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Technology Report

A Practical Guide to Build a Raspberry Pi Pico Based Potentiostat for Educational Electrochemistry and Electronic Instrumentation

Annemarijn Steijlen,* Margreet Docter, Jeroen Bastemeijer, Maciej Topyła, Monika Moraczewska, Thijn Hoekstra, Marc Parrilla, and Karolien De Wael*

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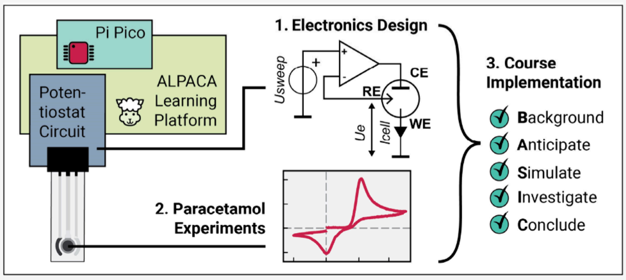
ABSTRACT: This manuscript presents the first practical guide to build a Raspberry Pi Pico based potentiostat for electrical and electrochemical instrumentation education. The circuit enables us to perform different types of voltammetry such as cyclic and square wave voltammetry. Voltammograms of paracetamol tablets in a neutral buffer solution were successfully recorded and compared to lab equipment. Thereafter, the effect of different scan rates and different concentrations was studied as a proof of concept. Furthermore, the experiments were expanded with measurements of other pharmaceutical tablets such as vitamin C. Over 80 nanobiology bachelor students successfully built their own potentiostat in an electronic instrumentation course. They validated their systems successfully with electrochemical experiments using paracetamol as a conventional pharmaceutical that can be performed in a classroom. The students acquired a valuable understanding of the electronic building blocks and system architecture within electrochemical instrumentation, equipping them with the requisite knowledge to effectively optimize instrumentation parameters in their future research work.



KEYWORDS: *Undergraduates, Interdisciplinary, Multidisciplinary, Hands-On Learning, Problem Solving, Decision making, Electrochemistry, Potentiostat*

INTRODUCTION

Modern electrochemical equipment became easy to operate without understanding the fundamental electronic principles of the electrochemical techniques, due to the digitalization of measurement technologies and the emergence of user-friendly interfaces. The ease-of-use of these devices often results in the treatment of the equipment as a black box[1] and the exact copying of parameter inputs, hampering true understanding of the technique and preventing well-considered optimization of the right parameters to a particular measurement. This not only applies to potentiostats, but also to other electronic equipment which is widely used in chemical analysis education.[2] Therefore, it is of great importance to teach future scientists the basics of electronic instrumentation to understand the opportunities and limitations of the equipment that they use.[3] An example of these future scientists are the students of the nanobiology bachelor program of the TU Delft. In this program, the students are educated in engineering, physics and bioscience to study the complexity of living systems. Within our electronic instrumentation course for the nanobiology students, we not only teach passive and active electronics, but also focus on the instrumental part, including programming and data acquisition. Next to the theoretical aspects, students build, measure and evaluate the different electronic concepts in practical sessions. In a 3-week final project, these electronic concepts are combined to design a final instrument for a real-life measurement application.[4−6] The aim of our new final project is to build a Raspberry Pi Pico based potentiostat that can perform cyclic voltammetry (CV) and square wave voltammetry (SWV) for rapid and portable chemical analysis. The students learn to understand the different analog and digital building blocks of the potentiostat, and to integrate them in a fully functioning electronic system. The potentiostat demonstrates the relevance of understanding electronics toward a system for a real-life application: the electrochemical detection of paracetamol in pharmaceutical tablets. The case study of paracetamol was chosen because it is an accessible analyte which can be quantitatively detected in a neutral buffer solution.[7−9] Furthermore, the required chemicals do not necessarily need to be handled in a chemical lab and can be used in a general classroom.

