



Simultaneous electroanalytical determination of luteolin and rutin using artificial neural networks



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ABSTRACT

In this study, we propose an electroanalytical method to quantify simultaneously luteolin and rutin, two flavonoids which are present in a pharmaceutical formulation. The methodology is based on square wave voltammetry at glassy carbon electrodes modified with multiwalled carbon nanotubes dispersed in polyethylenimine. Both flavonoids show quasi-reversible surface redox couples in 10% ethanol + 1 mol L⁻¹ HClO₄ aqueous solutions, which are defined in potential regions very close to each other. The adsorption process of flavonoids on the modified electrode surface was carried out using an accumulation potential of 0.55 V (vs. Ag/AgCl, 3 mol L⁻¹ KCl), and an accumulation time of 20 min.

Considering that luteolin and rutin electrochemical responses show a high degree of overlapping, we processed the electrochemical signals using artificial neural networks. We used a supervised network, feed-forward network with Levenberg-Marquardt back propagation training. Values of 92.6 ± 0.4 and 92 ± 1 mg per tablet were determined by the artificial neural networks methodology for luteolin and rutin, respectively. According to values declared by the manufacturer, differences of 7.4 and 8.0% were calculated for luteolin and rutin, respectively. Results obtained with electroanalytical methodologies were in very good agreement with those obtained by HPLC.

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1. Introduction

Flavonoids are benzo-γ-pyrone derivatives containing piranic and phenolic rings in their molecular structures. In most of the cases, flavonoids are molecules that have two benzene rings (A and B) linked through a chain of three carbon atoms (ring C when carbon atoms form a cycle). Flavonoids are extensively found in nature such as in fruits, seeds, and vegetables [1].

Luteolin (3',4',5,7-tetrahydroxy-flavone; LUT) belongs to the subclass of flavonoids known as flavones and is rated as one of the most bioactive flavonoids. It is found mainly in parsley, celery, thyme, and peanut hulls [2]. Its chemical structure is shown

in Fig. 1a. LUT has a resorcinol group in the benzene ring A, and a catechol group in the benzene ring B. LUT has beneficial effects on human health, such as cardiovascular protection, anti allergic, and anticancer activities, anti-ulcer effects, and prevent cataracts [3]. LUT also inhibits platelet aggregation by vasodilating action [4].

Rutin (3',4',5,7-tetrahydroxyflavone-3-O-β-D-rutinoside; RU) (Fig. 1b), a natural flavone derivative, is also considered one of the most bioactive flavonoids [5]. RU has different physiological activities such as anti-inflammatory, anti-tumor, anti-bacterial, antioxidant, and anti-allergic. RU also acts as a stimulant of the immune system [6], and has several pharmacological activities, including vaso-active, anti-viral and anti-protozoal [7].

Flavonoids have mainly been determined in fruits, vegetables and different beverages by reverse-phase high-performance liquid chromatography (HPLC) with ultraviolet detection [8], coulometric array detection [9] or amperometric detection [10], and to a lesser extent, using various other techniques, such as: spectrophotometry, thin-layer chromatography (TLC), gas chromatography (GC), capillary electrophoresis (CE) and electrochemical methods [11].

The LUT analytical determination has been reported by TLC [12], GC [13], gas chromatography–mass spectrometry (GC-MS) [14],

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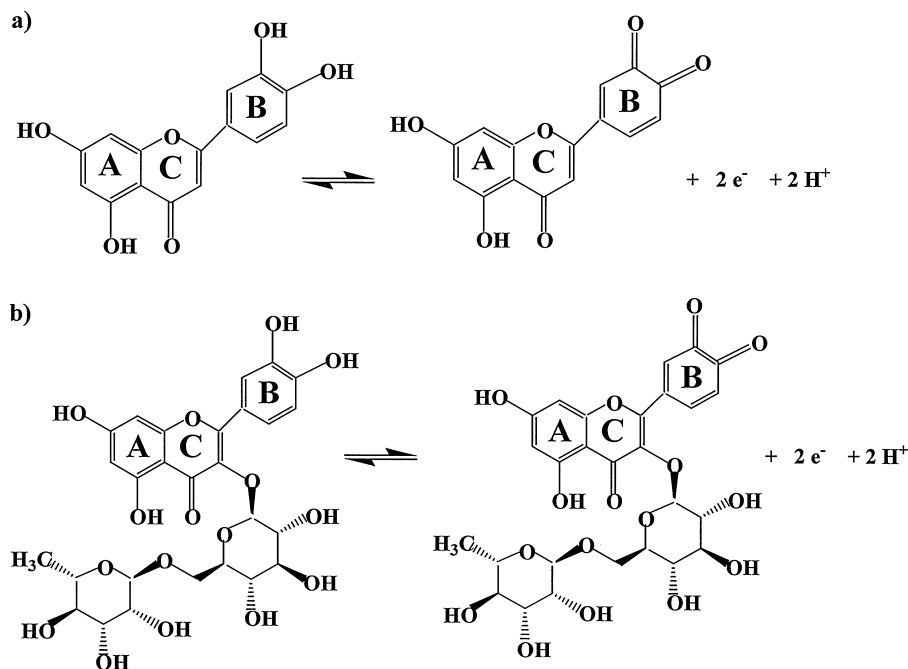


Fig. 1. Chemical structures of flavonoids and products of the first peak of electrochemical oxidation of luteolin (a) and rutin (b).

