Electrochimica Acta 219 (2016) 170–177

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Point-of-use electroanalytical platform based on homemade potentiostat and smartphone for multivariate data processing

Gabriela F. Giordano[a,b], Marcia B.R. Vicentini[a], Rui C. Murer[a], Fabio Augusto[b], Marco F. Ferrão[c], Gilson A. Helfer[d], Adilson B. da Costa[d], Angelo L. Gobbi[a], Leandro W. Hantao[a,b], Renato S. Lima[a,b,*]

[a] Laboratório de Microfabricação, Laboratório Nacional de Nanotecnologia, Centro Nacional de Pesquisa em Energia e Materiais, Campinas, São Paulo 13083-100, Brazil
[b] Instituto de Química, Universidade Estadual de Campinas, Campinas, São Paulo 13083-970, Brazil
[c] Instituto de Química, Universidade Federal do Rio Grande do Sul, Porto Alegre, Rio Grande do Sul 91501-970, Brazil
[d] Programa de Pós-graduação em Sistemas e Processos Industriais, Universidade de Santa Cruz do Sul, Santa Cruz do Sul, Rio Grande do Sul 96815-900, Brazil

ARTICLE INFO

Article history:
Received 5 August 2016
Received in revised form 18 September 2016
Accepted 24 September 2016
Available online 1 October 2016

Keywords:
Android app
Bluetooth
Chemometrics
Honey certification
Principal Component Analysis

ABSTRACT

We herein report a potential point-of-use platform for multivariate analyses by presenting homemade potentiostat and smartphone. This system combined high-performance detection (linear sweep, cyclic, and square wave voltammetry) with great simplicity, low-cost, portability, autonomy (6 h), and cable-free (wireless communication) device. In addition, the smartphone showed ability for processing complex and multivariate data. To the best of our knowledge, this paper is the first reporting about the development of a totally integrated point-of-use system with chemometric data processing on smartphone. This feature is essential for in-situ assays by allowing the real-time accomplishment of the entire analytical measurement at remote places. Such ability further reduces the occurrence of model overfitting by non-expert users. As proof-of-concept, our system was successfully applied to fingerprint Brazilian honey samples according to their botanical and geographic origins. The method relied on the unsupervised technique of principal component analysis (PCA) and the assays were performed by cyclic voltammetry using a single and non-modified working electrode of gold.

1. Introduction

Point-of-use platforms have been widely explored over the past decade in many science fields [1,2]. Such technologies provide fast, cheap, portable, and simple analyses into a single affordable testing system bypassing the necessity for specialized personal. In this regard, the ability to perform analytical measurements at resource-limited environments (e.g. developing regions or emergencies) is a crucial advantage of the point-of-use methods compared with conventional bench top approaches [3,4]. Currently, smartphones represent an outstanding alternative for the accomplishment of these assays by combining user-friendly operation, low cost, portability, and colorimetric detection with the acquisition and handling of the resulting data. The smartphones are supported by powerful processors, moderate storage capacity, wireless connectivity, real-time geo-tagging, secure data management, open-source operational system, and cloud computing [5,6]. These devices show computational capability and operation interface better than regular cellphones [7], which were initially applied in point-of-use assays [8]. Other important aspect towards the deployment of smartphone-based analytical platforms (SMAP) concerns the continuous increase in the number of smartphone's users. Currently, 1.91 billion people own at least one smartphone. Such number is estimated to be 2.56 billion until 2018, approximately one-third of the world population [9].

Smartphones have been used in analytical chemistry to conduct optical detection because they incorporate the two functional units for this type of operation, namely: source (white LED-emitting light from flash) and detector of radiation (digital camera) [10]. Apart from optical measurements [5,6,10–12], further smartphone-mediated applications include the control of microfluidic systems [13], the recording of images with 2-μm resolution [14], and linkage with portable potentiostats for electrochemical analyses [3,15,16]. The electroanalytical methods are particularly

---

[*] Corresponding author at: Rua Giuseppe Máximo Scolfaro, 10.000, Polo II de Alta Tecnologia, Caixa Postal, Brazil.
E-mail address: renato.lima@lnnano.cnpem.br (R.S. Lima).

http://dx.doi.org/10.1016/j.electacta.2016.09.157

interesting for the development of point-of-use platforms by exhibiting portability, low-cost, operational simplicity, satisfactory analytical performance, and versatility [17]. This latter property is mainly imparted by the different types of electrode material and electrode surface modification that can be used to improve the selectivity and sensitivity [18]. Such platforms have been remarkably explored in numerous fields for both qualitative and quantitative analyses [19], including experiments for classifying patterns in complex matrices such as milk [20], beverages [21], and honey [22].

With regard to the SMAPs integrating electrochemical detection, Lillehoj et al. recently customized an Android App to control a potentiostat, which was used for electro-polymerization, electric-field pulsed mixing, and amperometric detection [15]. The connection between the modules of this system was limited by a cabled USB connection. In other study, Nemiroski et al. coupled a portable potentiostat to a mobile phone through a standard audio cable for voice-assisted data transmission [3]. The results were sent by SMS to the user and the data processing was conducted by a personal computer. Despite the potential of these methods to point-of-use applications, further key advances are required for in-situ and real-time multivariate analyses. Ideally, the smartphone should be able to process multivariate advanced data with the intent to ensure the accomplishment of the entire in-situ experiment regardless of personal computers.