Previously, researchers developed simple Arduino-based potentiostats for research[10,11] and for educational purpo-

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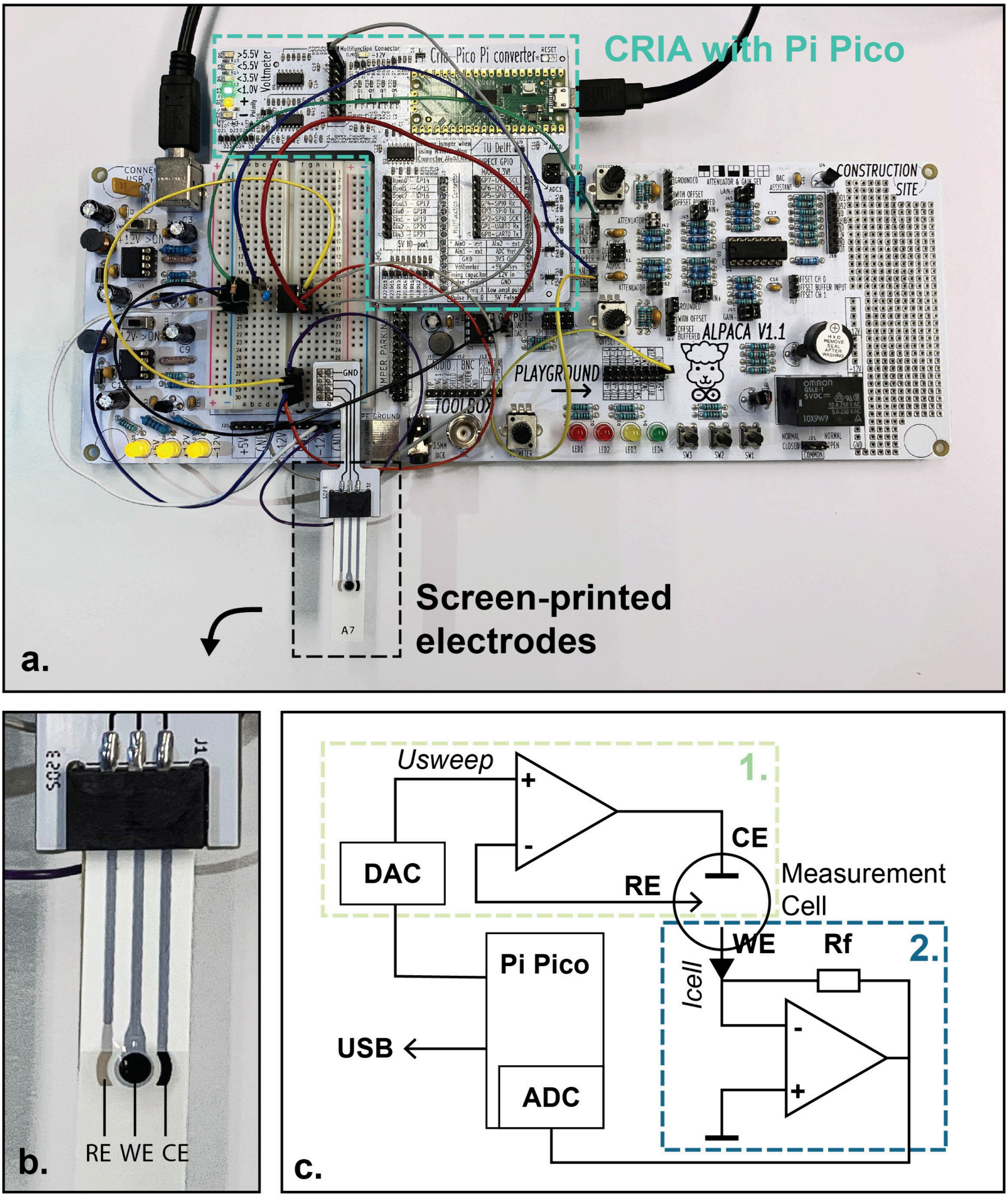

