



# Electrochemical sensor for dodecyl gallate determination based on electropolymerized molecularly imprinted polymer



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## ABSTRACT

An electrochemical sensor based on molecularly imprinted polymer (MIP) film for dodecyl gallate detection at the surface of a glassy carbon electrode (GCE) was proposed in this paper. The GCE was modified with f-MWCNT and the MIP synthesis was performed in situ by means of electropolymerization using ortho-phenylenediamine as the monomer. The stepwise preparation of the MIP and NIP (non-imprinted polymer) was characterized electrochemically by means of cyclic and square wave voltammetry employing ferrocyanide/ferricyanide as a redox probe. The selective capacity performance of the MIP and its imprinted effect to the template molecule (analyte) was compared to the NIP. They were also characterized by scanning electron microscopy technique (SEM). The analytical performance of the MIP sensor performed using square wave voltammetry showed linear range from 0.50 to  $8.0 \times 10^{-9}$  mol L<sup>-1</sup>, with a correlation coefficient of 0.9921. The sensor presented detection and quantification limit of  $0.22 \times 10^{-9}$  and  $0.67 \times 10^{-9}$  mol L<sup>-1</sup>, respectively. The apparent dissociation constant ( $K_D$ ) calculated was of  $1.26 \times 10^{-4}$  mol L<sup>-1</sup> and  $5.27 \times 10^{-1}$  mol L<sup>-1</sup> for the MIP and NIP respectively.

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## 1. Introduction

Chagas' disease, caused by protozoan *Trypanosoma cruzi*, is one of the major health problems in Latin America [1]. Transmission occurs mostly by triatominae insect vectors, but also through blood transfusion, congenital routes and organ transplants [2].

Treatments for Chagas disease are extremely limited and often ineffective. No vaccines have been produced thus far to protect the population at risk from contracting the trypanosomiasis in the endemic regions, where the insect vector has not yet been controlled. The current chemotherapy treatment still relies on the use of nifurtimox and a benzimidazole derivative, which is orally administered in the acute phase and short-term chronic phase [3,4]. These drugs frequently produce toxic side effects and have very limited efficacy in the treatment of chronic patients. The commercial pro-

duction of nifurtimox has been discontinued in some countries like Brazil, Chile, Argentina and Uruguay [5].

Taking into account the problems mentioned above, investigation on new compounds, mainly based on natural products, for the treatment of Chagas disease have been done [6,7]. Research has indicated that extracts and pure compounds obtained from plants, such as gallic acid and catechin derivatives, have expressive activities against *T. cruzi* and demonstrate no side effects [6,8,9].

Güida and coworkers presented, for the first time, the *in vivo* trypanocidal activity of epigallocatechin gallate (EGCg) obtained from a murine model of experimental Chagas disease. The results shown suggested that this compound could actually induce a programmed cell's death (PCD)-like processed in *T. cruzi* epimastigotes [9].

The ester derivatives of gallic acid, such as octyl gallate (OG), propyl gallate (PG) and dodecyl gallate (DG) are used as antioxidants in cosmetics, as food additives, and also as antioxidants in the pharmaceutical industry [10]. Andreo and coworkers investigated the antitrypanosomal activity of gallic acid and its esters against epimastigote forms of *Trypanosoma cruzi*. The authors evaluated both the trypanocidal potential after esterification of gallates and the mechanisms of action of these compounds in *T. cruzi* organisms.

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The antitrypanosomal effects of nonyl, decyl, undecyl, and dodecyl gallates were compared to benznidazole and results showed that the esters presented more significant  $IC_{50}$  (1.46–2.90  $\mu$ M for esters and 34.0  $\mu$ M for benznidazole) [11].

Analytical methods have a significant role in drug quality control as well as in the evaluation and interpretation of bioavailability, bioequivalence and pharmacokinetic data, therefore the development of simple, sensitive, rapid and reliable methods for the determination of these parameters has great relevance. Current techniques commonly used for detecting synthetic phenolic compounds mainly include high performance liquid chromatography [12], gas chromatography [13] and capillary electrophoresis [14]. Although these techniques have the advantages of high sensitivity, they may present some drawbacks, such as complex pretreatment steps, long assay time, expensive experimental equipment, and large amounts of reagents consumption. Therefore, alternative methods for simple, rapid and cost-effective detection of the synthetic phenolic antioxidants (propyl gallate and dodecyl gallate, for example) are still being researched [15,16].

Electrochemical methods have also been used for polyphenol detection directly on the electrodes surface, as graphite electrode, in grape and olive extracts matrices containing anthocyanins and green tea extract with catechines [17]. However, the main disadvantage of the phenol electrochemical oxidation is the deactivation of the electrode surface (“electrode fouling”) due to the formation of a passivating polymeric film [18]. This phenomenon is one of the main drawbacks of graphite based electrodes and can be overcome by modification of electrode surface [19,20].

A molecularly imprinted polymer (MIP) as the recognition element, synthesized by electropolymerization process presents attractive advantages like simple preparation, reproducibility of the polymeric film, high mechanical and chemical stability and low costs [21–23]. The development of MIP based electrochemical sensors can be improved using nanomaterials or nanocomposites to enhance the sensitivity of these sensors [16].

Carbon nanotubes (CNTs) has attracted considerable attentions in many fields owing to its special properties, such as good electrical conductivity, high surface area, chemical stability, outstanding charge transfer characteristics and low electrical resistance [24,25]. CNTs can significantly increase the active surface area and enhance the electron transfer efficiency, so as to improve the sensitivity of the electrochemical sensor [26,27].

