



Research article

Low-cost smartphone-controlled potentiostat based on Arduino for teaching electrochemistry fundamentals and applications

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ABSTRACT

Accessibility to potentiostats is crucial for research development in electrochemistry, but their cost is the principal drawback for their massive use. With the aim to provide an affordable alternative for resource-constrained communities, we present a low-cost, portable electrochemical workstation that integrates an open-source potentiostat based on Arduino and a smartphone application. This graphical user interface allows easy control of electrochemical parameters and real-time visualization of the results. This potentiostat can perform the most used electrochemical techniques of cyclic and linear voltammetry and chronoamperometry, with an operating range of $\pm 225 \mu\text{A}$ and $\pm 1.50 \text{ V}$, and results that are comparable with those obtained with commercial potentiostats. Three applications reported here demonstrate the capacity and the good performance of this low-cost potentiostat as a teaching tool: identification of redox pairs, electrochemical characterization of pencil graphite electrodes, and detection of heavy metals using an electrodeposited film of bismuth on the pencil graphite electrode. Furthermore, detailed schemes of the device and its software are entirely available, expecting to provide an open-source potentiostat easy to replicate to further support education in electrochemical fundamentals and instrumentation.

1. Introduction

Electrochemical instrumentation is essential for numerous real-world applications, including environmental monitoring [1], industrial process control [2], analytical chemistry [3], sensors development [4], energy-storing systems [5, 6], catalysis [7], and others [8, 9]. Although commercial potentiostats are essential for expanding research in these and other electrochemical applications, their usage is widely restricted in a low-income setting due to their high cost, ranging between \$1 000 - \$10 000, having the least expensive only basic functionalities [10].

In this context, advances have been made towards developing low-cost versions of potentiostats capable of performing fundamental electrochemical analysis [8, 10, 11]. To give an example, DStat (\$120) is a potentiostat with a software based on Python that can perform cyclic voltammeteries and chronoamperometric techniques [12]. Similarly, SweepStat (\$55) uses an Arduino Teensy and an interface designed in LabView that performs cyclic and linear voltammetry and chronoamperometry [11]. While these and other open-source potentiostats may still not overcome the capacity of commercial potentiostats, they are certainly an excellent tool for introducing general topics of

electrochemical techniques to undergraduate students. On the other hand, the low cost of these devices is a determinant factor for their use in resource-constrained communities, helping with their scientific development [10, 13].

Open-source tools have helped develop this kind of educational, scientific instrumentation [14, 15]. For instance, Arduino microcontroller boards have expanded the functionality of electronic-controlled potentiostats [13, 16], allowing an increment in the number of methodologies addressed with these while maintaining an affordable price. The spread and the increasing capacity of smartphones have provided a portable and affordable platform for several applications in the electrochemical field [16, 17]. Also, the growing efficiency of smartphone applications as educational strategies [14, 18] has allowed the use of smartphones as functional complements to potentiate the usage and portability of low-cost potentiostats [19].

Despite the benefits and the expansion of the Do-it-Yourself (DiY) culture around these educational tools, there is only a small number of projects about open-source potentiostats development with enough available information for their replication. This replicability is particularly important because a successful reproduction of these open-source

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devices by students and professors in low-resource laboratories could ensure a better learning process of electrochemical methods [20].

Motivated by this situation, we present in this article a low-cost (\$23-\$25), portable potentiostat based on Arduino. This equipment uses a free smartphone application for its control and manipulation. The application allows the selection among different electrochemical methods, the input of electrochemical parameters, and the real-time display of the obtained data. We have named this device Paqari Stat after the Runa Simi word *paqari*, which means *dawn*. Paqari Stat can perform several basic electrochemical experiments, electrochemical characterization tests, and different electroanalytical assays described in this work.

2. Development of the potentiostat

2.1. Hardware development

The functional design of Paqari Stat includes an adaptation of a widely cited work developed by Meloni [13], and extra components to support its ability to control voltage variations via Bluetooth. Paqari Stat is controlled by an Arduino Nano board that regulates the potential applied to a three-electrode electrochemical cell. The Arduino Nano is a microcontroller that has a USB-mini B port for its programming and power supply. This microcontroller has digital and analogical pins used for the input or output of information, depending on their assigned programming. The electric circuit of Paqari Stat (Figure S1) connects with the Arduino Nano microcontroller following the schemes of Figures S2 and S3.

