necessary modifications on-the-fly.

Upon completion of the proposed laboratory unit, the students learn how to build, calibrate, and use the instrument for a titration experiment along with acquiring a working knowledge of the software. The methods learned in the project can also be used to construct the hardware and software necessary to automate, remotely control, and integrate a variety of analog sensors into the Internet.

MATERIALS

A detailed description of the required materials is provided as [Supporting Information](#) (Table S1). It is assumed that the instructor and students have access to PC computers, Internet, and common undergraduate chemistry laboratory glassware and supplies needed to perform titration experiments. A summary of required materials to build one automatic titrator is given in the following.

- (1) Microcontroller board
- (2) Ethernet interface
- (3) Solderless plug-in breadboard
- (4) Breadboard jumper wire set
- (5) Solenoid valve
- (6) pH probe
- (7) Analog proto board adapter
- (8) Digital DC power supply 12 V
- (9) Resistors: 4 Ohm and 270 Ohm
- (10) Bipolar transistor
- (11) Silicone tubing
- (12) Sodium hydroxide solution, 0.1M
- (13) Hydrochloric acid solution, 0.1M
- (14) pH Buffer solutions (pH 4.0, 7.0, 10.0)
- (15) Beakers, 50 mL
- (16) Buret

UNIT OVERVIEW

In this unit, students build a pH meter and automatic titration solution dispenser and program it to control the instrument directly from the PC computer or remotely over the Internet. Once constructed and calibrated by students, the instrument is used for titration experiments in the laboratory operating as an interactive Web site (standalone web server) fully controlled over the Internet.

Hardware Design

The Arduino¹³ Mega 2650 R3 microcontroller (Figure 1) serves to convert the analog signal to digital (A/D) and process the information.

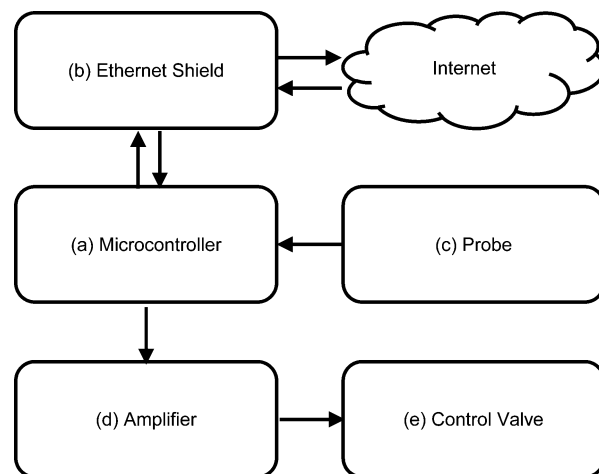


Figure 1. Hardware design: (a) a microcontroller connected to the Internet through the (b) Ethernet shield receives the measurements from the probe, for example, (c) a pH sensor, and controls the flow of the titration solution through the (d) amplifier and (e) valve. The amplified signal can be used to operate various actuators, pumps, servo motors, heaters, etc.

A pH probe is used as a sensor and is connected via a built-in amplifier to the microcontroller board analog input. The hardware design features versatility for the sensors, which can be connected to the instrument. Practically any analog sensor (temperature, salinity, pressure, etc.) can be used in addition to, or instead of, a pH probe. The current implementation is compatible with Vernier analog sensors and can be modified to work with other brands. The microcontroller is connected to the Arduino¹³ Ethernet shield R3, a network interface card, which enables network (e.g., Internet) communication of the instrument.

The flow of the titration solution from a standard buret is controlled by a solenoid valve, which is controlled by the same microcontroller through a current amplifying circuit. In alternative applications, the amplified electrical signal, which controls the valve, could be used to control various actuators (pumps, servo motors, heaters, etc.). The overall hardware design is very flexible and could be used for modifications of a variety of laboratory projects. In the unit, students learn the basics of building of chemistry laboratory instrumentation, assembling the pH sensor and volumetric control circuits, calibrating them, and carrying out a titration experiment. These activities are intended to help students critically evaluate and reinforce the concepts on acquisition and treatment of experimental data.

Software Design

The software used in the unit includes C-like Arduino¹³ scripts¹⁴ (commonly referred as “sketches”) that are uploaded to the microcontroller to initially calibrate the instrument (Figure 2a).