Figure 1. Electronics design. (a) The measurement setup with ALPACA (Advanced Learning Platform for Analog Circuits and Automation), connected to a Cria board with a Raspberry Pi Pico and a screen-printed electrode for the voltammetric measurements. (b) A close-up of the screen-printed electrodes with a Ag/AgCl pseudoreference electrode (RE) and carbon working electrode (WE) and counter electrode (CE). (c) The circuit diagram. The input potential is applied via CE and RE, while the current is flowing from CE to WE and WE is at ground potential. (1) The circuit controlling the input voltage (Usweep) with a regulator OPAMP and (2) the circuit to measure the cell current (Icell) with a transconductance amplifier.

ses.[12−17] Unfortunately, they generally do not report the implementation of building and validating these electronics by the students in a course. In this paper, we present the first guide to build a Raspberry Pi Pico based potentiostat for CV as well as SWV and its implementation in the electronic instrumentation course for bachelor students.

First, we present the electronics design of the potentiostat. Second, the functioning of the instrument is demonstrated with electrochemical paracetamol measurements. Thereafter, the implementation of designing and building this potentiostat and performing electrochemical measurements as a final assignment in the electronic instrumentation course is explained, followed by the student evaluations of this new final project. On the one hand, this practical guide can teach electronic instrumentation across different disciplines such as applied physics, technical medicine and nanobiology. On the other hand, the guide offers comprehensive insight into novice researchers in the field of electrochemistry regarding the electronic design aspects of the potentiostat. This enables relating the instrument parameters with electrochemical principles, facilitating the selection of optimal instrument settings for their research endeavors.

■ ELECTRONICS DESIGN

The ALPACA Platform

In this paper, we use the Advanced Learning Platform for Analog Circuits and Automation (ALPACA) to build the potentiostat. The ALPACA was created during COVID-19 times, as an effective alternative for on-campus practicals. All circuit diagrams of the ALPACA are available open access.[5,6] For alternative implementations, the Raspberry Pi Pico based potentiostat can also be made without the ALPACA. In Supplementary data SD-1, the schematics and main components for this alternative setup can be found, including a detailed explanation.

The ALPACA is designed and built around a breadboard for building electronic circuits, and a microcontroller (for control and acquisition) (Figure 1a). To support stand-alone safe use, onboard power supplies for +5 V and ±12 V were realized. Via a digital-to-analog converter (DAC), a continuous voltage output or variable waveform can be generated. To ensure safe voltage levels to ensure that the operational amplifiers (OPAMPs) function with a ±12 V supply, while the microcontroller only accepts <3.3 V for Raspberry Pi Pico, the following was realized: voltage level adaption and removal of negative voltage of the output of the onboard amplifiers. A Raspberry Pi Pico was added via a small additional "Cria" board, including a coarse voltmeter displaying the voltage levels through 5 LEDs turned on/off (<1, < 3.3, > 5 V, ± polarity).

A Raspberry Pi Pico was chosen over an Arduino to directly program in Python, the preferred and main programming language used in the TU Delft nanobiology curriculum. Since the process of transitioning between MicroPython for acquisition and Python3 for analysis proved to be cumbersome and inconvenient, a dedicated ALPACA kernel was developed, which is available via Github.[18,19] This kernel is used via Jupyter notebooks, which integrate text explanations, concise instructional YouTube videos, and code, facilitating a comprehensive learning experience. This approach allowed us to seamlessly combine theoretical concepts, visual demonstrations, and practical implementation within a single platform, enhancing student engagement and understanding.

The Potentiostat

A potentiostat allows researchers to study electrochemical reactions under controlled conditions. In voltammetry, the voltage at the working electrode (WE) will be varied with respect to the reference electrode (RE), while the current is measured between WE and a counter electrode (CE). It can be used to study and control oxidation and reduction reactions in a solution. In this project, we use low-cost disposable screen-printed electrodes with a carbon working and counter electrode and a Ag/AgCl pseudoreference electrode (PalmSens, The Netherlands) (Figure 1c). A droplet of the solution of interest is placed on top of this planar electrode system to perform the measurement.

