



# Determination of pentahydroxyflavones using coated chitosan multi-wall carbon nanotubes and an ionic liquid glassy carbon electrode by adsorption stripping voltammetry (AdSV)



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## ABSTRACT

In this work, the determination of pentahydroxyflavones on a glassy carbon electrode modified with chitosan and multi-walled carbon nanotubes (Ch-MWCNT) was studied. The presence of ionic liquids (LIs) on the surface of the modified electrode (Ch-MWCNT-LI-GCE) increased the oxidation current by nearly 20%. The pH and electrochemical parameters (adsorptive potential and time accumulation) were optimized based on the oxidation of morin to obtain the following values: pH, 3.2;  $E_{ads}$ ,  $-0.10$  V; and  $t_{ads}$ , 70 s. The detection limit was  $0.54 \times 10^{-7}$  mol L<sup>-1</sup> and the RSD was 1.7%. The new method was used to quantify pentahydroxyflavones in plant tissue samples.

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## 1. Introduction

For many years polyhydroxyflavones have been considered as important diet constituents. In fact, they have been reported to have antioxidant, antibacterial and anticarcinogenic properties. Moreover, they have been tested as treatments for diseases such as Parkinson's [1]. On the other hand, it is suspected that their biological activity is associated with their ability to inhibit oxidation processes with reactive oxygen species such as free radicals [2].

Morin and quercetin are polyphenolic compounds whose structure is shown in Fig. 1. They are flavonoids, members of the flavone subclass. Both have very similar structures and behaviors, the only difference being the position of a hydroxyl group on ring B [3]. They are considered potent chelators of metal cations, and free radical inhibitors [3,4]. On the other hand; they have been used as ligands in the quantification of metals such as lead, zinc and copper by electroanalytical techniques [5].

High performance liquid chromatography (HPLC) is one of the most used techniques for the quantification of pentahydroxyflavones in various matrices, obtaining detection limits below  $1.0 \times 10^{-6}$  mol L<sup>-1</sup>, but involving high equipment and handling costs [6]. Therefore, electroanalytical methods are a low operating and instrumentation cost option offering high sensitivity and selectivity. In this connection, adsorption voltammetry (AdV) techniques offer the advantage of greater sensitivity because they are conducted in two stages, first the adsorption of the

analyte on the surface of the modified electrode, and then the desorption of the analyte into the bulk solution. Thus it has been possible to quantify morin and quercetin using innovative modified electrodes and nano-structured electrodes with nano-silver particles [7], carbon nanotubes (MWCNT) with surfactants [8], and paste carbon [9], with detection limits below  $1.0 \times 10^{-7}$  mol L<sup>-1</sup>. In recent years the use of ionic liquids has increased in analytical chemistry, especially as green or alternative solvents [10]. Due to their wide electrochemical potential and conductivity windows [11], they have proved useful in the modification of electrodes used in the quantification of metals such as lead and cadmium [12,13,14], where detection limits between 0.02 and 8.9  $\mu$ g L<sup>-1</sup> have been reported. The use of ionic liquids in pentahydroxyflavone quantification has only been described for HPLC with diode array detection [6]. The aim of this study is to detect and quantify pentahydroxyflavone in real samples. On the other hand, modified electrodes using ionic liquids have not yet been reported for morin or quercetin.

## 2. Experimental part

### 2.1. Apparatus

Adsorptive stripping voltammograms and cyclic voltammograms were obtained using a Metrohm VA Computrace in a three-electrode setup. A modified glassy carbon electrode with multi-walled carbon nanotubes, chitosan and ionic liquid (Ch-MWCNT-IL-GCE) was used as the working electrode ( $\varnothing$  3 mm). Ag/AgCl/KCl (3 mol L<sup>-1</sup>) and

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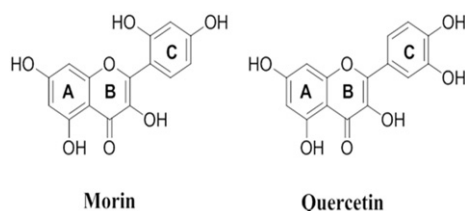


Fig. 1. Chemical structures of morin and quercetin.

platinum wire were used as reference and auxiliary electrodes, respectively. The pH measurements were made with an Orion-430 digital pH/mV meter equipped with a combined pH glass electrode.

## 2.2. Chemicals

A Milli-Q system (18.2 Ohm, Millipore, USA) was used to obtain the water used for sample preparation and dilution of reagents. Nitric acid and phosphoric acid were analytical grade, while ethanol was HPLC grade (Merck). The stock solutions of morin and quercetin (Sigma-Aldrich) were freshly prepared each working day by dissolving the reagents in ethanol ( $0.3 \text{ mmol L}^{-1}$ ). Chitosan (low molecular weight) and the multi-walled carbon nanotubes (MWCNT's  $\varnothing$  5–10 nm, length 0.5–20  $\mu\text{m}$ , and purity  $\geq 95\%$ ) were obtained from Sigma-Aldrich. Ionic liquids 1-ethyl-3-methylimidazoliumtrifluoromethanesulfonate ([EMIM]F<sub>3</sub>MSO<sub>3</sub>), 1-butyl-3-methylimidazoliumtetrafluoroborate ([BMIM]BF<sub>4</sub>), and 1-butyl-3-methylimidazoliumhexafluorophosphate ([BMIM]PF<sub>6</sub>), were purchased from Merck with purity  $\geq 99\%$ . Phosphate buffer solutions were used to investigate pH in the 2.0–4.5 range. These buffers were prepared with  $0.10 \text{ mol L}^{-1}$  phosphoric acid and sodium phosphate solution, adjusting to the required pH with NaOH solution ( $0.5 \text{ mol L}^{-1}$ ).