Two main modules are used to interface the instrument with the Internet (Figure 2b). The first of these two modules is uploaded to the microcontroller after the calibration. The module provides the basic functionality for reading the sensor

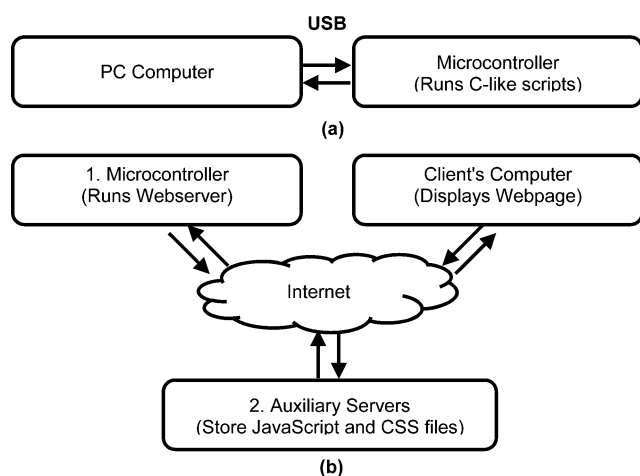


Figure 2. Software design: (a) C-like scripts are uploaded to the microcontroller over the USB interface to calibrate the instrument; (b) the microcontroller (1) communicates sensor readings and information on its status to the client over the Internet using the built-in Web server. Auxiliary servers (2) are used to store JavaScript and CSS files that are used to operate the instrument and analyze the obtained data.

(e.g., pH probe) by sending control signals to the actuator (e.g., valve that controls the flow of the titrant) and providing basic network connectivity. The second module consists of JavaScript and Cascading Style Sheet (CSS) files¹⁵ that are located on separate auxiliary Web servers (e.g., faculty Web server) and are called automatically by the microcontroller to generate the graphical user interface of the Web site (generate HTML code)¹⁵ to operate the instrument, to visualize, to analyze, and to store the results of measurements on the client's computer or smartphone.

A client requests the webpage on the Web server by typing in the IP address or hostname of the microcontroller (Figure 2). The Web server generates basic HTML and JavaScript code that references the scripts stored on the auxiliary sever. The webpage containing the user interface controls and displays the live data feed from the microcontroller. The auxiliary server is necessary because the Web server on the microcontroller is not powerful enough to generate all HTML, CSS, and JavaScripts reasonably fast when the full page is requested. Another feature of the code is to automatically update real-time sensor and volumetric readings displayed on the client computer using the Asynchronous JavaScript and XML (AJAX) mechanism.¹⁶ The detailed description of the scripts and listings of source codes are provided in Supporting Information S2.

HAZARDS

Electrical Safety

Even though the circuits in this unit use low voltage (up to 12 V) and do not pose direct risk of the electric shock, appropriate electrical safety precautions have to be taken. Electrical tape should be used to insulate wires and electrical circuits should not be left exposed at any time. Circuits should not be installed in locations where flammable vapors or other easily ignitable materials are present. Operators should also be cognizant that solutions of acids and bases conduct electricity and may short circuits.

Corrosive Solutions

Solutions of acids (e.g., HCl) and bases (e.g., NaOH) are corrosive. When working with these chemicals, safety goggles,

gloves, and a lab coat should be worn to prevent direct skin and eye contact. These solutions may also corrode circuits and exposed wires.

DESCRIPTION OF LABORATORY SESSIONS

A total of 19 chemistry majors have conducted this experiment over two different semesters, two in one semester (as a pilot project), and 17 in the other semester. The laboratory was completed over three laboratory sessions (165 min each) that included prelab, experimental work, and postlab discussions. For the experimental work, the class was divided into teams of two so that each student would have experience with all steps of the experiment.

The detailed procedures for the laboratory sessions are provided in the section S.1 of the Supporting Information. The following three laboratory sessions describe the assembly, testing, calibration, and use of the instrument by students in the titration experiment.

Session 1: Assembly and Calibration of the pH Sensor

The goal of this session is to give students a basic knowledge and understanding of the microcontroller board and electronic circuit components (Figure 3).

