



Adsorptive stripping voltammetry for simultaneous determination of hydrochlorothiazide and triamterene in hemodialysis samples using a multi-walled carbon nanotube-modified glassy carbon electrode



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ABSTRACT

Hemodialysis is the most commonly used method for the treatment of chronic kidney disease. In this procedure, some patients use diuretics to control weight gain and blood pressure. In this work, a voltammetric sensor based on a glassy carbon electrode modified with carbon nanotubes (GCE/MWCNT) is described for the simultaneous determination of the diuretics hydrochlorothiazide (HCT) and triamterene (TRT). The oxidation of the diuretics on the GCE/MWCNT surface was observed at 1.01 and 1.17 V for HCT and TRT, respectively, allowing simultaneous determination, which was not possible with the unmodified glassy carbon electrode. The GCE/MWCNT electrode provided 6-fold and 10-fold gains in anode peak intensity for HCT and TRT, respectively, compared to the unmodified electrode. After optimization of the conditions (pH, accumulation time, and accumulation potential), analytical curves were constructed for the analytes in the range from 1.0×10^{-7} to 2.0×10^{-5} mol L⁻¹. The detection limits for HCT and TRT were 2.8×10^{-8} and 2.9×10^{-8} mol L⁻¹, respectively. A high performance liquid chromatography method with diode array detection was also developed for the determination of HCT and TRT in hemodialysis samples, for comparison with the electroanalytical method.

1. Introduction

Hemodialysis is a treatment for chronic kidney disease (CKD), which affects 10% of the world's population [1,2]. Ensuring the quality of dialysis water can be a challenge, since each patient is exposed to between 18,000 and 36,000 l of water per year [3], and high water quality is extremely important in order to avoid exposure of these individuals to chemical and microbial contaminants [4]. The literature reports several analytical methods for the detection of metal contaminants, with the aim of minimizing the possibility of patient exposure [5–8]. However, to the best of our knowledge, there have been no reported studies concerning the detection of pharmaceutical compounds such as diuretics in the water used for dialysis. The control of diuretics is important, since these drugs may be used as part of the hemodialysis treatment, in order to control weight gain and blood pressure [9]. Therefore, it is necessary to develop methods able to detect and quantify diuretics such as hydrochlorothiazide (HCT) and triamterene (TRT) in samples of hemodialysis water.

Methods have been reported for the determination of HCT and TRT based on chromatography [10,11], spectrophotometry [12], capillary electrophoresis [13], amperometry [14], and voltammetry [15,16]. In

addition to the need for methods for the determination of these diuretics, in recent years increasing attention has been given to the development of green analytical methods, with the goal of reducing environmental pollution [17].

Electrochemical analytical techniques are attractive because in addition to avoiding the generation of large amounts of residues, they offer high sensitivity, good reproducibility, low cost, and the possibility of miniaturization [18–22]. Further improvements in these techniques in terms of sensitivity, selectivity, enhanced surface area, and catalytic effects can be achieved by modifying the surfaces of the electrodes with specific materials [23–26]. Multi-walled carbon nanotubes (MWCNT), first discovered in 1991 [27], are especially attractive as electrode modifiers, due to their excellent electronic, thermal, mechanical, and catalytic properties [28,29]. From the electrochemical perspective, their use increases the active area and improves electron transfer reactions, resulting in higher detection capability and better peak separation [30,31].

This work describes the development of an electrochemical sensor based on a glassy carbon electrode modified with carbon nanotubes for the simultaneous determination of hydrochlorothiazide and triamterene at very low concentration in hemodialysis water, synthetic urine,

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and other aqueous samples of environmental interest. In addition, a high performance liquid chromatography method with diode array detection (HPLC-DAD) was developed for determination of the compounds, and the figures of merit were compared to those for the proposed electrochemical sensor.