As indicated in Figure 1b, the circuit includes a transimpedance amplifier that connects to the working electrode and collects the analogical measurements recorded from the cell. The ADC module of the Arduino Nano board transforms these measurements into digital signals. The Bluetooth module transfers these digital signals to a smartphone application, where the data is plotted in real-time. The initial determination of the working parameters of the electrochemical techniques is

also made through this application, which will be further explained in the next section. Figure 1a indicates all the electrochemical workstation elements proposed in this article. The operation range of Paqari Stat goes from -1.5 V to $+1.5$ V, with a limit current between -225 μ A and $+225$ μ A. A 10 kOhm resistor was used for the equipment calibration, as indicated in Figures S4, S5, and S6.

The negative voltage values required to perform most of the electrochemical procedures, as cyclic voltammetry, in the anodic and cathodic direction, linear sweep voltammetry, and chronoamperometry, are achieved by the use of two voltage converter (ICL7660) and two operational amplifiers (LM324). One voltage converter is coupled to one operational amplifier, which invert the voltage polarity delivered by the Arduino from $+5$ V to -5 V, allowing the production of positive and negative voltage values in this device. The remaining voltage converter and operational amplifier enable the extension of power supply options for the equipment, which can use a smartphone, a battery, or an AC connection for its powering. The inclusion of a Bluetooth module and all these features improve the functionality, autonomy, and portability of the potentiostat, which maintains a small and portable size (Figure 1c). The Supporting Information file includes a more detailed explanation of hardware development.

2.2. Software development

Introduction to the usage of electrochemical methodologies presents several difficulties, most of them inherent to the control and management of the lab equipment used during these procedures. In contrast with other DiY instruments that rely only on the direct manipulation of the equipment [10, 11, 13, 21, 22, 23, 24], Paqari Stat uses the smartphone application Paqari Lab to control and receive the data. This application works in any smartphone with an Android 7.0 or higher operational system. The MIT APP Inventor 2 platform, a free, simple cloud-based tool, was used for the smartphone application development. This application can be downloaded following the instructions in the Supporting Information file.

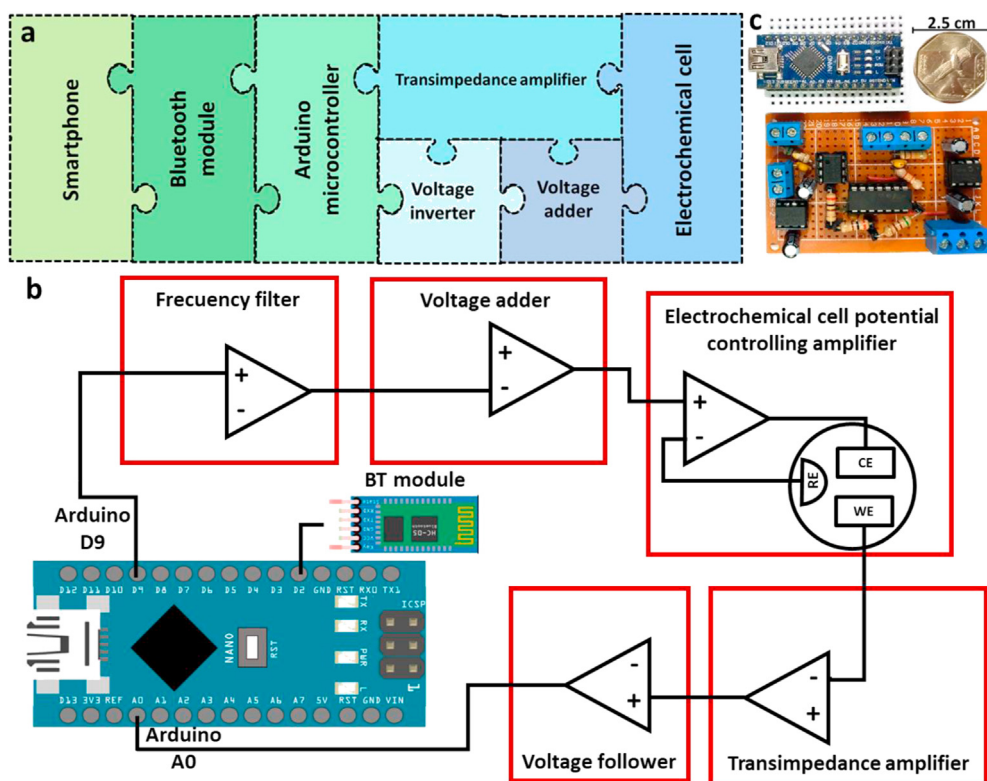


Figure 1. (a) Functional diagram of Paqari Stat, an Arduino-based potentiostat. (b) Simplified circuit diagram of the smartphone-controlled Paqari Stat. (c) Size proportion of the circuit board of Paqari Stat.

