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Design and implementation of low-cost portable potentiostat based on WeChat

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Abstract: The potentiostat is critical in the development of electrochemical systems; however, its cumbersome detection and high cost considerably limit its large-scale application. To provide an affordable alternative to developing countries and resource-constrained areas, this study designs an electrochemical detection system based on smartphones, which uses Bluetooth Low Energy to convert open-source potentiostat data based on PSoC-5LP. The WeChat application on the smartphone provides an interface for entering experimental parameters and visualizing the results in real time. The smartphone-based electrochemical detection system has a simple design and reduces the size (10×3×0.3 cm^3) and the cost of the hardware ($ 18). The system performs the most commonly used cyclic voltammetry for electrochemical detection, with results that are comparable to those obtained using a commercial potentiostat and an error rate of 1.3 %. In the classical teaching experiment of electrochemical determination of ascorbic acid in orange juice samples, the measured value of the system is 0.367±0.012 mg/mL, compared with the standard reference value of 0.37 mg/mL, which is obviously a convincing value. Therefore, this system is a low-cost, reliable alternative to a potentiostat for research, education or product integration development.

Keywords: cyclic voltammetry; point-of-care testing; smartphone; Bluetooth.

INTRODUCTION

Electrochemistry studies chemical reactions at the interfaces of electronic and ion conductors and charge transfer between molecules and electrodes.[1] It may be used in wearable devices and for analysis in applications such as clinical diagnosis, environmental, industrial, and food monitoring, and quality control.[2–6] Data are obtained by monitoring electron transfer at the conductor interface and

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the redox peak intensities of substances involved in the reaction. A critical monitoring device in bioelectrochemical research is the potentiostat, which measures the current passing between the two electrodes by controlling the voltage between the working and counter electrodes (WE and CE, respectively).[7] Although progress in electronic technology reduced the volume of the traditional commercial potentiostat,[8,9] the use of commercial potentiostats remains cumbersome and costly, resulting in clear limitations in cost, portability, and analysis time. Furthermore, their components and circuits are confidential. Hence, for researchers who conduct rapid electrochemical analysis in the field and require the use of a potentiostat for research, education, or product integration development, there are clear, considerable challenges in using a commercial potentiostat.

Point of care testing (POCT) technology is critical in promoting electrochemical detection. This is a rapid detection technology that is used in the field, instead of being limited to the laboratory setting.[10] Compared with the traditional central laboratory,[11] POCT exhibits the advantages of small equipment, simple operation, lower sample consumption, lack of required pre-processing, and instant reporting of results, particularly with the short duration of sample analysis.[12]

Currently, >67 % of the global population own mobile phones, and >50 % of the population own smartphones with advanced computing and connectivity capabilities.[13,14] The rapid development of smartphones resulted in them becoming the most widely used mobile devices. Smartphones exhibit the advantages of programmable systems, high-speed computing, and sizable data storage, and may be used as integrated platforms to receive, analyze and display data. They are critical portable devices and the most sought-after analytical equipment in the field of biosensing.[15,16] Currently, smartphones are mainly involved in the design of optical biosensor systems.[17,18] In recent years, with the progression of electrochemical research, the wireless combination of smartphones and portable potentiostats *via* Bluetooth favors on-site electrochemical analysis in areas with limited resources,[19] which effectively achieves POCT. Additionally, this may overcome the limitations of commercial electrochemical workstations to a considerable extent. The emergence of this design promotes the application of smartphones in the field of bioelectrochemical sensing.[20–23]

WeChat Mini Program is an application service that may be run in WeChat. It was developed by Tencent and launched on January 9, 2017. Its emergence overcomes the multi-platform and compatibility issues that exist in the development of native applications for smart mobile terminals. Native application development tools (such as Android studio) employ Java language as the basic development language, with the concomitant disadvantages of Java language development, such as high memory usage and running on virtual machines.[24] Conversely, WeChat applet development employs JavaScript language as the basic development language, which relies on browser engines for compilation, analysis, and rendering, and enables the creation of better interactive pages, which users appreciate.

