



Simultaneous determination of ascorbic and uric acids and dopamine in human serum samples using three-way calibration with data from square wave voltammetry



Adrian Marcelo Granero ^{a,1}, Gastón Darío Pierini ^{a,1}, Sebastián Noel Robledo ^{b,1}, María Susana Di Nezio ^c, Héctor Fernández ^{a,*}, María Alicia Zon ^{a,*}

^a Departamento de Química, Facultad de Ciencias Exactas, Físico-Químicas y Naturales, Universidad Nacional de Río Cuarto, Agencia Postal N°3, 5800 Río Cuarto, Argentina

^b Departamento de Tecnología Química, Facultad de Ingeniería, Universidad Nacional de Río Cuarto, Agencia Postal N°3, 5800 Río Cuarto, Argentina

^c Departamento de Química, INQUISUR, Universidad Nacional del Sur, B8999CPB, Bahía Blanca, Argentina

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ABSTRACT

We present for the first time a novel analytical method based on a model of three-way calibration using second-order data generated from the combination of records of forward (oxidation) and reverse (reduction) currents using a glassy carbon electrode modified with a dispersion of electrochemically reduced graphene oxide (GCE/RGO) as the working electrode, which can be obtained from a square wave voltammetry single experiment. This methodology was used for the simultaneous determination of ascorbic (AA) and uric (UA) acids, and dopamine (DO) in the presence of glucose (interfering species) in lyophilized human serum samples.

The serum samples have analyte different concentration levels (normal and pathological levels). The forward and reverse currents were pre-processed using AsLS and COW, to generate the second order data and finally the data were modeled with the U-PLS algorithm. Recovery studies were made in order to validate the proposed method. Recovery percentages between 92.4 and 120% were obtained.

The present method has the advantage to generate second order data through a simple voltammetric experiment. Among the advantages of the proposed method can be mentioned speed, easy data acquisition and the possibility of using modified electrodes with nano-structures.

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1. Introduction

Ascorbic acid (AA) is an essential vitamin in the diet of humans and it is present in mammalian brain along with various neurotransmitter amines. It has been used in the prevention and treatment of the common cold, infertility, mental illnesses, cancers and respiratory viral infections [1,2].

Uric acid (UA; 7,9-dihydro-1H-purine-2,6,8-(3H)-trione) is the main final product of purine metabolism and, it is a very important substance for the human body. Abnormal levels of UA may be associated with many diseases, including Lesch–Nyhan syndrome, gout and hyperuricemia [3].

Dopamine (DO) is a neurotransmitter that plays an important role in central nervous system. Its determination is very important because of

the necessity to monitor HIV infection, neurotransmission processes and diagnose Parkinson's disease [4,5].

AA, UA and DO usually coexist in biological matrixes. They are considered as crucial molecules for physiological processes in human metabolism [6]. Thus, the development of sensitive and selective detection methods for these bio-molecules is highly important in healthcare, biological analysis and clinical diagnostics.

Electrochemical techniques have received considerable interest for simultaneous detection of different analytes because of their high sensitivity, simple operation, rapid response and low cost. Potential pulses techniques are within electrochemical techniques mainly used for the development of analytical methods. The main advantage of the pulse voltammetric techniques is their ability to discriminate against charging currents. Thus, a higher sensitivity of the measured signal is achieved [7]. One of these pulse voltammetric techniques is called square wave voltammetry (SWV), which was invented by Ramaley and Krause [8]. In the last three decades, the advances in both analog and digital electronics allowed to SWV to be used in countless developments related to the quantification of various analytes [9–11].

* Corresponding authors.

E-mail addresses: agranero@exa.unrc.edu.ar (A.M. Granero), gpierini@exa.unrc.edu.ar (G.D. Pierini), srobledo@ing.unrc.edu.ar (S.N. Robledo), sdinezio@criba.edu.ar (M.S. Di Nezio), hfernandez@exa.unrc.edu.ar (H. Fernández), azon@exa.unrc.edu.ar (M.A. Zon).

¹ These authors contributed equally to this work.

As previously mentioned, AA, UA and DO are substances of great interest, so that the development of analytical methods for their simultaneous determinations is important in several areas such as science, health and clinical diagnosis.

However, the development of electrochemical methods is not easy because the oxidation peaks of AA, UA and DO exhibit overlapping at solid electrodes resulting in a poor selectivity [12]. Thus, several types of modified electrodes have been developed in recent years for the simultaneous determination of these analytes. Carbon based nanomaterials [13–15], noble metals [16,17], metal oxides [18,19], metal complexes [20] and polymers [21,22] have been used as effective electrode modifiers for the simultaneous determination of AA, UA and DO.

Recently, many materials based on graphene and its derivatives have been proposed to determine AA, UA and DO [23–25]. Reduced graphene oxide (RGO), a derivative of graphene, is usually obtained by chemical oxidation/exfoliation of graphite and subsequent reduction of graphene oxide (GO). Thermal, chemical and electrochemical reductions are among the usual methods of reducing GO to obtain RGO [26–30]. RGO has been successfully used for the simultaneous determination of AA, UA and DO in different real samples [31,32]. Chemometric tools are interesting complementary techniques, such as two or multi-way analysis, that allow the simultaneous determination of several analytes having overlapping electrochemical signals or when there are strong interactions between these analytes or molecules present in the matrix analyzed [33,34].