2. Experimental

2.1. Reagents and equipment

All chemicals used in this work were analytical grade and the solutions were prepared using ultra-pure water (Milli-Q® system, Millipore). Triamterene (purity $\geq 99.9\%$), hydrochlorothiazide, and dimethylsulfoxide were obtained from Sigma-Aldrich. Acetic acid, phosphoric acid, boric acid, and potassium chloride were from Merck. Sodium hydroxide and N,N-dimethylformamide were from Synth. Multi-walled carbon nanotubes (MWCNT) were obtained from DropSens. Standard solutions of 0.01 mol L^{-1} triamterene and hydrochlorothiazide were prepared by dissolution of the compounds in dimethylsulfoxide and acetonitrile, respectively, and were subsequently diluted in 0.10 mol L^{-1} Britton–Robinson (B–R) buffer, used as supporting electrolyte. The B–R buffer was prepared by mixing appropriate amounts of 0.10 mol L^{-1} sodium hydroxide with orthophosphoric acid, acetic acid, and boric acid (all at 0.10 mol L^{-1}). Measurements of pH were performed with a Tecnopon mPA 210 pH meter. The electrochemical experiments (using voltammetric techniques and electrochemical impedance spectroscopy) employed an Autolab PGSTAT 302 N potentiostat equipped with a FRA32 AC module and controlled using NOVA software. The chromatographic analyses were performed using a Shimadzu LC10ATVp high performance liquid chromatograph equipped with a diode array detector (HPLC-DAD) and controlled using CLASS-VP software.

2.2. Preparation of the modified electrode

A 1 mg portion of MWCNT was macerated in a Petri dish for 15 min and was then placed in 1 mL of N,N-dimethylformamide, with ultrasonication for 30 min. A $2.5 \mu\text{L}$ aliquot of the resulting MWCNT composite was placed on the surface of a previously cleaned glassy carbon electrode, followed by drying of the film at $60 \text{ }^\circ\text{C}$ for 20 min in an oven.

2.3. Sample preparation and analysis

2.3.1. Tap water sample

An aliquot of tap water fortified with HCT and TRT was transferred to a 10 mL electrochemical cell, giving a final concentration of $3 \mu\text{mol L}^{-1}$ of the diuretics. Voltammograms were recorded in 0.10 mol L^{-1} B–R buffer (pH 4.0), under magnetic stirring, using linear sweep adsorptive stripping voltammetry with application of an accumulation potential of 0.80 V for 40 s. The concentrations of HCT and TRT were obtained using the standard additions method.

2.3.2. Water treatment plant sample

A 10 mL sample of water collected from a water treatment plant in the city of Araraquara (São Paulo State) was fortified with $15 \mu\text{mol L}^{-1}$ of HCT and TRT. A 2 mL aliquot of the sample was transferred to an electrochemical cell containing 8 mL of B–R buffer solution, resulting in final concentrations of $3 \mu\text{mol L}^{-1}$ of the diuretics, and analysis was performed as described in Section 2.3.1.

2.3.3. Artificial urine sample

The artificial urine sample was prepared by mixing the following reagents in 250 mL of water: 0.73 g NaCl, 0.40 g KCl, 0.28 g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 0.56 g Na_2SO_4 , 0.35 g KH_2PO_4 , 0.25 g NH_4Cl , and 6.25 g urea [32,33]. A 10 mL aliquot was then fortified with 8.40×10^{-7} and $9.87 \times 10^{-7} \text{ mol L}^{-1}$ of HCT and TRT, respectively (equivalent to

250 ng mL^{-1}). For the electrochemical analysis, 4 mL of the urine sample, without any previous treatment, was placed in an electrochemical cell containing 6 mL of 0.10 mol L^{-1} B–R buffer (pH 4.0), resulting in concentrations of 3.36×10^{-7} and $3.95 \times 10^{-7} \text{ mol L}^{-1}$ of HCT and TRT, respectively. Analysis was performed as described in Section 2.3.1.