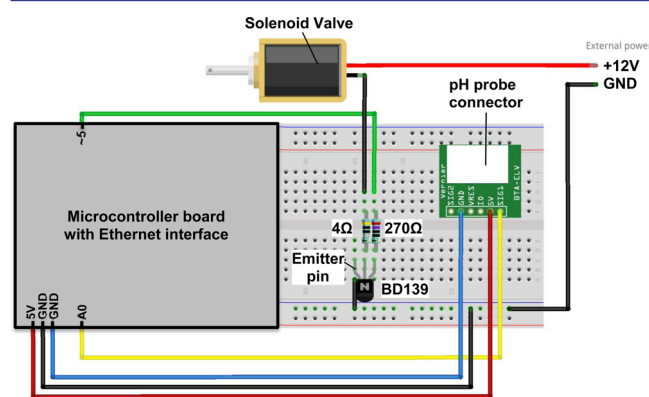


Figure 3. Circuit assembled on the breadboard is connected to the pH probe (not shown) and solenoid valve. For details, see Supporting Information (S1 Laboratory Sessions).

Objectives for the session include: (i) gaining a general understanding of the electronic components; (ii) acquiring an overview of the project; (iii) creating the circuit set up capable of taking pH measurements; and (iv) calibration of the pH probe using the circuit and pH calibration script.

The different sections of the Arduino¹³ microcontroller board¹⁴ and electronic components¹⁸ were explained to students. The students received a brief overview of the pH calibration C-like Arduino¹³ code. Although the students may perform the pH calibration without learning the code, it is highly desirable that the students understand how the pH measurements are being made and be able to troubleshoot the code if necessary. After assembling and troubleshooting the circuit, students calibrated the pH sensor with the calibration script. The circuit scheme, a detailed procedure for assembling the circuit, and suggested sample questions are given in S1.1. The full listing of the pH calibration script is provided in S2.1. Upon completion, students were able to create a simple circuit by connecting the microcontroller board and a pH sensor. In this session, students have assembled and tested their circuits in given time allotment. Students generally reported this

laboratory session was challenging as they had not had previous opportunities to design electronic circuits with microcontrollers.

Session 2: Construction of the Titrant Dispenser

The goal of this session is to provide students with hands-on practice in application of the previously acquired knowledge about the microcontroller circuit to building the more complex part of the automatic titrator—the titrant dispenser circuit (Figure 3) and volumetric assembly (Figure 4). Objectives for

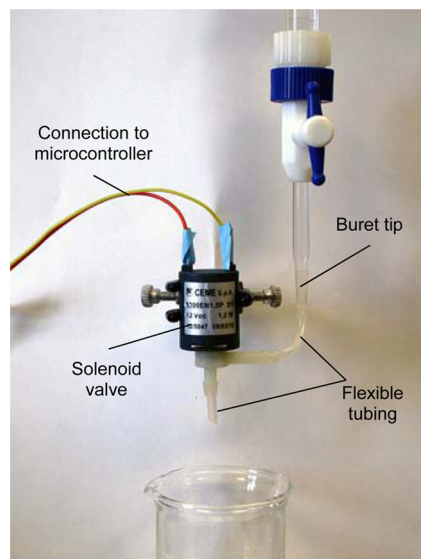


Figure 4. Solenoid valve assembly.

the session include: (i) assembling the buret and valve set-up required to automate the volume dispersions; (ii) introducing new electrical components (resistors, transistors, and a solenoid valve) into the circuitry and gain a basic understanding of their operation; (iii) applying the newly learned information along with previously acquired understanding of the circuit to modifying the circuit to control the volume of titrant dispensed; and (iv) calibrating the volume of titrant dispensed by creating a calibration curve for the titrant dispenser.

In this session, students also studied the code that controls the opening and closing of the valve and how it is translated into the volume of dispensed titrant solution. The volume of titrant dispensed is dependent on the time the valve is in the open state (12 V applied to the valve).

The time that voltage is applied should be short enough so that the volume dispensed by the valve is small enough to observe the equivalence point (there is an option in the program to accelerate the titration at the beginning and end to avoid having to dispense too small volumes of titrant for the entire duration of the titration). The default recommended time to apply voltage to the valve is 500 ms. However, this value can be adjusted in the volume calibration script if necessary.

Because of variations in room temperature, atmospheric pressure, titrant viscosity, and density, the volume of titrant that is dispensed may vary. It is necessary to calibrate the volume dispensed versus the number of voltage pulses applied to the valve to open it. The calibration script keeps a continuous count of the pulses that open the valve upon the user's request. After ensuring that the dispenser is functional, students calibrated it with the sodium hydroxide solution.