This study involves the design of a portable, low-cost, smartphone-based electrochemical cyclic voltammetry (CV) system. This system consists of the following main components: smartphone, handheld detector and three-electrode system. The smartphone is used to receive and process data *via* the WeChat applet and display the results. The handheld detector is based on an embedded development board; it is used to perform CV based on the applied excitation voltage, detect feedback within the three-electrode system, and transmit the obtained data to the smartphone. The three-electrode system participates in the chemical redox reaction in the electrolyte solution and measures electron transfer during the reaction. The performance of this system is verified by comparing the results with those of commercial electrochemical systems. Moreover, the practicability of the system in educational application is verified.

EXPERIMENTAL

Design of smartphone-based electrochemical detection system

The overall system operation is shown in Fig. 1. The chemical reaction in the electrochemical cell generates an analog electrical signal, which is recorded using the handheld detector and converted into digital signals. These signals are transmitted to the smartphone *via* Bluetooth. The WeChat applet then visualizes the data on the screen of the smartphone.

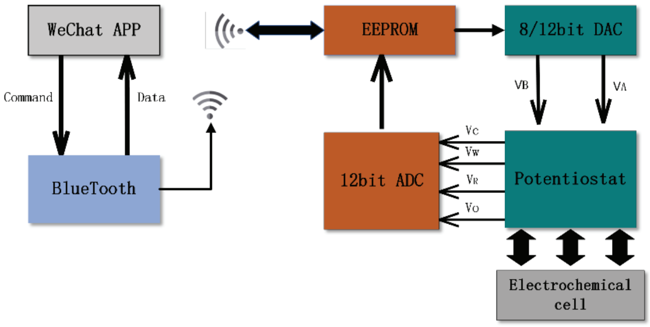


Fig. 1. Electrochemical detection system based on a smartphone.

Design of the hand-held cv detector

The design of the detection module is the key to the portability of the entire system. Therefore, the design employed a small PSoC-5LP development board (part number CY8CKIT-059, purchased from Future Electronics, Shanghai, China), and the microcontroller unit CY8C5888LTI-LP097. The low-cost chip exhibited satisfactory experimental accuracy. Additionally, the programmable system on a chip (PSoC) Creator programmable environment (Cypress Semiconductor, San Jose, California) configured by PSoC 5LP integrated various functional circuit modules, including operational, transimpedance, and programmable gain amplifiers, comparators, mixers, segment liquid crystal displays, CapSense touch sensors, digital-to-analog converters (DACs), and analog multiplexers (AMuxs),[25] which satisfied the requirements of detection module design.

To control the voltage between the electrodes, a voltage control circuit was designed, as shown in Fig. 2a. The circuit may employ 8-bit voltage DAC (VDAC) or 12-bit voltage DAC (DVDAC). DVDAC can control the voltage that may rapidly switch between two values. This renders the DVDAC output voltage a weighted average of the input values, that may be used for improving the accuracy of the DA conversion. However, this type of switching produces noise and causes interference to signal. Thus, a small capacitor C(100nF) should be placed at the output to improve the voltage resolution, and the circuit may also be used to select the DAC to employ an AMux sensing electrode. The operational amplifier may buffer the voltage and provide a feedback electrical signal from the reference electrode (RE).[26,27]

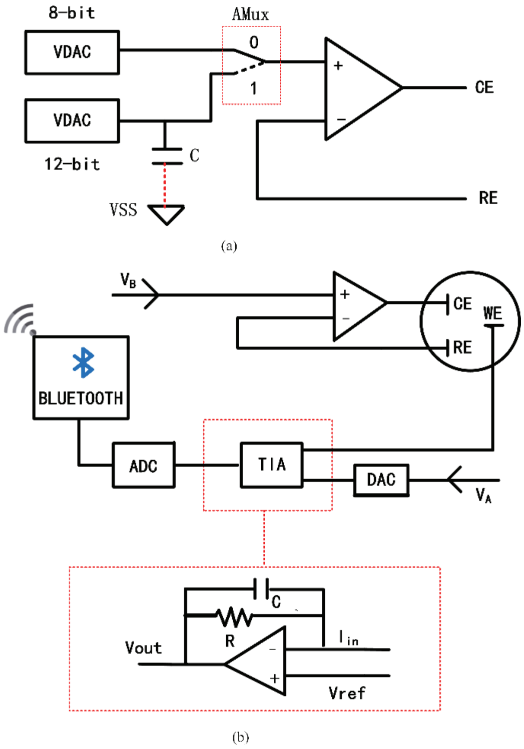


Fig. 2. a) Voltage control circuit. b) Potentiostat circuit diagram.