From a chemical point of view, the RE is regarded to be the zero potential, such that the reaction voltage resembles the WE potential. The cell current flows from CE to WE. No current will flow through RE, ensuring that RE maintains a stable potential. However, the practical implementations of the circuit are such that not the RE but the WE is at zero potential (ground-potential) as shown in Figure 1d. The OPAMP serves as a regulator (Figure 1d (nr. 1). It will adjust its output voltage to maintain an equal potential on the inverting and the noninverting input. The OPAMPs (TL072, Texas Instruments, USA) output is connected to the CE. The inputs are connected to the control-voltage/sweep-voltage and to the RE. The potential at the WE is at 0 V (ground-potential), which facilitates the measurement of the cell-current from an electronics point of view. Note that having the WE at ground potential is contradictory to the chemical definition of the potential, in which the RE is at ground potential. To apply the correct electrochemical potential to the sweep-input, we have to apply the inverted chemical potential to the sweep input of the OPAMP.

Figure 1d (nr. 2) shows how the current through the electrochemical cell (Icell) is measured with a transconductance amplifier circuit. The feedback resistor (Rf) determines the transfer-ratio of current to voltage. The inverting function ensures that the negative current is transferred to a positive output voltage which can be converted by the ADC (analog-to-digital converter). When the noise levels are found to be too high, a capacitor can be added parallel to Rf.

For generating the voltage sweep we use the DAC on the ALPACA (MCP4822, Microchip, US). To perform an oxidative scan (i.e., negative control voltage in our setup) an inverting amplifier is deployed. To record I_{cell}, the Raspberry Pi Pico built-in ADCs are used. These can digitize an analog voltage in the range of 0 V until 3.3 V with a resolution of <1 mV (12 bits).

One way to do the voltammetric measurement is by applying a linear potential sweep. However, performing SWV or even differential pulse voltammetry is an option too. The advantage of the ALPACA is that it can do all of these modes. The mode can be changed by changing the digital waveform (in software) which is sent to the DAC, no changes are necessary in the hardware. The processing of the data should be adjusted according to the chosen voltammetry mode. In this course, students have successfully performed CV and SWV measurements.

■ ELECTROCHEMICAL MEASUREMENTS

Materials and Methods

Phosphate-buffered Saline (PBS) pH 7 (20 mM, 0.1 M KCl) was created with analytical grade reagents from Sigma-Aldrich (Merck, Belgium), including disodium hydrogen phosphate, potassium dihydrogen phosphate and potassium chloride. Solutions were made with 18.2 MΩ/cm doubly deionized water (Milli-Q, Merck Millipore). Standard 500 mg paracetamol tablets were purchased at the pharmacy (Kruidvat, The Netherlands). Vitamin C tablets (600 mg per tablet, Davitamon, The Netherlands) and Ibuprofen tablets (Kruidvat, 400 mg, The Netherlands) were also used. Solutions of 0.5 mg/mL, 0.25 and 0.125 mg/mL paracetamol tablet (APAP) in PBS were made. Furthermore, a solution 5 mg/mL Vitamin C (VitC) tablet in PBS and 5 mg/mL Ibuprofen tablet (IBU) in PBS were made.

Reference measurements were performed using a single-channel EmStat Blue potentiostat and the PSTrace software (PalmSens, The Netherlands). ItalSens IS-C Screen-Printed Carbon Electrodes were used (PalmSens, The Netherlands). The electrodes were disposable and were replaced after each measurement. The used droplet volume is 80 μL in each experiment. However, a constant droplet volume is not critical, as long as the droplet covers all electrodes, and hence the students can use a simple disposable pipet during the practical sessions.