Students can interact with the equipment through the application Paqari Lab, easing the selection process of electrochemical methods (chronoamperometry and linear and cyclic voltammetry) and the input of functional parameters (scan rate, operating voltage window, potential step, cycle number, and others). This application displays the experimental data in real-time, but this can also be exported with a .csv extension to the smartphone or a desktop computer. Figure 2 shows the process of communication between the smartphone and the potentiostat via Bluetooth.

3. Experimental

3.1. Electrochemical validation

Cyclic voltammetry measurements were conducted to validate and compare the performance of Paqari Stat with the commercial potentiostat Autolab PGSTAT320N. This electrochemical technique was carried out using a conventional three-electrode cell, with a glassy carbon electrode (GCE) as the working electrode ($S = 0.07 \text{ cm}^2$), a platinum wire as the auxiliary electrode, and an $\text{Ag}/\text{AgCl}_{\text{sat}}$ electrode as reference. The electrolyte used for this test included an equimolar solution of $\text{K}_4[\text{Fe}(\text{CN})_6]$ and $\text{K}_3[\text{Fe}(\text{CN})_6]$ 5 mM in KCl 0.1 M. Five successive voltammograms were performed during this validation in the potential rate between -0.1 V and 0.6 V (vs. $\text{Ag}/\text{AgCl}_{\text{sat}}$) with increasing scan rates from 10 to 100 mV/s.

3.2. Electrochemical application

The characterization of electroactive species in a ferricyanide/ferrocyanide redox couple $[\text{Fe}(\text{CN})_6]^{3-/4-}$ electrolyte was conducted using the electrochemical system described in the previous section. For this measurement, the GCE was replaced by a carbon fiber rod electrode, and the potential rate was expanded to the range between -0.75 V and 1.2 V (vs. $\text{Ag}/\text{AgCl}_{\text{sat}}$) using a scan rate of 50 mV/s.

The performance of a set of pencil graphite electrodes (PGE) H, HB, B, 2B, and 4B ($S = 0.03 \text{ cm}^2$) was compared with a GCE using a cyclic voltammetry technique. These measurements were performed in a

ferricyanide/ferrocyanide redox couple electrolyte ($[\text{Fe}(\text{CN})_6]^{3-/4-}$), with a potential rate between -0.15 V and 0.6 V (vs. $\text{Ag}/\text{AgCl}_{\text{sat}}$) and a scan rate of 50 mV/s. Each PGE was treated previous to its use as working electrode in the cyclic voltammeteries. For this pre-treatment, each pencil's graphite tip was polished with a polishing pad until a completely flat surface was achieved. This polishing step was repeated two more times, and at each repetition, the rugosity of the polishing pad was decreased. The obtained flat surface of the graphite section was isolated by covering the rest of the pencil material with enamel (Figure S7).

After this analysis, a pencil graphite electrode was chosen and used in the subsequent electrochemical techniques. The reaction medium for all these techniques consisted of an HClO_4 0.01 M solution, adjusted to a pH 1 with a diluted solution of HNO_3 to avoid bismuth hydrolyzation [25]. $\text{Bi}(\text{NO}_3)_3$ was added to this acid solution until a Bi^{3+} 0.1 M concentration was obtained.

Detection of Pb and Cd was made using the $\text{HClO}_4/\text{Bi}(\text{NO}_3)_3$ solution previously prepared by adding to it consecutive volumes of standard solutions of Pb and Cd. After applying a chronoamperometric technique ($E_{\text{app}} = -1.2 \text{ V}$, $t_{\text{acc}} = 300 \text{ s}$), these three metals (Bi, Pb, and Cd) were deposited on the selected PGE. Pb and Cd were detected during the sequential oxidation of the PGE by using a linear sweep voltammetry technique with a potential rate of -1.2 V and 0 V (vs. $\text{Ag}/\text{AgCl}_{\text{sat}}$) and a scan rate of 10 mV/s.

All the electrochemical measurements presented in this work were obtained with Paqari Stat. As a comparison, these tests have also been replicated with the commercial potentiostat Autolab PGSTAT320N, and the results are shown in the Supplementary information file (Figures S8, S9, S10, and S11).