2.3.4. Hemodialysis sample

The hemodialysis sample was collected during the hemodialysis of a patient at the Araraquara Regional Hemodialysis Reference Center (São Paulo State). A 10 mL aliquot was fortified with $15 \mu\text{mol L}^{-1}$ of HCT and TRT.

For the electroanalytical measurements, a 2 mL aliquot of the sample (without previous treatment) was placed in an electrochemical cell containing 8 mL of 0.10 mol L^{-1} B–R buffer (pH 4.0) and was analyzed as described in Section 2.3.1. For measurements using the HPLC-DAD method, the sample was pretreated by filtering first through a $0.45 \mu\text{m}$ filter and then through a $0.22 \mu\text{m}$ filter. The analysis was performed using an injection volume of $20 \mu\text{L}$ of the sample, a Phenomenex Kinetex PFP column ($150 \times 4.6 \text{ mm}$; $5 \mu\text{m}$) heated at $35 \text{ }^\circ\text{C}$, and a mobile phase consisting of methanol (eluent A) and 0.01 mol L^{-1} acetate buffer (pH 5.6) (eluent B), at a flow rate of 1.2 mL min^{-1} . The eluent gradient was as follows: 0–2 min 5% A, 2–12 min 5–100% A, 12–14 min 100% A, 14–20 min 100–5% A.

3. Results and discussion

3.1. Characteristics of the GCE/MWCNT modified electrode

Electrochemical impedance spectroscopy (EIS) measurements were recorded using $5 \text{ mmol L}^{-1} \text{ Fe(CN)}_6^{3-/4-}$ in $0.1 \text{ mol L}^{-1} \text{ KCl}$. The charge transfer resistance (R_{ct}) of the unmodified GCE was 288Ω (Fig. 1). After modification of the electrode with MWCNT, R_{ct} decreased to 36.2Ω , which could be explained by the excellent intrinsic conductivity of MWCNT. The Nyquist plots for all electrodes were fitted using the Randles circuit (Fig. 1 insert).

3.2. Electrochemical behavior of HCT and TRT at the GCE/MWCNT electrode

The electrochemical behaviors of $100 \mu\text{mol L}^{-1}$ HCT and TRT were first investigated individually by cyclic voltammetry in 0.10 mol L^{-1} B–R buffer (pH 4.0), as shown in Fig. 2. For the glassy carbon electrode (GCE), HCT (Fig. 2.I.a) showed an anodic peak (E_{ap}) at 1.06 V , corresponding to oxidation of the $-\text{NH}-$ group [34], while no peak was observed in the cathodic scan, indicative of irreversible behavior [35]. For

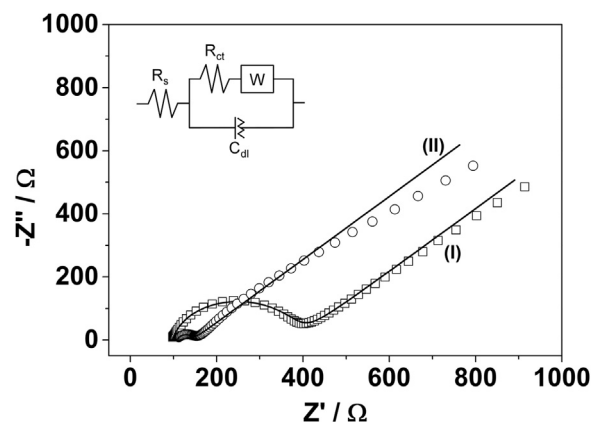


Fig. 1. Nyquist plots using $5.0 \times 10^{-3} \text{ mol L}^{-1} \text{ Fe(CN)}_6^{3-/4-}$ redox probes in $0.10 \text{ mol L}^{-1} \text{ KCl}$ solution for GCE (a) and GCE/MWCNT (b). Conditions: 10 kHz – 0.03 Hz ; 5 mV rms sinusoidal modulation at OCP.

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