Results and Discussion

First, cyclic voltammograms (CVs) were recorded within the range of −0.5 to 1.2 V with the Raspberry Pi Pico based potentiostat using a scan rate of 500 mV/s (and a step size of 5 mV). Figure 2a shows the applied potential sweep. Figure 2b presents the voltammograms. The graph shows that for a blank measurement (i.e., only buffer solution) the I_{cell} is very small (<10 μA), which motivated a careful and manual adjustment of the current-to-voltage converter's gain with the resistor *Rf* as a necessary part of the student's workflow. When a 0.5 mg tablet APAP/ml is added, the signal is much stronger, and the gain must be reduced by approximately an order of magnitude (x10) to capture the signal's entire range. The curve for the APAP tablet shows a clear oxidation peak at 0.52 V (peak current, I_{peak} = 85.5 μA), which is followed by a reduction peak around 0 V (I_{peak} = 45.2 μA). The Raspberry Pi Pico-based potentiostat measures a similar voltammogram (yellow) as the PalmSens potentiostat that was used as a reference (black). The CVs show that the process is quasi-reversible (peak separations >500 mV, $I_{peak,oxidation}/I_{peak,reduction} > 1$).[20] Figure 2c shows the voltammogram of 0.5 mg tablet APAP/ml at different scan rates. Higher currents are observed for faster scan rates. This corresponds to the theory: faster scan rates lead to a decrease in the diffusion layer, which results in higher currents.[20]

Second, the microcontroller was programmed to perform SWVs. A typical square wave signal consists of a square wave signal superimposed on a linear ramp. SWV is a fast and sensitive technique that can be used for quantitative detection of analytes in the micromolar range. It is a differential technique which can discriminate against charging currents/nonfaradaic processes.[21,22] A potential (E_{cell}) from 0 to 1.2 V is applied over time, as displayed in Figure 3a. To make the square wave visible, Figure 3b shows a detailed view of the time window from 14.5 to 15 s. The amplitude of the square wave (A) is 25 mV, the step size (E_{step}) is 5 mV and the frequency is 10 Hz. In Figure 3c, the cell current (I_{cell}) is plotted over time for a measurement of 0.5 mg tablet/ml APAP. The detailed view of the window from 14.5 to 15 s in Figure 3d shows the effect of the alternating potential on I_{cell}. This plot provides insight into the progression of the reaction, which can be used to optimize SWV parameters. To retrieve the square wave voltammogram, the current at the end of the downward pulse ($I_{reverse}$) needs to be subtracted from the current at the end of the upward pulse ($I_{forward}$). The black boxes in Figure 3d highlight the sampling window of 3 ms for these currents. In this window, three measurements are recorded and averaged to compensate for the high-frequency noise of the readout. Figure 3e shows $I_{forward}$ and $I_{reverse}$ plotted against potential. The final square wave voltammogram