4. Results and discussion

4.1. Validation of Paqari Stat

Cyclic voltammetry in a $[\text{Fe}(\text{CN})_6]^{3-/4-}$ solution is essential for validating the capacity of the equipment to conduct electrochemical techniques [8, 10, 13, 16, 24]. Therefore, this technique was used to compare

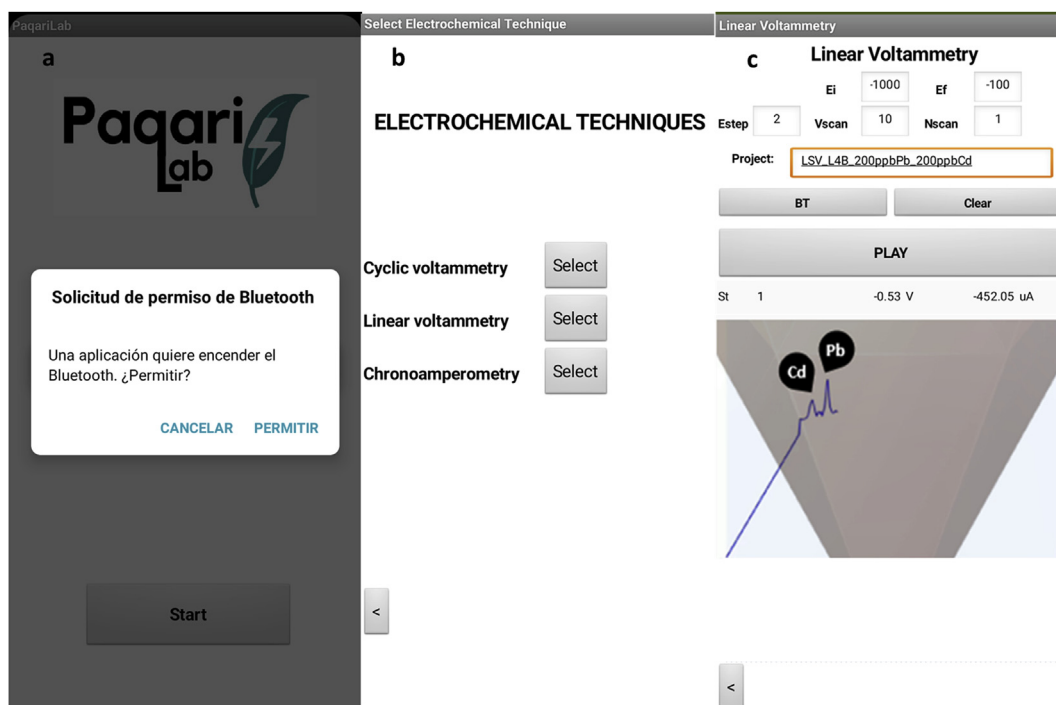


Figure 2. Screenshot of the mobile application used to control the potentiostat: (a) Bluetooth activation to recognize the equipment, (b) electrochemical technique selection, and (c) input of parameters and real-time display of the analytical measurements.

Paqari Stat and a commercial potentiostat. Figure 3 displays the last measurement of five cycles obtained with increasing scan rates from 10 to 100 mV/s with Paqari Stat and a commercial potentiostat.

Introduction courses in electrochemistry usually use this ferricyanide/ferrocyanide redox couple to illustrate the concept of reversibility in a redox reaction. In this redox couple, half-reactions rapidly exchange electrons with the working electrode [26], and the reaction that occurs is $[\text{Fe}(\text{CN})_6]^{3-} + e^- \leftrightarrow [\text{Fe}(\text{CN})_6]^{4-}$. The cyclic voltammetric response of this redox couple shows the oxidation $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ and reduction $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ peaks of the electroactive species, generating the characteristic current-potential profile of this reaction [26].

In systems like this ferricyanide/ferrocyanide couple, the Randles-Sevcik equation (Eq. (1)) gives the relationship between the peak current and the square root of the scan rate:

$$I_p = 0.446nFAC \left(\frac{nFvD_o}{RT} \right)^{1/2} \quad (1)$$

In this equation, the number of transferred electrons during the reaction (n), the concentration (C , $\text{mol}\cdot\text{cm}^{-3}$), the diffusion coefficient of the electroactive species (D_o , $\text{cm}^2\cdot\text{s}^{-1}$), and the scan rate (v , $\text{mV}\cdot\text{s}^{-1}$) determine the proportionality of the peak currents (I_p , A) and the electroactive area of the electrode (A , cm^2). The linearity between the obtained peak current and the square root of the scan rate indicates that this