The preparation of electropolymerized MIP consists of applying successive voltammetric cycles in a pre-established potential range. For this, a conventional electrochemical cell with three electrodes is used in an electrolytic solution at controlled pH, containing the functional monomer and template. After this step, a polymeric film is formed on the working electrode surface. The last stage is the removal of the template from the polymeric structure by successive washing using a solvent in which the analyte presents high solubility [28].

An electrochemical sensor for propyl gallate was developed using ortho-phenylenediamine (o-PD) to form the MIP on a glassy carbon electrode surface modified with Pt and Au nanoparticles, graphene and carbon nanotubes. After optimizing several parameters, the authors reported a detection limit of  $2.51 \times 10^{-8}$  mol L<sup>-1</sup>, linear range from  $7 \times 10^{-8}$  to  $1 \times 10^{-5}$  mol L<sup>-1</sup> and good results for detection of PG in food samples [29].

This work describes the development of an electrochemical sensor using molecularly imprinted polymer technology as element recognizer for dodecyl gallate determination. The MIP was synthesized by electropolymerization of o-phenylenediamine around the analyte on the glassy carbon electrode, which was firstly modified with functionalized carbon nanotubes. The method proved to be useful for the detection and quantification of the galloyl group.

## 2. Material and methods

### 2.1. Reagents and solutions

Potassium ferricyanide ( $K_3[Fe(CN)_6]$ ), potassium ferrocyanide ( $K_4[Fe(CN)_6]$ ), dodecyl gallate (DG) ( $C_{19}H_{30}O_5$ ), ortho-phenylenediamine (o-PD), epigallocatechin gallate (EGCG) ( $C_{22}H_{18}O_{11}$ ) and N-benzyl-2-nitro-1H-imidazole-1-acetamide ( $C_{12}H_{12}N_4O_3$ ) were obtained from Sigma-Aldrich (St.Louis, USA). Tetradecyl gallate (TG) ( $C_{21}H_{34}O_5$ ) was synthesized following the procedure described by Ximenes et al. (2010) [30]. Multiwall carbon nanotubes (MWNTs) were purchased from DROPSSENS. Ultrapure water obtained from a Millipore water purification system (resistance 18.2 M $\Omega$  cm) was utilized in all assays for dilution of the samples. All chemicals were of analytical grade.

### 2.2. Apparatus

All voltammetric experiments were performed using a potentiostat-galvanostat  $\mu$ AutoLab (Echo Chemie, B.V., Netherlands, NOVA software) connected to a personal computer and a conventional three-electrode configuration. The morphological characterization of the GCE surface was performed employing field emission scanning electron microscopy (FEG-SEM; Jeol JSM 6330F).

### 2.3. Electrochemical measurements

The 50 mL electrochemical cell consisted of a 3 mm diameter glassy-carbon working electrode (GCE), a Pt wire counter electrode and an Ag|AgCl|KCl<sub>sat</sub> reference electrode inserted through a Teflon cover. The stepwise of the MIP and NIP (non-imprinted polymer) construction was obtained by the cyclic voltammetry (CV) and square wave voltammetry (SWV) analysis performed using ferrocyanide/ferricyanide as a probe. This solution was prepared in KCl (0.1 mol L<sup>-1</sup>) and  $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$  (0.01 mol L<sup>-1</sup>). CV for electropolymerization was scanned from -0.4 to +1.0 V at 50 mV s<sup>-1</sup>. SWV was obtained under a frequency of 100 Hz, amplitude of 50 mV and step potential of 8 mV and was employed to monitor the analytical performance of the MIP and NIP sensor in different dodecyl gallate concentrations prepared in an ethanol:water (60:40) solution. The CV was also carried out in order to characterize MIP modification on the electrode's surface using a potential range from -0.10 to +0.6 V at 50 mV s<sup>-1</sup>. All electrochemical experiments were carried out at  $25 \pm 1$  °C.

### 2.4. Fabrication of the imprinted electrode

The carboxylic group of MWCNTs was functionalized using H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> (3:1). The 100 mg solution of crude MWCNTs was added to 250 mL of the acid mixture and stirred for 12 h. Subsequently, the nanotubes were washed with ultrapure water, filtered by vacuum and dried at 70 °C [31]. After this step, the functionalized nanotube was called f-MWCNTs. Then, the GCE surface was manually polished with sandpaper (4000 grit) for 2 min and washed with ultra-pure water. Then, f-MWCNTs (5 mg) was added into 2.5 mL of dimethylformamide and the suspension was submitted to ultrasonic treatment for 30 min in order to obtain a homogeneous suspension. Finally, 5  $\mu$ L of this suspension was added on the GCE surface and dried at room temperature to obtain a multiwall carbon nanotube/glassy carbon electrode (f-MWNTs/GCE). Before the electrosynthesis of MIP on the f-MWNT/GCE, the mixture of o-PD (0.005 mol L<sup>-1</sup>, acetic acid/acetate buffer solution (ABS, pH 5.4)) and dodecyl gallate (0.05 mol L<sup>-1</sup>, ethanol/water; 9:1) was incubated for 3 h. After this, the electropolymerization was performed using cyclic voltammetry from -0.40 to 1.00 V at 50 mV s<sup>-1</sup> for 20 cycles

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