The core circuit design of the module is shown in Fig. 2b. The circuit mainly consists of a voltage control circuit, transimpedance amplifier (TIA), Digital to analog converter (DAC), and an analog-to-digital converter (ADC). When the module is used in CV detection, the output amplifier of the voltage control circuit adjusts the potential of the CE and feeds back the potential to the RE to ensure that the potential of the RE is consistent with the output of the reference potential of the DAC. The transimpedance amplifier (TIA) mainly measures the electrical signal feedback at the WE, converts the ADC signal to a digital electrical signal, and uploads it to the smartphone terminal *via* Bluetooth communication.

Bluetooth communication module and three-electrode system

The Bluetooth communication module transferred the data between the potentiostat and WeChat applet. This system employed the HC-08 module owing to the following: 1) the small, low-cost microprocessor exhibited low power consumption. 2) Compatibility with Apple and Android, which are two mainstream smartphone operating systems, yielding numerous possibilities in system software design. 3) It could provide a wide bandwidth for data transmission and transmit all original data to the smartphone within the working distance of the communication module.

The electrochemical cell module generally consists of two- or three-electrode systems. However, in a two-electrode system, the polarization current passing through the electrodes causes voltage changes, interfering with the constant voltage between the electrodes, which causes large experimental errors. Compared with the two-electrode system, the three-electrode system possesses an RE, which provides a stable reference potential during measurement, eliminates the large error of electrode potential caused by polarization current to stabilize the working electrode, and ensures the accuracy of the measurement.[28] The electrochemical cell module of this system was designed as a three-electrode system. The details of the electrode materials are as follows: the WE was a glassy carbon electrode (Shanghai Chuxi Industrial Co., Ltd; diameter: 10 mm; length: 80 mm), the CE was a platinum electrode (Shanghai Chuxi Industrial Co., Ltd; diameter: 1 mm; length: 60 mm), and the RE was a saturated calomel electrode (Shanghai Chuxi Industrial Co., Ltd; diameter: 9 mm; length: 120 mm).

Design of the WeChat applet

This study developed a WeChat applet (Fig. 3b–d) by using WeChat developer tools (Tencent, China, Version 1.03). It connects a smartphone to a handheld CV detector *via* Bluetooth to control CV, process real-time data, and plot cyclic voltammograms. The basic process of the software application (Fig. 3a) is as follows: first, open the application software, initiate Bluetooth, enter the detection interface and pair with the Bluetooth module of the lower computer. Second, log in using a WeChat account, and select CV detection mode. Enter the parameter-setting interface, and after accurately entering the specific initial parameters, click "OK" to enter the detection interface. Subsequently, the lower computer detects according to the set detection method and corresponding parameters, and the measured data is transferred via Bluetooth. Subsequently, the WeChat applet on the mobile phone plots and presents the voltage–current curve.