The detailed procedure for assembling the circuit and suggested sample questions are given in S1.2. The full listing of the volumetric calibration script is provided in S2.2.

A survey of calibration plots indicated that half of the students had to repeat the volumetric calibration procedure to achieve satisfactory accuracy of measurements. In general, the pH measurements obtained with the assembled instruments had been as accurate as standard laboratory instrumentation that gave students sense of accomplishment and excitement.

Session 3: Network Integration. Titration Experiment

In this session, students connect the assembled circuit to the Internet so that the microcontroller can host the Web site. Objectives of this session are (i) to configure the microcontroller to connect to the Internet; (ii) to learn the basic user interface controls made available through the Web site; (iii) to perform a titration using the Web site; and (iv) to use the titration curve, the first and second derivative graphs, and the table of data points to determine the equivalence point.

There are various controls on the Web site intended to automate the titration (Figure 5). The student can input the final volume, which allows the student to set the end point volume for the titration if they are using the automatic titration feature. The Web site displays the plots of the titration curve, the first and second derivatives, as well as the table of stored values. The full description of the web interface is given in S1.3. Upon completion, students have logged in to the Web site and utilized it to run a titration (obtaining the titration curve and table and determine the equivalence point of their titration).

This usually is the most complex part of the project for students. The software development is out of the scope for the present project. The two high-achieving students who ran pilot experiments were interested in learning the code in detail and even suggested modifications to increase precision of measurements, while others just used the code as provided by the instructor. As a standard manual titration experiment, it was somewhat tedious, while the automatic titration procedure, once properly setup, provided much faster and easier titration with equality accurate results. This provided clear motivation for students using the built autotitrator.

RESULTS

The results shown in this article represent data collected by students.

Calibration of the pH Probe

The theoretical pH calibration equation derived from the Nernst equation (see S3) is written as

$$pH = -\frac{1}{k_N T} E + \frac{E_0}{k_N T} \quad (1)$$

where E is the voltage of an ideal pH electrode, E_0 is the standard electrode potential, $k_N = \ln(10)(R/F)$ is the Nernst factor, R is the gas constant, F is the Faraday constant, and T is the absolute temperature. Eq 1 provides an important insight: the calibration coefficients depend on temperature. Further improvements of the instrument may include addition of a temperature probe to account for temperature variations.

For the example run described here, the pH probe was calibrated by students with three pH buffers with pH = 4.0, 7.0, 10.0 (Thermo Scientific). An average of six replicate pH measurements for each buffer was used in the calibration plot (Figure 6). Linear regression coefficients from the best fit