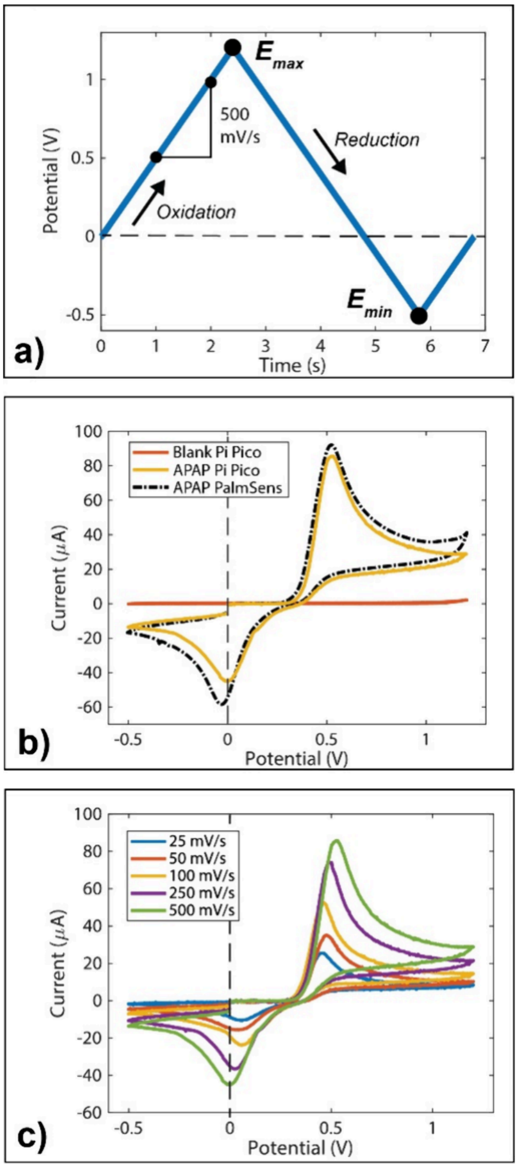

Figure 2. (a) Applied potential sweep between (E_{min} = −0.5 V and E_{max} = 1.2 V) with a scan rate of 500 mV/s. (b) Voltammograms of the buffer solution (blank, orange) with the new setup (Pi Pico), 0.5 mg tablet/mL of paracetamol (APAP) with the new setup (yellow), and the reference measurement with a 0.5 mg tablet of APAP/mL with a PalmSens commercial potentiostat (black dotted line). (c) Voltammograms of a 0.5 mg tablet of APAP/mL at different scan rates with our new setup.

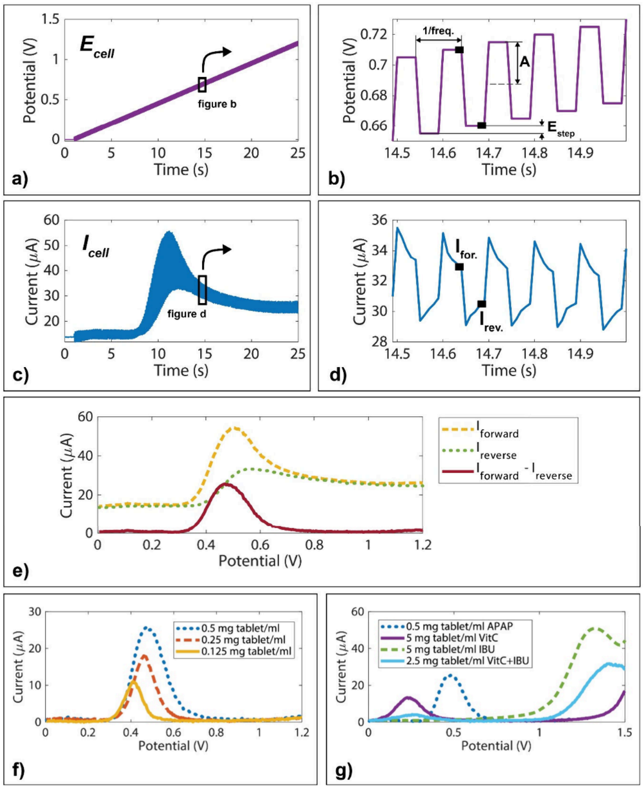

Figure 3. (a) Applied potential sweep for square wave voltammetry (SWV) from 0 to 1.2 V. (b) Applied potential between 14.5 and 15 s (zoom in) with an amplitude (A) of 25 mV, step size (E_{step}) of 5 mV, and a frequency of 10 Hz. The black boxes represent the sampling windows for the reverse and forward currents to construct the square wave voltammogram. (c) The cell current (I_{cell}) plotted over time. (d) I_{cell} between 14.5 and 15 s (zoom in). The forward current ($I_{for.}$) is sampled at the end of the upward pulse, and the reverse current ($I_{rev.}$) is sampled at the end of the downward pulse. (e) The construction of the square wave voltammogram. $I_{forward}$ and $I_{reverse}$ are plotted separately. The final curve shows the difference between $I_{forward}$ and $I_{reverse}$. (f) SWVs of solutions with different concentrations APAP (0.125, 0.25, and 0.5 mg tablet/mL). (g) SWVs of solutions with alternative pharmaceutical tablets (vitamin C tablets (VitC) and ibuprofen tablets (IBU). VitC and IBU can also be detected in a binary mixture (2.5 mg tablet/mL).