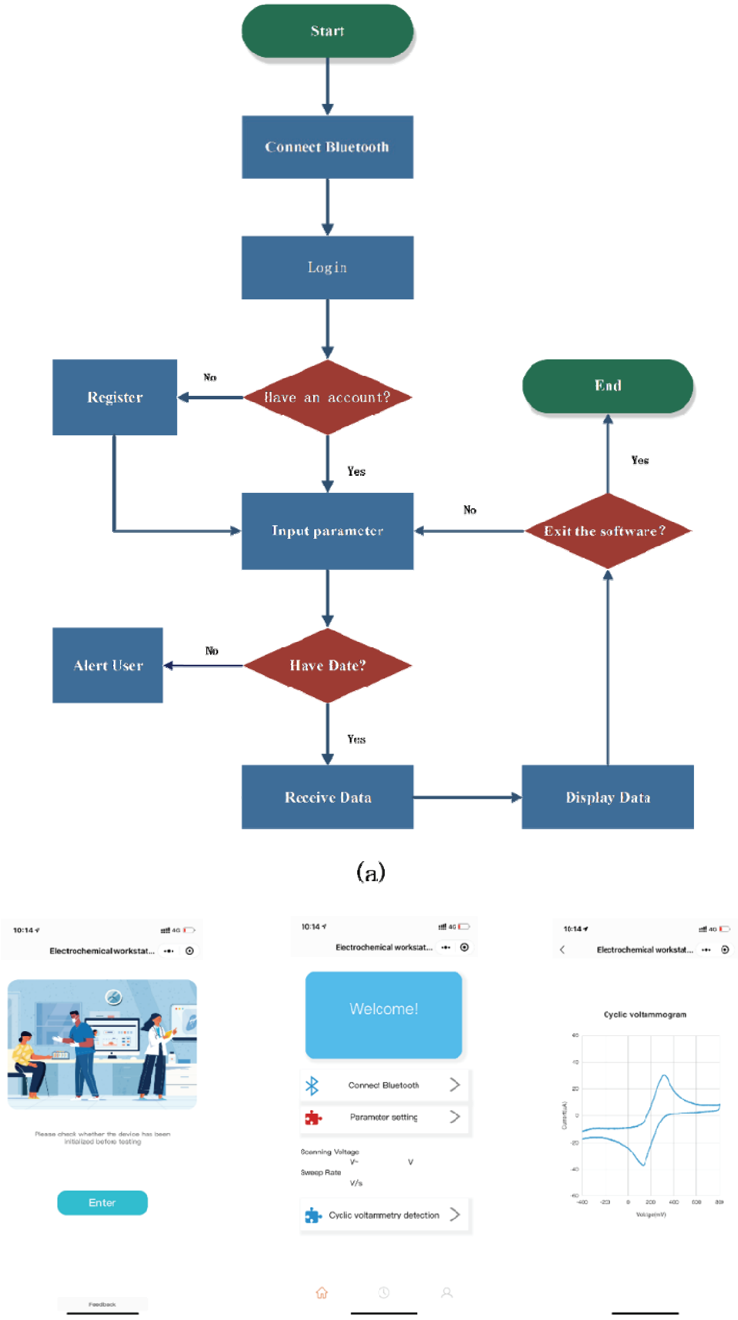
System performance evaluation

To evaluate the performance of the system, a commercial potentiostat and the system were used to perform CV studies on a 5 mM potassium ferricyanide solution and the results were compared to obtain the peak oxidation current error rate of the system. The experimental sweep voltage range was 800 to –400 mV, sweep rate was 50 mV/s. The error rate equation is:

$$\text{Distinction} = \frac{I_\text{d} - I_\text{c}}{I_\text{c}} \quad (1)$$

where I_d is the oxidation peak current measured using the system and I_c is the oxidation peak current measured using the commercial potentiostat.

The ferrocyanide cyclic voltammograms were recorded at 0.31, 0.62, 1.25, 2.5 and 5 mM (sweep rate of 50 mV/s, sweep voltage of –400–800 mV) and different scanning rates at 5 mM (sweep rate of 10–100 mV/s and sweep voltage of –1000–800 mV) using the system.



(a)

(b) (c) (d)

Fig. 3. a) WeChat applet operation. b–d) WeChat applet interface.

RESULTS AND DISCUSSION

In the ferricyanide/ferrocyanide redox pair, the half reaction (2):

$$[\mathrm{Fe(CN)}_6]^{3-} + \mathrm{e}^- \leftrightarrow [\mathrm{Fe(CN)}_6]^{4-} \tag{2}$$

rapidly exchanges electrons with the WE.[29] The CV response of the redox pair shows the oxidation $Fe^{2+} \rightarrow Fe^{3+}$ and reduction $Fe^{3+} \rightarrow Fe^{2+}$ peaks of the electroactive substances, resulting in the characteristic current-potential curve of the reaction.[29] Fig. 4a shows that the detection results of the smartphone-based electrochemical CV detection system and those of the commercial potentiostat exhibit similar characteristic reversible redox peaks, but there are some differences in the traces. These differences, several of which may be owing to electrochemical changes over time within the electrodes,[30] may also be caused by a slight voltage offset of the on-board amplifier of the embedded development board. Fig. 4b shows the measured oxidation peak currents – the difference is 0.47 µA with an error rate of 1.3 %.