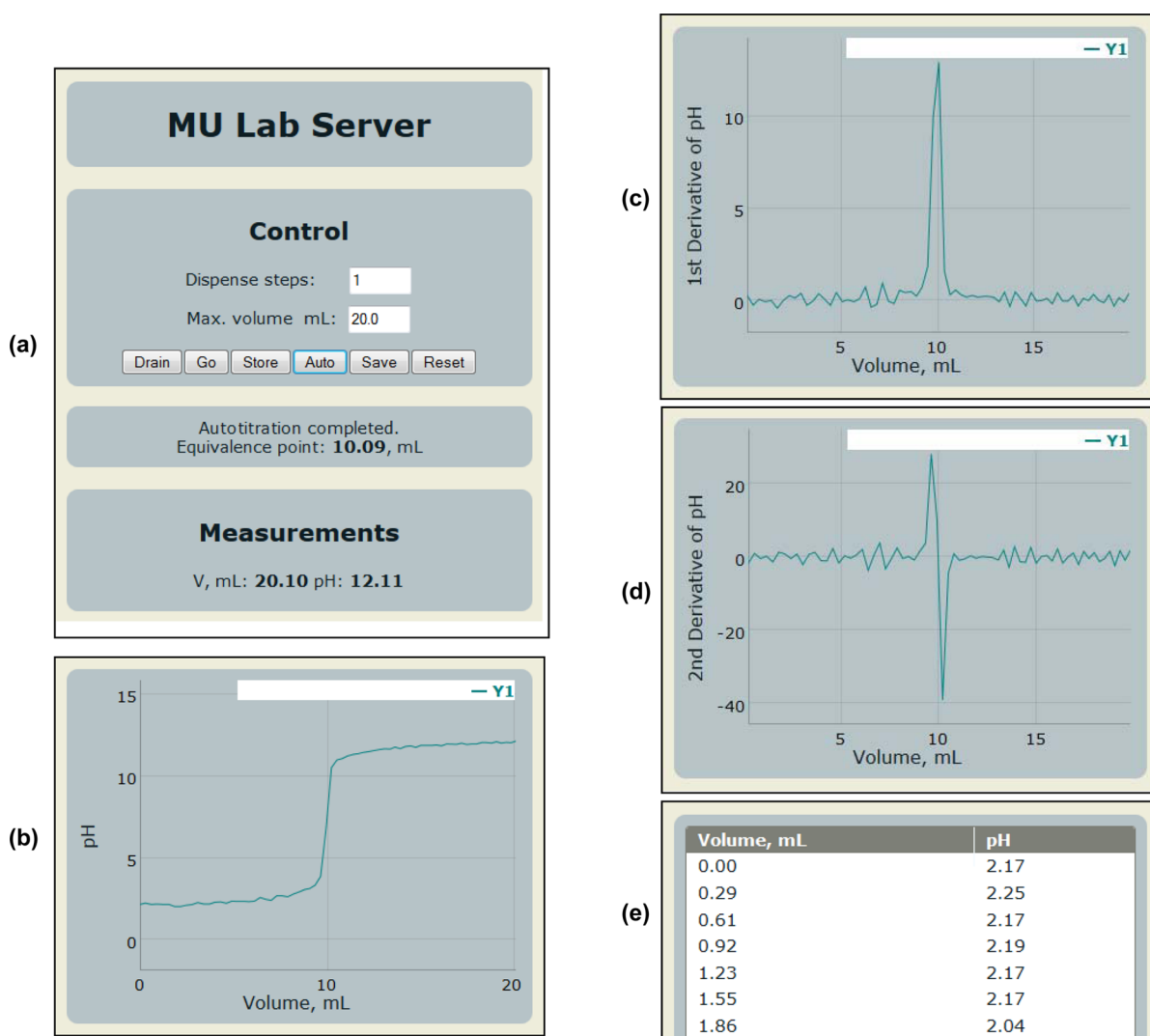


Figure 5. Screenshots of the webpage generated by the instrument: (a) user interface controls, volumetric and pH measurements; (b) titration curve; (c) first and (d) second derivatives of the titration curve; (e) tabulated titration data.

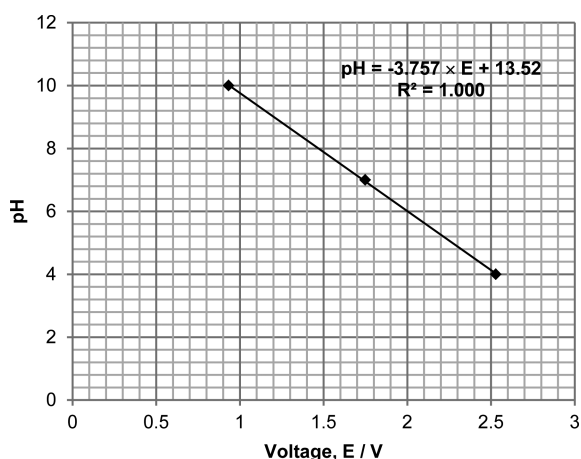


Figure 6. pH calibration values. The linear fitting parameters were used in the titration scripts.

equation, $\text{pH} = -3.757 \times E + 13.52$, were used in the scripts (S2). The measured coefficients are close to the default calibration values for the pH sensor:¹⁹ $\text{pH} = -3.838 \times E + 13.72$. The theoretical maximum accuracy for pH, based on the

microcontroller built-in 10 bit analog-to-digital converter with 5 V reference voltage and using the measured calibration value, is $(5.000 E/2^{10}) \times (3.757) \approx 0.02$ pH units. However, the actual obtainable accuracy is limited by the accuracy of the pH sensor itself which is ± 0.2 pH units.¹⁸ It is recommended that the pH sensor be calibrated before each laboratory session.

Calibration of the Titration Dispenser

The volume dispensed from the buret may need to be recalibrated each time a new solution is used for titration. The dispensed volume measurement was calibrated by specifying the number of pulses sent to the valve and manually reading the liquid level in the buret after each set of pulses. The calibration plot is shown in Figure 7. The optimum value for the valve open-time was determined from this calibration to be 500 ms. This value for valve open time will dispense about 0.35 mL when the buret is filled, and 0.15 mL when the buret is close to empty. Several measurements of the volume were taken and plotted against the voltage pulse count, and the coefficients from a second order polynomial best fit curve were entered into the code for the following the automatic titration.