Thus, several analytical methods have been developed by combining chemometric tools with electrochemical techniques for the determination of different analytes in complex matrices, using data of first and second order. For example, tocopherols were determined in edible vegetable oils [35], AA, UA, DO, and nitrite in human serum samples [36], flavonoids in pharmaceutical formulation [37], heavy metals in propolis [38], and ethiofencarb in the presence of interfering [39].

In this work, we discuss for the first time a novel analytical method based on a model of three-way calibration. It uses second-order data generated from the combination of records of forward (oxidation) and reverse (reduction) currents, which are obtained in the same experiment of square wave voltammetry. The proposed method is used for the simultaneous determination of AA, UA, and DO in lyophilized human serum samples.

2. Experimental and theoretical considerations

2.1. Experimental details

2.1.1. Reagents

AA, UA, DO, KMnO_4 , H_2SO_4 , Na_2HPO_4 , NaH_2HPO_4 , H_3PO_4 , H_2O_2 , and HCl, were purchased from Sigma–Aldrich. HClO_4 , ethanol, methanol, and acetic acid were Merck p.a. Ultrapure water ($\rho = 18 \text{ M}\Omega \text{ cm}$) was obtained from a Millipore–Milli Q system. Stock solutions of AA, UA and DO were prepared in ethanol, protected from light, and kept in the refrigerator. Working solutions were prepared daily by adding different aliquots of stock solutions to pH 7.00, 0.2 M phosphate buffer solution (PBS).

Graphene oxide (GO) was synthesized from graphite flakes by using a method developed by Marcano et al. [40].

2.1.2. Apparatus and software's

SW voltammetric experiments were performed with an Epsilon potentiostat (BASi–Bioanalytical System, USA) and run with the BAS Epsilon EC Windows software version 1.60.70. A C3 cell stand (BASi–Bioanalytical System, USA) was used for all experiments.

The electrodes were inserted into the cell through holes in its Teflon cover. The working electrodes were glassy carbon disks (GCE), GCE modified with a dispersion of GO (GCE/GO) and GCE modified with a dispersion of electrochemically reduced GO (GCE/RGO). A platinum

wire and Ag/AgCl, 3 M NaCl (BAS, RE-5B) were used as counter and reference electrodes, respectively.

The MVC1 free algorithms package was employed to first order data analysis [41]. The MVC2 package was used to obtain second order models [41,42]. Artificial neural networks (ANN) were implemented from MATLAB 7.8 software.

2.1.3. Preparation of electrodes

Pretreatment of GCE: the electrodes were polished with alumina slurries of 0.30 and 0.05 μm for 1 min each, and sonicated in water during 30 s.

Preparation of GCE/GO: the polished GCE was modified with GO dispersion (GCE/GO) by dropping an aliquot of 5 μL of the dispersion on the top of the electrode and allowing to dry during 30 min at 37 °C.

Preparation of GCE/RGO: the GCE/RGO was electro-generated by applying at GCE/GO a potential of -1.70 V during 5 min in a pH 7.00 0.20 M PBS.

2.1.4. Procedure

The AA, UA and DO accumulation at the electrode surface was performed at open circuit potential during 5 min under stirring conditions. The voltammetric stripping was also performed in pH 7.00 0.20 M PBS.

SW voltammograms were recorded in the potential range from -0.4 to 0.8 V . Other parameters of SWV were: amplitude of the square wave, $\Delta E_{\text{sw}} = 0.025 \text{ V}$, staircase potential, $\Delta E_s = 0.005 \text{ V}$ and frequency, $f = 20 \text{ Hz}$.

2.2. Theoretical details

2.2.1. Generation of second-order data with SWV

Among several types of square wave voltammetry are of Osteryoung (OSWV) [43] and Barker (BSWV) [44]. However, the most frequently used is OSWV, which usually is called SWV.

SWV is a dynamic technique in which one pulse train is applied to the working electrode as shown in Fig. 1. Forward currents (I_f) are those currents measured at the end of direct pulses (in Fig. 1, $m = 1, 3, 5, \dots$). In contrast, reverse currents (I_r) are those measured in the same cycle in lower pulses (in Fig. 1, $m = 2, 4, 6, \dots$). The parameters of interest are ΔE_{sw} , ΔE_s , the period of the wave (τ), and the pulse time (t_p), defined as half of the period. The time parameter can also be described alternately by the frequency (f), where $f = \tau^{-1}$ or $f = 1 / (2t_p)$ [45].

A very important aspect of SWV is that the forward and reverse currents can be examined independently of each other. The net current (I_n) is calculated as $I_f - I_r$ [43]. Forward and reverse currents have a diagnostic value and they are measured separately. Consequently, from a single SWV experiment it is possible to obtain three voltammograms, showing I_f , I_r , and I_n as a function of the potential (see Section 3.2.4.1). Thus, a SW

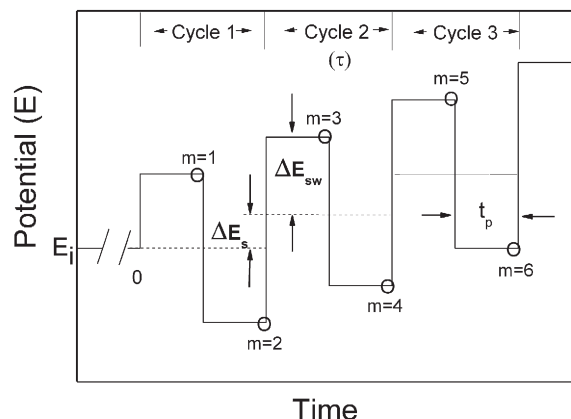


Fig. 1. Waveform and measurement scheme for square wave voltammetry.

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