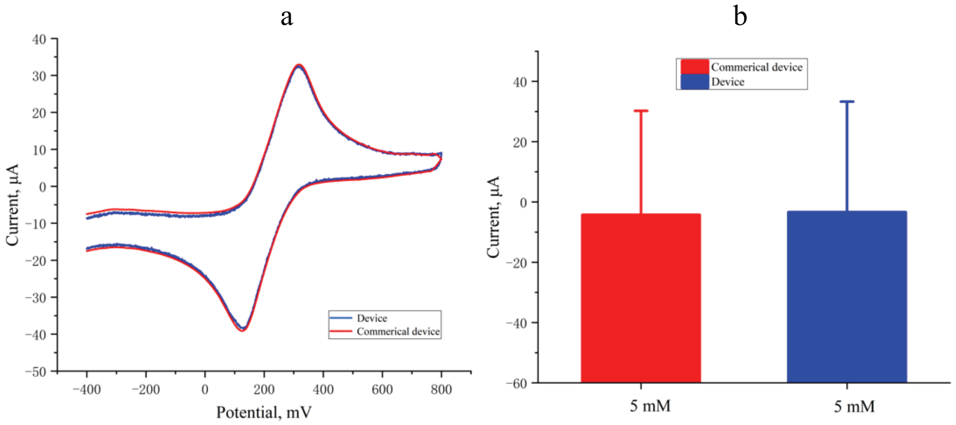


Fig. 4. a) Cyclic voltammograms obtained using the Proposed system and commercial potentiostat. b) Oxidation peak currents measured using the Proposed system and commercial potentiostat.

Table I summarizes the parameters of the proposed system and commercial potentiostat. The proposed system has lower cost, weight, and dimensions than the commercial potentiostat. However, its voltage range is narrower than that of the commercial device.

TABLE I. Comparison of parameters between self-made system and commercial Potentiostat

Potentiostat	Voltage range	ADC resolution	Cost, $	Weight, g	Dimensions, cm^3
PSoC-device	±2 V	12-bits[c]	18.03	65	10×3×0.3
Commerical-device	±10 V	24-bits	80–120	2000	37×23×12

As shown in Fig. 5a, the redox peak current increases with increasing sweep rate. A good relationship between the redox peak current and the square root of the sweep rate is observed (Fig. 5b). The correlation coefficients of the oxidation and reduction currents and the square root of the sweep rate are 0.9987 and 0.9966, respectively. According to the relationship between the peak current and square root of the scan rate based on the Randles-Sevcik equation,[31] the electron transfer reaction at the electrode surface is governed by diffusion.

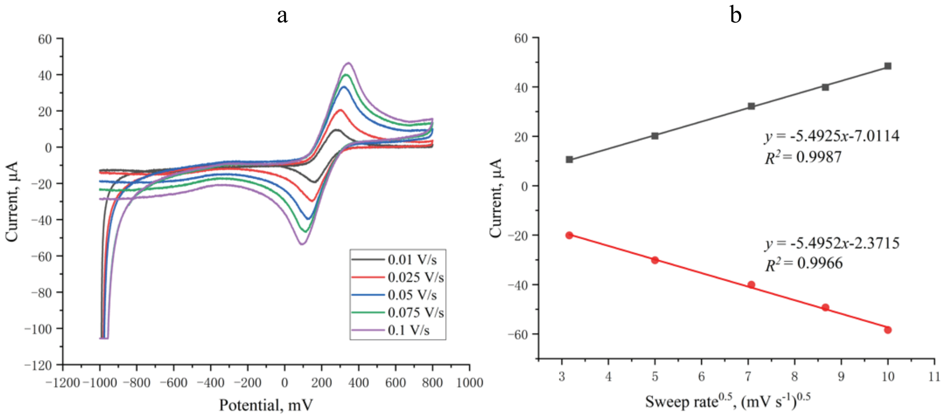


Fig. 5. a) Cyclic voltammograms of potassium ferricyanide solution at sweep rates of 10–100 mV/s. b) Linear relationships between the square root of the sweep speed and the peak redox currents. Black line, oxidation current; red line, reduction current.