## 2.3. Preparation of modified Ch-MWCNT-IL-GCE

Before measurement, the glassy carbon substrate electrode was thoroughly polished using a polishing pad with 0.3 and 0.05  $\mu\text{m}$  Al<sub>2</sub>O<sub>3</sub> slurries, rinsed with  $0.3 \text{ mol L}^{-1}$  HNO<sub>3</sub>, water and methanol for 5 min in an ultrasonic bath, and dried with N<sub>2</sub>. Preparation of the modified Ch-MWCNT-IL-GCE was performed as in Nagles et al. [15]. 2.0 mg of MWCNT composites were dispersed in 1.0 mL of chitosan solution (1% acetic acid) and sonicated for 60 min. 10  $\mu\text{L}$  of composite solution or 10  $\mu\text{L}$  of MWCNT-chitosan solution was placed on the electrode surface and the solvents were evaporated at room temperature for 15 min. Then 10  $\mu\text{L}$  of concentrated ionic liquid were placed on the surface of the recently modified electrode, and the solvents were evaporated at 50 °C and at room temperature (60 min). The electrode was washed to remove excess solvent. The modified Ch-MWCNT-IL glassy carbon electrode was submitted to 10 cycles of potential between 0.00 and 1.20 V ( $0.10 \text{ mV s}^{-1}$ ) to obtain a stable, reproducible and clean surface.

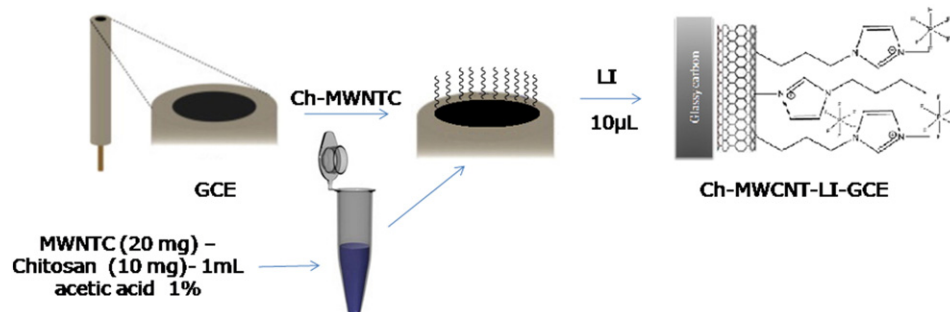


Fig. 2. Preparation of the modified electrode.

The same electrode was used in a series of measurements. The modified electrode preparation is shown in Fig. 2.

## 2.4. Flower and petal sample preparation

Five grams of dried flowers was treated with 30 mL of ethanol and crushed in a mortar. The extraction was carried out for 1 h and the material was filtered before each measurement to avoid interference.

## 2.5. Measurement procedure

9.0 mL of deionized water, 500  $\mu\text{L}$  of phosphate buffer solution ( $0.1 \text{ mol L}^{-1}$ ) and 100  $\mu\text{L}$  aliquots of morin and quercetin solutions ( $3 \text{ mg L}^{-1}$ ) were pipetted into the electrochemical cell and stirring at 500 rpm. After an equilibration time of 10 s, square wave adsorptive voltammograms and cycle voltammograms (scan rate  $100 \text{ mV s}^{-1}$ ) were recorded, while the potential was scanned from 0.0 to 1.2 V. Each voltammogram was repeated three times. Calibration curves were obtained and linear regression and limits of detection were calculated. The proposed method was applied to the determination of pentahydroxyflavones in yellow flower samples. To eliminate matrix effects the standard addition method was used. All data were obtained at room temperature ( $\sim 25^\circ\text{C}$ ).

## 3. Results and discussion

### 3.1. Characterization of the modified Ch-MWCNT-IL glassy carbon electrode with morin and quercetin solution

Preliminary experiments were carried out with morin and quercetin solutions to identify the general features that characterize the surface of the modified electrode using cycle voltammetry and adsorptive voltammetry.

Fig. 3a shows cyclic voltammograms (CVs) of morin solution ( $1.5 \times 10^{-4} \text{ mol L}^{-1}$ ) at  $100 \text{ mV s}^{-1}$  in phosphate buffer solution at pH 3.2, using GCE (dotted line) and Ch-MWCNT-GCE (solid line). The CV obtained with morin showed irreversible oxidation processes at 0.52 V (solid line), which results from a  $2e^-$  transfer, accompanied by the transfer of two protons [9]. The morin first oxidation peak corresponds to the oxidation of the -OH group of C<sub>3</sub> in ring C [18], but this oxidation current increased greatly when the GCE was modified with Ch-MWCNT, the new surface favoring charge transport. On the other hand, morin and quercetin have similar electroactive properties (Fig. 3b) on the glassy carbon modified electrode with Ch-MWCNT, the morin current peak (solid line) being higher. The oxidation potentials of the pentahydroxyflavonoids depend on properties of the substituents on rings B and C [16,17]. This suggests the importance of the 2-OH on ring B of morin and OH on ring C to quercetin pentahydroxyflavones [18]. Therefore morin was chosen for further optimization studies.

Fig. 4 shows net current square wave adsorptive voltammograms (SWAdVs) of morin solution ( $4 \times 10^{-6} \text{ mol L}^{-1}$ ) in phosphate buffer

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