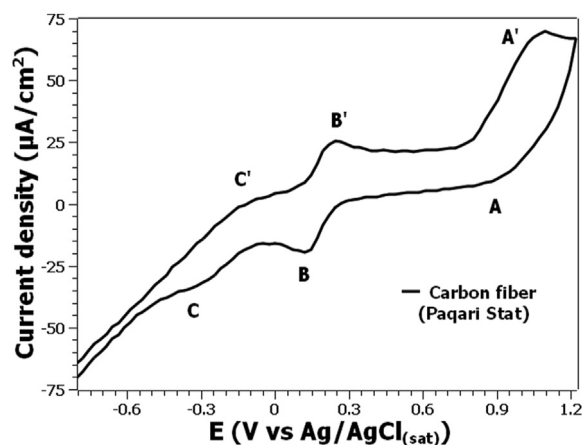


Figure 4. Cyclic voltammogram of a carbon fiber rod electrode in a ferricyanide/ferrocyanide electrolyte using Paqari Stat (scan rate of 50 mV/s).

is a diffusion-controlled process, a characteristic of the ferricyanide/ferrocyanide system [27]. As shown in Figure 3, this linear adjustment is present in the measurements made with Paqari Stat and the commercial potentiostat.

4.2. Characterization of electroactive species on a carbon fiber rod electrode

If the operating voltage window expands, several reactions evolve during the cyclic voltammetry performed in a ferricyanide/ferrocyanide couple, showing different peaks with distinct features. Figure 4 displays the obtained voltammograms of a carbon fiber rod (working electrode). This plot shows three anodic (A', B', and C') and three cathodic (A, B, and C) peaks. These correspond to the oxygen evolution process (A-A') [28], the ferricyanide/ferrocyanide redox couple (B-B') [26], and the reduction of oxygenated species (C-C') [29] on the working electrode, as reported in the literature. The reversibility of these reactions relates to their voltammogram features: peaks A-A' represent an irreversible reduction reaction, peaks B-B' show a quasi-reversible reaction, and the C-C' peaks, an irreversible oxidation reaction. For comparison, this experience was replicated with a commercial potentiostat, showing a good agreement with the position and the intensity of the peaks (Figure S8).

4.3. Heavy metals detection using a pencil graphite electrode

A commonly used electroanalytical method for heavy metals detection is polarography. This method uses a drop of mercury as a working

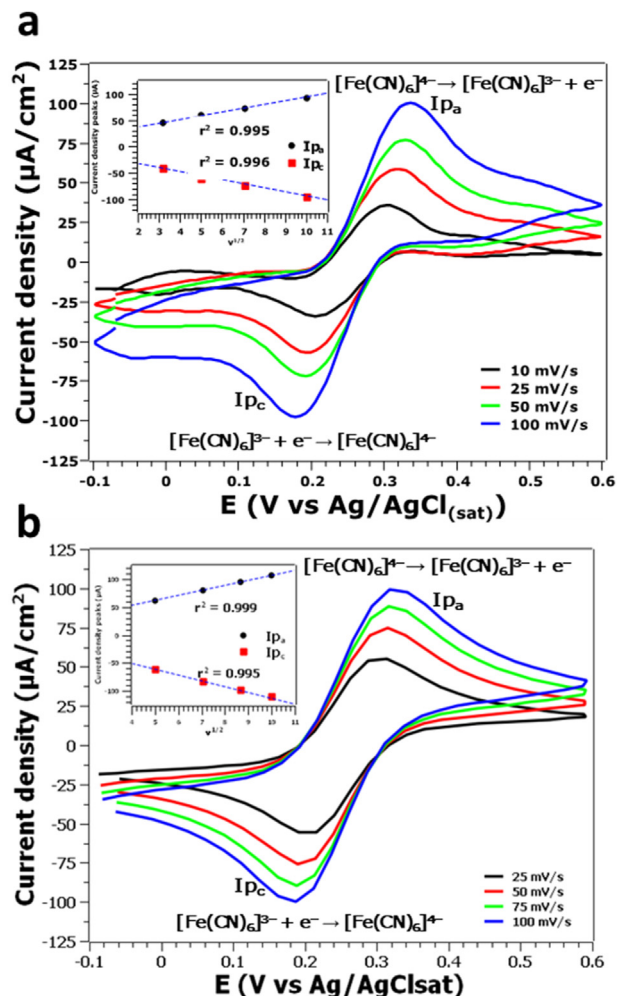


Figure 3. Cyclic voltammograms of a glassy carbon electrode (GCE) in a ferricyanide/ferrocyanide electrolyte obtained with (a) Paqari Stat and (b) a commercial potentiostat (Autolab PGSTAT320N). The internal inset of both images shows the Randles-Sevcik linear correlation between the peak current (I_p) and the square root of the scan rate ($v^{1/2}$).