Fig. 6a shows the peak currents of the system using 0.31–5 mM potassium ferricyanide solution. The data follow Fick's first law, as the electron diffusion rate is proportional to the reactant concentration, the current increases with the reactant concentration, and the oxidation and reduction peak currents exhibit linear relationships with the reactant concentration. The correlation coefficients are 0.99056 and 0.99502 (Fig. 6b), respectively. The system exhibits good stability.

To verify the applicability of the proposed system, in school general chemistry lab course, we used it to determine the concentration of ascorbic acid in orange juice. In the experiment, four 20 ml orange juice samples ((Nongfu Spring, China) were prepared. One sample was unmodified, whereas in the other three, 10 ml of ascorbic acid standard solutions with different concentrations (0.1, 0.2 and 0.3 mg/mL) were added. In order to increase the conductivity of the solution, an appropriate amount of KCl was added to the orange juice to make up the concentration to 1 M. Then, the system was used to detect the cyclic voltammograms of the four samples (Fig. 7 a) over the sweep voltage range of 200–900 mV and at the sweep rate of 100 mV/s. In order to quantify ascorbic acid in orange juice, the current corresponding to 550 mV was selected as the standard, because the samples contain ascorbic acid, a redox active substance in orange juice, and the oxidation of other substances in orange juice occurs, causing the current rise to >550 mV.[32]

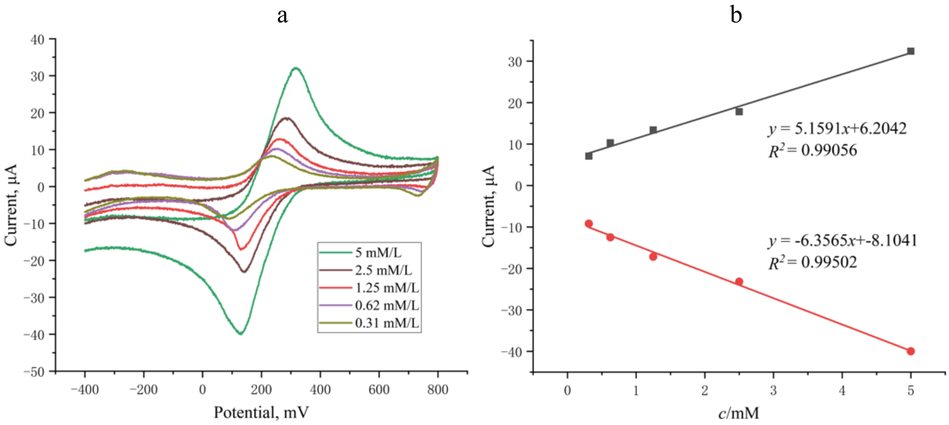


Fig. 6. a) Cyclic voltammograms of potassium ferricyanide solution at concentrations of 0.31–5 mM. b) Linear relationships between the potassium ferricyanide concentration and the redox peak currents. Black line, oxidation current; red line, reduction current.