Taking into account the relevance of the point-of-use methods, the potential of the smartphones and electroanalytical detectors for the accomplishment of such platforms, and the absence of simple and portable set ups to perform multivariate analyses, we herein report an inexpensive, hand-held, and portable electroanalytical SMAP using homemade potentiostat and smartphone with ability for processing multivariate data. This platform is potentially attractive for in-situ experiments by combining high-performance detection with great simplicity, low-cost, portability, autonomy, cable-free system, and capacity to conduct in real-time the entire analytical measurement at remote places.

The potentiostat relied on CheapStat, a recently engineered open source and “do-it-yourself” analytical tool [23]. While the most commercial potentiostats cost a few thousands of dollars, the CheapStat requires less than eighty dollars for its manufacturing. This platform originally used a personal computer (or a notebook) as both power supply and data collection. The version addressed in this paper shows improvements with regard to the device autonomy and data transmission. The autonomy was provided by using a battery (9 V) as power supply. Moreover, the proposed platform not only allowed cabled USB connection, but also wireless communication through a Bluetooth module that was integrated in the potentiostat’s hardware. This module allowed remote connection to smartphones or tablets, thus eliminating the use of additional network systems.

In relation to the advances in the smartphone’s software, we developed an *in-house* App for Android operational system (termed TongueMetrix) to collect, store, and process multivariate data. Such large and complex data require the use of chemometric techniques to extract useful informations from the obtained measurements. The current SMAPs do not grant such a processing ability as aforementioned [3,24–26]. This aspect hinders in-situ tests and represents a crucial downside for point-of-use technologies. Our TongueMetrix App ensures the on-site processing of multivariate data using principal component analysis (PCA). Furthermore, the App enables to share the data through the cloud (e-mail, google drive, or even social media) for backup or remote processing of the electroanalytical results. This option provides an operation center (OC) to explore more advanced chemometric tools, such as partial least squares-based approaches (PLS, PLS-DA) [27], independent component analysis (ICA) [28], multivariate curve resolution (MCR) [29], parallel factor analysis (PARAFAC) [28], and support vector machines (SVM) [30].

As a proof-of-concept, the SMAP addressed in this paper was applied in the pattern recognition of honey samples according to their botanical and geographic origins. Brazilian Federal Agricultural Research Company (EMBRAPA) and Brazilian Innovation Agency (FINEP) have launched projects with the intent to deploy reliable protocols for certificating the botanical and geographic sources of honey samples. Since the Brazilian producers export such products in bulk quantities at low prices, this effort aims to increase the market value of the honey products. The major procedures used for certification of honey are melissopalynology [31] and physicochemical assays (e.g. color, moisture, electrical conductivity, pH, total acidity, diastase activity, or hydromethylfurfural content) [32]. These methods are often laborious, time-consuming, and incompatible with in-situ analyses. Such features are critically adverse because different physicochemical properties of the honey depend on the storage time [33]. As a consequence, we believe our platform is a powerful alternative to detect unique patterns in honey samples related to their botanical and geographic origins. This application was performed by cyclic voltammetry using a single and non-modified working electrode of gold (Au). PCA analyses were performed by the smartphone to glean the most useful information from the complex set of resulting data.

2. Experimental

2.1. Chemicals, samples, and instruments

All chemicals were of analytical grade. Potassium ferrocianide trihydrate ($K_4Fe(CN)_6.3H_2O$) and potassium chloride (KCl) were provided by Merck (São Paulo, Brazil). Potassium phosphate dibasic (K_2HPO_4), potassium ferricianide ($K_3Fe(CN)_6$), and also sodium phosphate monobasic monohydrate ($NaH_2PO_4.H_2O$) were purchased from LabSynth (São Paulo, Brazil). Ultrapure water ($18.2\,M\Omega\,m^{-1}$) was obtained from a PURELAB water purification system (ELGA – Celle, Germany) with a resistivity higher than 18 $M\Omega$ cm.

Eight groups of honey samples (HS1-HS8) were evaluated. They covered three monofloral origins, namely: quince, orange, and coffee as shown in Table S1 (Supplementary Information). Such samples were obtained from two suppliers, EMBRAPA (certified by melissopalynology experiments) and a local apiary (Campinas, SP, Brazil).

The portable and homemade potentiostat was fabricated according to Rowe et al. [23]. Changes in hardware were performed to add external power supply and Bluetooth module for data transmission. The TongueMetrix App in smartphone managed the Bluetooth communication and the PCA treatment of the data.

AUTOLAB PGSTAT302N potentiostat/galvanostat (Metrohm AG – Herisau, Switzerland) was used as reference method. The reference electrode (RE) was Ag/AgCl in $3.0\,mol\,L^{-1}$ KCl (Metrohm AG). The working (WE) and counter electrodes (CE) were a gold disc electrode (diameter of 3.0 mm) and a platinum wire, respectively. These electrodes were used in the electrochemical measurements with the homemade potentiostat as well.

2.2. Cleaning of the working electrode

Prior to the analyses, the gold WE electrode was polished in alumina slurry (0.3 μm grade, Arotec, São Paulo, Brazil) and sequentially cleaned in ethanol and water ultrasound baths for 10 min each. Afterward, an electrochemical polishment was conducted in aqueous solution of $100.0\,mmol\,L^{-1}\,H_2SO_4$ by applying 10 cycles of cyclic voltammetry. In this case, the scanning