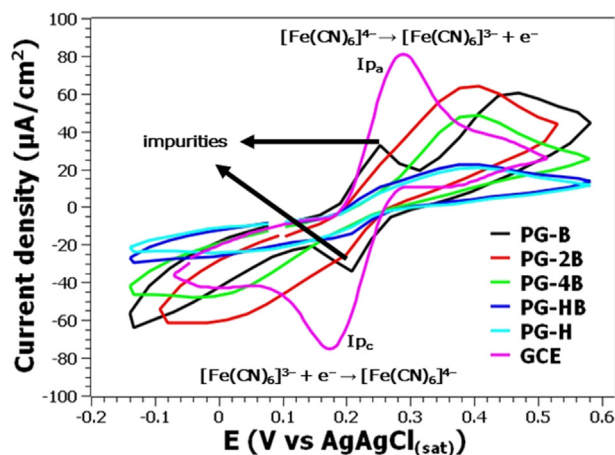


Figure 5. Cyclic voltammograms of pencil graphites (PG) H, HB, B, 2B, and 4B in a ferricyanide/ferrocyanide electrolyte using Paqari Stat.

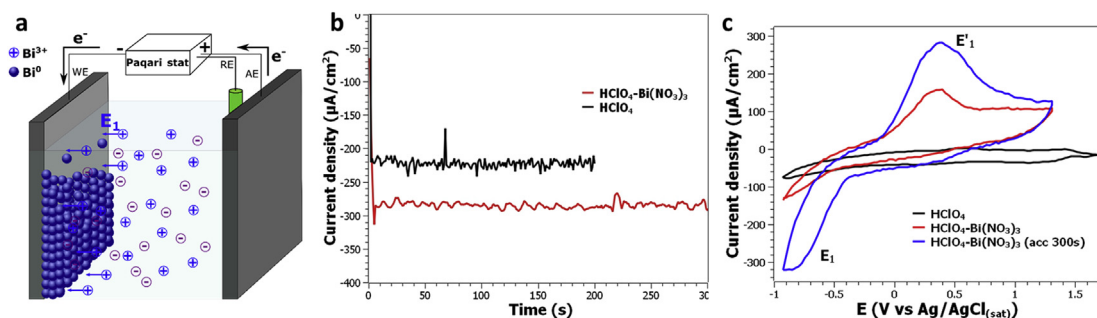


Figure 6. (a) Schematic representation of the pre-concentration of Bi^0 on the PG-4B (plateau). (b) Chronoamperometric measurement of the bismuth film deposition on the PG-4B electrode using Paqari Stat. (c) Cyclic voltammogram at 50 mV/s of the PG-4B in a solution without Bi^{3+} (black), with Bi^{3+} (red), and with Bi^{3+} and pre-accumulation by chronoamperometry (blue) using Paqari Stat.