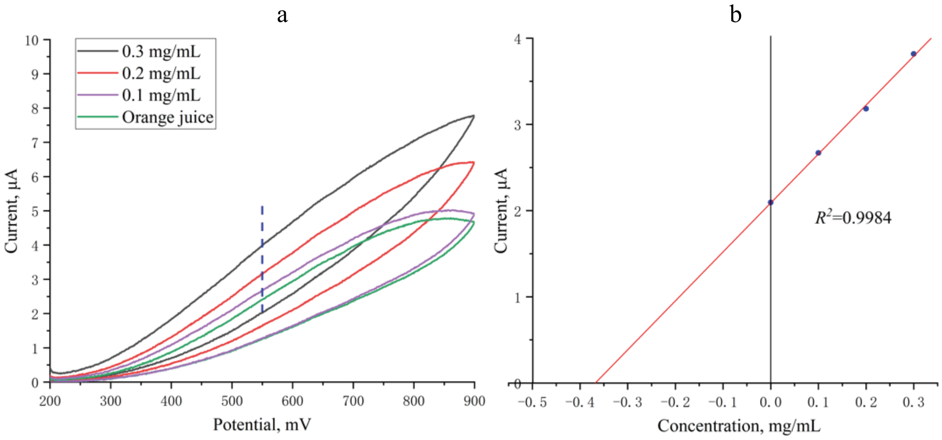


Fig 7. a) The original current traces of cyclic voltammetry experiments in four kinds of orange juice. b) The linearity of the oxidation current observed at 550 mV was compared with the linearity of the ascorbic acid standard solution.

The linear diagram of the current corresponding to 550 mV and that of the added ascorbic acid standard solution (Fig. 7b) is extrapolated to the zero current on the *x*-axis. The ascorbic acid concentration in the non-modified orange juice sample is measured to be 0.367±0.012 mg/mL. The result obtained through the proposed system is comparable to the ascorbic acid value of 0.37 mg/mL prescribed by the orange juice nutrition panel.

CONCLUSIONS

This study designed a chemical CV detection system based on a smartphone, which combines a handheld CV detection module with wireless Bluetooth Low Energy and a smartphone. To compare the performances of the system and that of the traditional commercial constant potential studies were conducted, using potassium ferricyanide electrolyte solution, with satisfactory results. Additionally, compared with the traditional commercial potentiostat, this system exhibited the following advantages: 1) the system hardware test equipment has small volume and low cost (US $18.03), and it can be used as an educational tool with special value. In the experiment of determining the content of ascorbic acid in orange juice, the value obtained by using this system is almost consistent with the standard value. From the perspective of education, the operation of the system is very simple, which is conducive to students' learning and use. 2) In addition to educational purposes, the system will provide a cheap POCT platform for electrochemical analysis in some developing countries. 3) The software design of the system was based on the WeChat interface, which enabled broad software compatibility with different systems. However, the system only realizes cyclic voltammetry detection, and other electrochemical detection methods, such as square wave voltammetry and differential pulse voltammetry, that need to be further developed. In addition, the system can develop in the direction of the Internet of Things in the future, thus it will be a good choice to use cloud services to process and store data.

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ИЗВОД

ДИЗАЈН И ПРИМЕНА ЈЕФТИНОГ ПРЕНОСИВОГ ПОТЕНЦИОСТАТА ЗАСНОВАНОГ НА АПЛИКАЦИЈИ WeChat

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Потенциостат је кључни инструмент у развоју неког електрохемијског система, међутим његове димензије и висока цена значајно ограничавају његову примену. Да би се обезбедила алтернатива која је ценовно прихватљива за земље у развоју и областима са ограниченим ресурсима, у овој студији је дизајниран систем за електрохемисјко мерење заснован на паметним телефонима који користе Bluetooth мале потрошње за конверзију података из потенциостата отвореног софтвера базираног на PSoC-5LP. Апликација WeChat за паметне телефоне обезбеђује интерфејс за унос експерименталних параметара и за визуелизацију резултата у реалном времену. Електрохемијски систем за мерење базиран на паметном телефону је једноставног дизајна, малих димензија (10×3×0,3 cm^3) и ниске цене хардвера (18 $). Систем омогућава извођење цикличне волтаметрије као најчешће коришћене методе за електрохемијску детекцију и даје резултате који су поредиви са комерцијалним потенциостатима са нивоом грешке од 1,3%. У класичном школском експерименту електрохемијске детекције аскорбинске киселине у соку од поморанџе измерена је вредност 0.367±0.012 mg/mL која је веома блиска стандардној референтној вредности од 0.37 mg/mL. Из тога следи да је овај систем јефтина и поуздана алтернатива потенциостату за истраживачки рад, образовање и интегрисани развој производа.

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