($I_{forward}$-$I_{reverse}$) is represented by the red graph. As can be seen in the graph, the capacitive contribution originating from nonfaradaic processes is successfully minimized by subtraction.[23] The oxidation peak of APAP is present at 0.47 V with an I_{peak} of 25.6 μA. SWV provides many opportunities for the students to experiment with this setup. For example, Figure 3f demonstrates that this system can potentially be used for quantitative detection of APAP. A clear distinction in the peak height in the voltammograms of different solutions between 0.125 mg (I_{peak} = 11.0 μA) and 0.5 APAP tablet/ml (I_{peak}= 25.7 μA) can be noticed. At higher concentrations, a larger amount of paracetamol is oxidized, resulting in a higher peak current and a higher peak potential. Furthermore, other pharmaceutical tablets can be easily analyzed. Measurements with Vitamin C (E_{peak} = 0.23 V) and Ibuprofen tablets (E_{peak} = 1.32 V) (both 5 mg tablet/ml) have been performed successfully (Figure 3g) and even a binary mixture of these substances showed peaks for both compounds (VitC: E_{peak} = 0.28 V, IBU: E_{peak} = 1.40 V). These measurements show the possibilities of the potentiostat. In the future, a broad range of detection methods for analytes such as hydrogen peroxide and glucose can be applied.[24,25] Furthermore, adding functionalities such as remote control can be explored.

IMPLEMENTATION IN THE ELECTRONIC INSTRUMENTATION COURSE

Course Implementation

The final voltammetry project of the electronic instrumentation course in the nanobiology bachelor curriculum of the TU Delft presents second year students with the ultimate challenge of applying their acquired electronics knowledge, skills and competencies to measure a biochemical reaction. It spans the last 3 weeks of a 20 weeks (semester) course of 6 ECTS. Each week consists of a 2-h theory session (which is initially a teacher-driven lecture and transitions to student-driven Q&A sessions) and a 4-h lab session. Within this voltammetry project, students embark on a guided inquiry process in which they: 1. construct a basic circuit, 2. progress to implementing advanced electronics and coding, and 3. record electrochemical reactions using their own device.

For the initial voltammetry practical session, we implemented the predict-observe-explain approach,[26] augmented with just-in-time theory and simulations in our Jupyter Notebook manual that is provided to the students (supplementary data, SD-2). These notebooks include text, code, movies, and are used for hardware control, data acquisition and analysis. Furthermore, it enables the students to create and electronic lab journal. Guiding questions assist students in synthesizing the provided building blocks. However, to stimulate independence and critical thinking, the manual of the final assignment for the second lab session merely provides directions and prompts for critical thinking, and for the third session, there is no manual. In every session, the students can always consult the teachers and teaching assistants for additional guidance.

The activities of the final project closely align with the overarching goals of the course, which include the ability to predict outcomes, design simulations and circuits, acquire and analyze data, resolve discrepancies, and evaluate and effectively communicate findings. Working in pairs (this year, 40 pairs +6 singles) promotes cooperation and ensures equal contribution from all team members. Assessment is based on a written report submitted by each group, following a predefined structure that correlates with a detailed rubric. Points are awarded for various aspects including design, implementation, understanding of basic electronics, programming skills, biochemistry knowledge, and any additional advancements made in these areas. Moreover, students are encouraged to share and reflect on their journey, allowing them to earn credits for ideas that may not have been fully implemented but demonstrate understanding. Demonstrating proficiency in troubleshooting is considered particularly valuable, as it showcases a deeper comprehension of the concepts being taught.

Evaluation

The voltammetry assignment was successfully implemented in the course in the academic year 2023−2024. The study to evaluate the course was approved by the Human Ethics Research Committee of Delft University of Technology. The students gave informed consent about sharing their experiences. The grade distribution of the students' reports about the final voltammetry assignment is shown in Figure 4, and the distribution per overall rubric item is displayed in Table 1.