HPLC [15–18], and CE [19] coupled with various detection techniques, such as UV spectrometry, electrochemical, etc.

The RU analytical determination has been carried out using different methodologies such as spectrometry [20,21], HPLC [22], CE [23], and chemiluminescence [24].

The electrochemical behavior of RU has been studied at electrodes of different materials such as bare glassy carbon [25], hanging mercury drop [26], and gold electrodes modified with single-walled carbon nanotubes [27]. In addition, electrochemical sensors and biosensors for the RU determination have been described in the literature [28,29].

On the other hand, several chemometric tools have been described to resolve systems where signals appear overlapped [30]. The most used chemometric techniques are deconvolution [31], multivariate curve resolution [32,33], and multivariate calibration [34,35]. The most popular chemometric tools are, particularly, in the field of electrochemistry, multivariate calibration based on different regression methods such as multilinear regression (MLR) [36], principal component regression (PCR) [37], continuum regression [38], partial least squares regression (PLS-1) [39], and artificial neural networks (ANNs) [30,40].

In addition, ANNs is a data processing system consisting of a large number of highly interconnected elements in an architecture inspired by the structure of the brain, and it is a powerful modeling tool for processing from complex to imprecise data [41]. The ANNs processing systems can be performed using a conventional set of independent analyses. However, it could be advantageous to replace this with a statistically designed experimental procedure in which several factors are simultaneously varied. This multivariate approach reduces the number of experiments and improves statistical interpretation of results [42].

In this study, we propose the simultaneous determination of LUT and RU in a pharmaceutical formulation at glassy carbon electrodes (GCE) modified with multi-walled carbon nanotubes (MWCNTs) dispersed in polyethylenimine (PEI) in 10% ethanol + 1 mol L⁻¹ HClO₄ aqueous solution using cyclic (CV), and square wave (SWV) voltammetries. Electrochemical impedance spectroscopy (EIS) is also used to compare the state of bare and modified GCE. Considering that surface voltammetric signals of LUT and RU show a high

overlapping, we used the ANNs methodology, and an experimental design to quantify the LUT and RU content in the pharmaceutical formulation. For comparison purposes, these studies were also carried out using HPLC.

2. Materials and methods

2.1. Reagents

LUT, RU, and a dispersion of PEI in water were purchased from Sigma–Aldrich. MWCNTs (diameter 30 ± 15 nm, length 1–5 μ m) were obtained from Nano-Lab (USA). HClO₄, ethanol, methanol, and acetic acid were Merck p.a. Acetonitrile was Sintorgan, HPLC degree. Ultrapure water ($\rho = 18$ M Ω cm) was obtained from a Millipore–Milli Q system. Stock solutions of LUT (3.5×10^{-3} mol L⁻¹) and RU (8.7×10^{-4} mol L⁻¹) were prepared in ethanol, protected from light, and kept in the refrigerator. They were stable for at least two months. Working solutions were prepared daily by adding different aliquots of stock solutions to 1 mol L⁻¹ HClO₄ aqueous solutions. The percentage of ethanol in all solutions was 10%.

2.2. Apparatus

CV and SWV experiments were performed with an Epsilon (BAS, USA) Potentiostat. EIS measurements were carried out in solutions containing equal concentrations (1×10^{-3} mol L⁻¹) of oxidized and reduced forms of the [Fe(CN)₆]^{4-/3-} redox couple, with 0.1 mol L⁻¹ KCl as the supporting electrolyte. EIS experiments were performed with an AutoLab PGSTAT 30 potentiostat, controlled by FRA 4.9 software. A 5 mV amplitude sine wave perturbation was applied to the electrode, whereas the dc potential was set at the formal potential of the redox couple, i.e., $E_f^0 = 0.240$ V vs. Ag/AgCl. The ac frequency was varied from 0.5 Hz to 10 kHz. Both, the in-phase (Z') and out of phase (Z'') impedance components were extracted from the experimental data. Values of the electron-transfer resistance (R_{ct}), and double layer capacitance (C_{dl}) for both the bare and modified GCE were extracted from a non-linear squares fitting

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