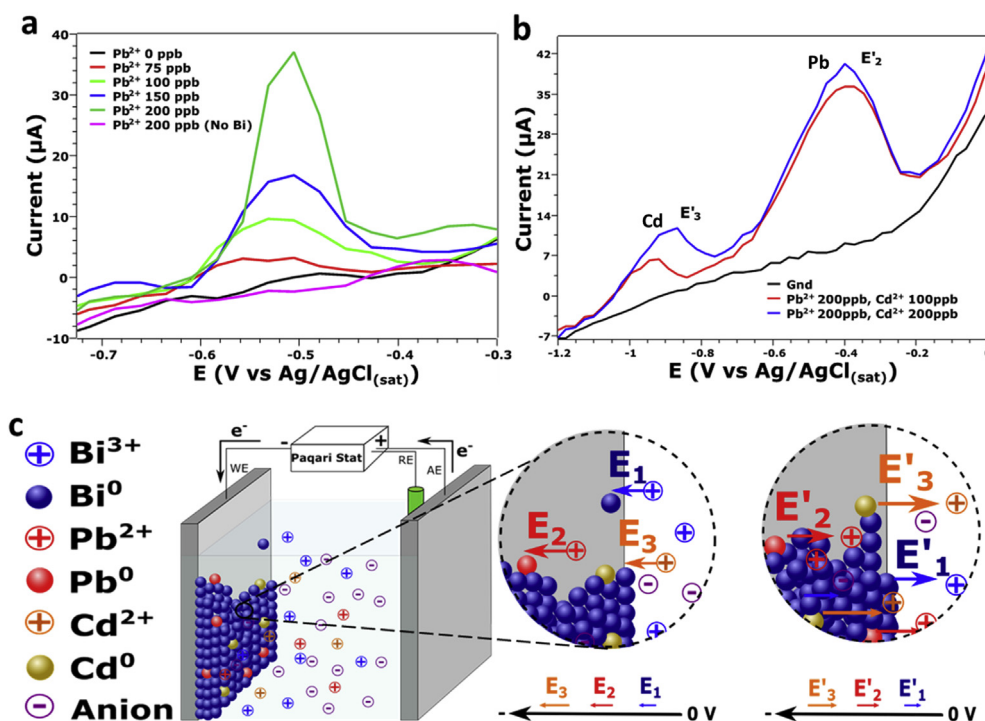


Figure 7. Detection of (a) a varying Pb concentration and (b) Pb and Cd by linear sweep voltammetry on a PG-4B electrode using Paqari Stat. (c) Schematic representation of the pre-concentration of Bi, Pb, and Cd by chronoamperometry and their voltammetric stripping.

electrode due to its capability to amalgamate with heavy metals [30, 31]. Although effective, this method is discontinued because of mercury toxicity. Other alternative approaches are currently used with similar mechanisms and minimal impact on the environment and the users, such as bismuth films deposited on carbon electrodes [32]. Here we present an experimental process for detecting heavy metals (Pb and Cd) using cyclic voltammetry, chronoamperometry, and linear sweep voltammetry methods performed by Paqari Stat.

4.3.1. Electrochemical performance study of pencil graphite as a working electrode

Pencil graphite presents features that make it suitable for its usage as electrodes in electrochemical applications. In these applications, these are commonly called pencil graphite electrodes (PGE). PGE are characterized by their excellent adsorption capacity, wide operating voltage window, low capacitive current, and low cost combined with high accessibility [33]. However, their electrochemical response might vary

depending on their type. Therefore, here we analyze the performance of five pencil graphites (PG) H, HB, B, 2B, and 4B as working electrodes using a simple, low-cost cyclic voltammetry technique. This electrochemical technique allows obtaining information about the charge transfer rate between the electrode and the electrolyte during the oxidative and reduction reactions [26]. Therefore, cyclic voltammograms will be used to determine the performance of the PGE by comparing their responses with the measurements obtained with a GCE.

Figure 5 presents the current-potential response of the five classes of PGE analyzed by Paqari Stat. According to the results, PG-H and PG-HB show a low current compared with other electrodes. On the other hand, PG-B, PG-2B, and PG-4B present good conductivity, like the GCE, but with significant separation between the anodic and cathodic peaks. The electrochemical responses of PG-B and PG-2B depict additional peaks at 0.15 V and 0.25 V, indicating the presence of impurities in them. According to these results, PG-4B showed the best electrochemical response, presenting good conductivity and no impurities. This result is

in concordance with the study of Vishnu et al. [34]. Therefore, PG-4B was selected as the working electrode for the subsequent experience.

4.3.2. Heavy metals detection using pencil graphite 4B

Pb and Cd can be detected with voltammetric methods through the in-situ formation of a bismuth film, as stated by Wang et al. [35]. Initially, a chronoamperometric technique is applied to the PG-4B electrode in a starting solution of HClO_4 , Bi^{3+} , and the metals of interest (Pb^{2+} and Cd^{2+}). If the applied potential during the chronoamperometry is greater than the reduction potential of the metallic ions (Bi^{3+} , Pb^{2+} , and Cd^{2+}), the in-situ deposition of these metals on the working electrode PG-4B forms an amalgam [36]. This amalgam results from the initial deposition of a bismuth film on the PG-4B. Pb and Cd are then consecutively deposited on this electrode. This pre-concentration in the amalgam allows Cd and Pb detection enhancement during their stripping by a linear sweep voltammetry technique. As these metals are in their reduced form when deposited on the PG-4B, a linear sweep voltammetry technique in the anodic direction oxidate them. The signal obtained from the oxidation during this technique allows detecting Cd and Pb on the PG-4B electrode. This multi-elemental detection of metals by voltammetric methods is only possible when there is a clear separation between the oxidation potentials of the analytes [37].

As stated previously, a bismuth film must be formed on the PG-4B electrode to effectively detect heavy metals in the solution. To demonstrate the formation of this bismuth film, the electrochemical responses obtained by chronoamperometry and cyclic voltammetry of the PG-4B electrode were analyzed. Figure 6b depicts the current registered during the chronoamperometry applied to the working electrode in an HClO_4 solution with (red) and without (black) the presence of Bi^{3+} . As observed, the solution with Bi^{3+} generates a more significant electric response. The current generated by reducing Bi^{3+} to Bi^0 on the electrode increases its electric response, creating an increment of current that is not observed in the solution containing only HClO_4 .