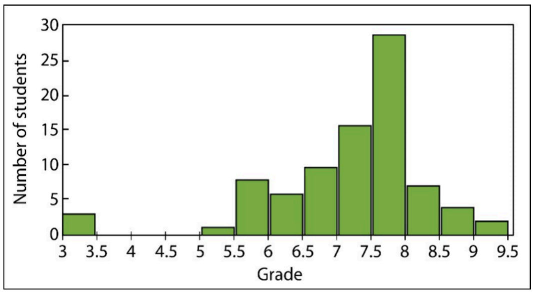

Figure 4. Distribution of voltammetry report grades in the academic year 2023−2024, *N* = 86, 40 teams of two and six students solo, on a 1−10 scale. >5.75 is considered a passing grade.

Table 1. Scores (in %) per Rubric Item for *N* = 86 Students, 40 Teams of Two and Six Students Solo

	mean score (%)	standard deviation (%)	weight factor
1. electronics, following the manual	87	6	5
2. Python, following the manual	79	9	5
3. protocol	76	11	1
4. paracetamol measurements	67	11	5
5. advanced electronics, beyond the manual	55	13	2
6. advanced coding, beyond the manual	49	20	2
overall	73	10	20

In the detailed rubric, which can be provided to teachers upon request, there are 20 subcategories with an equal weight factor. From scores per subcategory, we found that 95% of the students measured a paracetamol peak successfully. To accomplish this, the students successfully followed the manual to build the correct electronics and software code in Python. This explains the high scores in the first categories. For the last two categories, advanced electronics and advanced coding, the students were encouraged to design and implement more advanced features of the potentiostat, beyond the description in the manual. 89% of the students figured out how to use a capacitor to reduce noise. 74% of the students implemented the square wave signal generation.

The only rubric items scoring less than 60% were the variation of paracetamol concentrations, and implementing a subsequent step in the electronics and coding, such as the addition of a relay, or implementation of automated analysis of the square wave data.

The course response group (N = 8), composed of the nanobiology student association, gave the following feedback about the voltammetry project:

> *"Overall, the students liked the project, and they appreciated getting the opportunity to apply the skills from the course in a practical context. However, they think there were some issues with the expectations since they did not have a clear rubric and the goals of the project were ill-defined."*

In the anonymous (centrally organized) evaluation survey (N = 12), general opinions ranged from *"The content: I think it is very useful and interesting for us to have basic knowledge about electronics."*, to *"The correlation and relevance to our program could be better explained and defined"* without specifically mentioning the voltammetry project.

More interesting to read were the student journeys, found at the end of each report, which include detailed diaries mainly describing what happened, as well as careful reflection and insights into the student's learning process. A selection of journeys is given in supplementary data, SD-3 describing a challenging process, which in the end turned out to be manageable and rewarding. In short, the assignment of building a Raspberry Pi Pico based potentiostat was successfully implemented in the electronic instrumentation course of the nanobiology bachelor program. The students felt they understood their designs and measurements and were proud of their results.

■ CONCLUSION

We designed and fabricated a Raspberry Pi Pico based potentiostat for education in electrochemistry and electronic instrumentation. As a proof of concept, CVs (0.5 mg tablet/ml APAP in neutral phosphate buffer) with screen-printed electrodes were recorded and successfully compared to the results of a commercial potentiostat. Further experiments included the variation of scan rates, performing SWVs, varying analyte concentrations and measuring alternative pharmaceutical tablets such as VitC tablets, showing the potential of performing real-life experiments in a classroom with this setup. In the final assignment of the nanobiology electronic instrumentation course, over 80 students were asked to build this potentiostat. They gained insight into the electronic building blocks of the potentiostat and successfully recorded CVs and SWVs of paracetamol tablets. This course provided indispensable knowledge in instrumentation to conduct dependable research in their respective fields that can lead to the development of new miniaturized analysis tools for a broad variety of applications (e.g., health, environment, and/or security analysis).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available at https://pubs.acs.org/doi/10.1021/acs.jchemed.4c00624.

How to build the Raspberry Pi Pico based potentiostat without the ALPACA (SD-1), instructions for de voltammetry assignment (SD-2) and student reflections (SD-3) (PDF)

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Notes

The authors declare no competing financial interest.

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