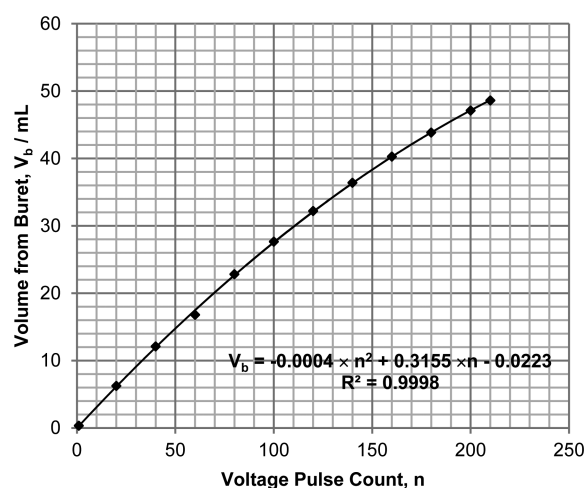


Figure 7. Volume calibration curve as a function of the voltage pulse count applied to the valve. The quadratic fitting parameters were used in the titration scripts.

Titration Curve

Test titrations were performed in both the manual and the fully automatic modes. A representative titration curve obtained in the fully automatic mode is shown in Figure 8. The equivalence

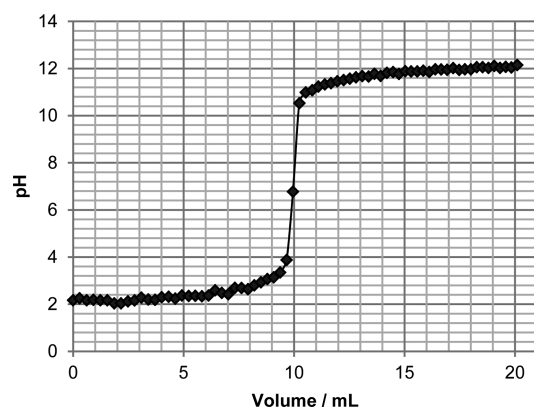


Figure 8. Titration of 10 mL of 0.1 M HCl with 0.1 M NaOH.

point was determined using the maximum of the first derivative plot. In the run shown in Figure 8, the titration of 10 mL of a HCl 0.1 M standard solution with 0.1 M NaOH standard solution gave an equivalence volume of 10.0 ± 0.2 mL (2% error) in agreement with that calculated from the HCl concentration. Students performed the titration in both manual and automated modes.

CONCLUSIONS

This experiment provides an opportunity for students to engage in construction, automation, and remote control standard analog sensors (e.g., a pH probe) and actuators (e.g., a solenoid valve).

An open-source affordable hardware and software platform has been used to integrate undergraduate laboratory experiments with the Internet. The developed platform enhances physical chemistry or instrumental analysis laboratory undergraduate courses and prepares students for future graduate research or professional careers where skills in electronics and

digital data acquisition and processing, as well as the knowledge of modern software and hardware technologies, are essential.

Included in the physical chemistry laboratory course, an example of the application along with the detailed instructions, sample questions, and source codes of the developed platform for a titration experiment is presented. The methods described can be easily modified for other types of experiments, for example, by replacing the pH probe with a temperature sensor and the solenoid valve with a heating element, the platform could be used to carry out experiments in thermodynamics including calorimetric measurements of the heat of neutralization, investigation of phase transitions, etc.

The described multiweek laboratory unit helps to develop a sense of ownership in students. Critical thinking is encouraged when students work on assembling and calibrating the instrument, debugging the software, and troubleshooting hardware problems. In our experience, when a team of two students works on the project, positive peer pressure contributes to keeping students motivated. It is critical to offer meaningful, reasonably challenging assignments in the proposed unit by splitting complex tasks into several steps. We have observed that the challenge of the project and the tangible results obtained provide students with a genuine sense of accomplishment when completed.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00494.

Detailed materials list, procedures and sample questions for laboratory sessions, and source code listings (PDF, DOCX)

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Notes

The authors declare no competing financial interest.

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