Further verification of the bismuth film formation is made by cyclic voltammetric measurements (Figure 6c). For this, three conditions were evaluated: a bare PG-4B electrode in an HClO_4 solution (black), a bare PG-4B electrode in an $\text{HClO}_4/\text{Bi}(\text{NO}_3)_3$ solution (red), and a PG-4B electrode with a previous chronoamperometry in an $\text{HClO}_4/\text{Bi}(\text{NO}_3)_3$ solution (blue). As shown, a bare PG-4B electrode presents no response during the voltammetry in the HClO_4 solution due to the absence of electroactive species on its surface. If the cyclic voltammetry is performed in an $\text{HClO}_4/\text{Bi}(\text{NO}_3)_3$ solution, Bi is observed for the appearance of low-intensity oxidation and reduction peaks. However, if the Bi^0 is previously deposited on the PG-4B electrode by chronoamperometry, the signal shows clear and intense oxidation and reduction peaks with a lower separation between them. The differences between the results are explained by the pre-accumulation of Bi^0 on the working electrode by applying a voltage over the reduction potential of bismuth (E_1) during chronoamperometry (Figure 6a).

The sensitivity of the methodology for detecting heavy metals was tested by performing linear sweep voltammetry after the chronoamperometry in a solution with a varying concentration of Pb^{2+} (Figure 7a). In the presence of Bi^{3+} in the solution, the oxidation signal increases with the increment of the Pb^{2+} concentration. In comparison, the solution with a Pb^{2+} 200 ppb concentration did not display an oxidation signal during the stripping because of the lack of Bi^{3+} in the solution. This response is related to the low oxygen interference and small background current of the bismuth film [38]. Therefore, this technique allows detecting Pb^{2+} concentration variations in the solution, changing the signal response during the linear sweep voltammetry if a bismuth film is initially formed on the PG-4B electrode.

In a starting solution that contains Bi^{3+} , Pb^{2+} , and Cd^{2+} (Figure 7b), the applied voltage during the chronoamperometry (-1.2 V) is higher than the reduction potential of Bi, Pb, and Cd (E_1 , E_2 , and E_3 , respectively). Consequently, an amalgam of these reduced metals ($\text{Bi}^{3+} \rightarrow \text{Bi}^0$, $\text{Pb}^{2+} \rightarrow \text{Pb}^0$, and $\text{Cd}^{2+} \rightarrow \text{Cd}^0$) is formed on the PG-4B electrode. The

scheme presented in Figure 7c shows that these metals are detected during their oxidation when the potential is scanned in the anodic direction ($\text{Bi}^0 \rightarrow \text{Bi}^{3+}$, $\text{Pb}^0 \rightarrow \text{Pb}^{2+}$, and $\text{Cd}^0 \rightarrow \text{Cd}^{2+}$). Due to their oxidation potential values (E'_1 , E'_2 , and E'_3 , respectively), Cd is the first one to be oxidized and detected, followed by Pb and Bi at the end.

5. Conclusion

This work presents a low-cost, DiY version of a potentiostat capable of performing basic electrochemical techniques, such as cyclic and linear voltammetry and chronoamperometry. A free-access smartphone application is used for the control via Bluetooth of this potentiostat called Paqari Stat. This application allows the selection of electrochemical techniques, the input of electrochemical parameters, and the real-time visualization of the experimental data obtained via Bluetooth. The performance of Paqari Stat has been compared with a commercial potentiostat (Autolab PGSTAT320N) using a cyclic voltammetry technique with a ferricyanide/ferrocyanide redox couple and a glassy carbon electrode, a widely used practice in electrochemical courses. The results obtained by both potentiostats are in good agreement and show that the performance of Paqari Stat is adequate for performing electrochemical measurements. This work reports the use of Paqari Stat in a teaching experience that uses a pencil graphite electrode to detect heavy metals. The experience begins with the electrochemical characterization of commercial pencil graphite electrodes (H, HB, B, 2B, and 4B), which showed that the 4B pencil has the best electrochemical performance. A chronoamperometric technique is then used for the in-situ formation of a bismuth film and the consequent reduction of the heavy metals present in the aqueous solution. This bismuth film increases the detection sensitivity of the heavy metals when these are oxidized by applying a linear sweep voltammetry technique. The experiments evidence this open-source, low-cost potentiostat capacity that can be used as a valuable tool for introductory classes in electrochemistry.

Declarations

Author contribution statement

Allison V. Cordova-Huaman & Victor R. Jauja-Ccana: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Adolfo La Rosa-Toro: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data.

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Data availability statement

Data included in article/supp. material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

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