



# Construction of novel sensitive electrochemical sensor for electro-oxidation and determination of citalopram based on zinc oxide nanoparticles and multi-walled carbon nanotubes



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## ABSTRACT

A new chemically modified carbon paste electrode (CMCPE) was applied to the simple, rapid, highly selective and sensitive determination of citalopram in human serum and pharmaceutical preparations using adsorptive square wave voltammetry (ASWV). The ZnO nanoparticles and multi-walled carbon nanotubes modified CPE (ZnO-MWCNT/CPE) electrode was prepared by incorporation of the ZnO nanoparticles and multi-walled carbon nanotubes (MWCNT) in carbon paste electrode. The limit of detection and the linear range were found to be 0.005 and 0.012 to 1.54  $\mu\text{mol L}^{-1}$  of citalopram, respectively. The effects of potentially interfering substances on the determination of this compound were investigated and found that the electrode is highly selective. The proposed CMCPE was used to the determination of citalopram in human serum, urine and pharmaceutical samples. This reveals that ZnO-MWCNT/CPE shows excellent analytical performance for the determination of citalopram in terms of very low detection limit, high sensitivity, very good repeatability and reproducibility over other methods reported in the literature.

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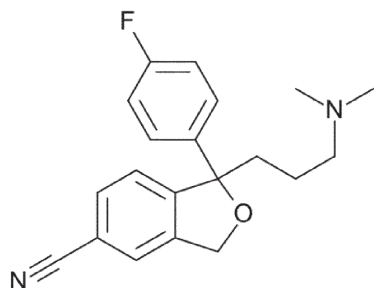
## 1. Introduction

Analysis of drugs in pharmaceutical products and biological samples is growing in importance, both in the development of more selective and effective drugs and in understanding their therapeutic and toxic effects [1–4]. Knowledge of drug levels in body fluids, such as serum, allows the optimization of pharmacotherapy and provides a basis for studies of patient compliance, bioavailability, pharmacokinetics, and the influence of co-medications. The treatment of depressive disorders is usually accomplished with antidepressants [5,6]. Therapeutic drug monitoring is underutilized in the field of psychiatry because the therapeutic ranges of antidepressants seem quite broad, leading to the generally accepted notion of low toxicity [7]. Citalopram (CIT, Scheme 1) is an antidepressant drug, which selectively potentiates serotonin neurotransmission by inhibiting serotonin reuptake. It offers similar therapeutic efficacy and a more favorable tolerability profile than the tricyclic antidepressants [8]. Citalopram is a racemic mixture, its pharmacological effect resides mainly in the *S*-(1) enantiomer and, to a lesser degree, in the *S*-(1)-desmethyl citalopram [9]. Nevertheless, for bioequivalence studies the recent guidance [10] recommends measurement of the race-mate using an achiral assay.

The advantages of the therapeutic profile of one important antidepressant, citalopram [11–13], have led to its increasing use in the treatment of depression. However, even if this compound has fewer undesirable side effects, it can lead to major intoxications [11]. Therefore, the development of a rapid and specific method allowing the screening and the determination of this new antidepressant drug in biological fluids could be of great interest either in therapeutic drug monitoring use or in toxicological screening in the case of a suicide involving this compound [14]. Analytical methods for the detection of anti-depressants are not only of interest in the field of clinical toxicology, but also in forensics because they are often involved in intoxications [15–19]. The methods described for the determination of citalopram in biological samples involve gas chromatography and high performance liquid chromatography [20,21]. One of the important steps in an analytical method is the extraction of the compounds of interest from the sample matrix. Liquid–liquid extraction (LLE) and solid-phase extraction (SPE) are the most common techniques for isolation and enrichment of citalopram prior to chromatographic analysis [22–29]. These methods have many disadvantages, as they are tedious, labor-intensive and time-consuming. Formation of emulsion is a major drawback during LLE process. This method also requires the use of large amount of highly purified solvents, which are often hazardous and lead to the production of toxic laboratory waste. However SPE needs a large volume of samples to obtain high enrichment factors. This could

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Scheme 1. Structure of CIT.

be a major limitation especially when biological samples are being analyzed. Therefore development of simple, fast and sensitive methods was necessary.

Over the past five decades, carbon paste, i.e. a mixture of carbon (graphite) powder and a binder (pasting liquid), has become one of the most popular electrode materials used for the laboratory preparation of various electrodes, sensors, and detectors [30–32]. In recent years, to improve the sensitivity, selectivity, detection limit and other features of CPE, chemically modified carbon paste electrodes (CMCPES) have been used. For example, within the electrode structure various materials such as chelating agents, ion exchangers or functionalized nanoparticles have been used as modifiers [33–37].

The operation mechanism of such CMCPES depends on the properties of the modifier materials used to impart selectivity and sensitivity towards the target species. Initially, non-conductive reagents, such as mineral oil or paraffin oil were used as binders [30].

Nowadays, due to the unique properties of carbon nanotubes (CNTs) such as ordered structure with high aspect ratio, ultra-light weight, high mechanical strength, high electrical conductivity, high thermal conductivity, metallic or semi-metallic behavior and high surface area, they have been widely used for the development of chemically modified electrodes [38–40]. The combination of these characteristics makes CNTs unique materials with the capability to promote electron transfer reaction and improve sensitivity in electrochemistry, and thus they are widely used to prepare modified electrodes. Moreover, extensive efforts have been devoted to design novel CNTs modified electrodes to improve the voltammetric determinations of organic [40–42] and inorganic compounds [38,43]. In comparison to the conventional CPEs, the carbon nanotube paste electrodes have shown a considerable enhancement in electrochemical signals leading to improvement of the detection limit in the voltammetric measurements.

In the present work, we investigated the performance of a ZnO and multi-walled carbon nanotube modified CPE using a room temperature ionic liquid (RTIL) as the binder (ZnO–MWCNT/CPE<sub>IL</sub>) as the working electrode for the determination of trace amounts of CIT by adsorptive square wave voltammetry (ASWV). The created selectivity in this method makes the electrode very suitable for the detection of trace amounts of CIT in various real samples. To the best of our knowledge, this electrode represents the better limit of detection and selectivity rather than other reported methods for electro-determination of CIT [44,45]. Also, in this paper, harmful substances, such as mercury, were not used to construct the electrode for the termination of this compound. The prepared modified electrode was successfully applied to the voltammetric determination of CIT in pharmaceutical and clinical samples. To the best of our knowledge this is the first report on the investigation of the electrochemical behavior of CIT at the modified CPE surface. The combination of the above-mentioned characteristics makes modified CPEs as a unique sensor with the potential for the diverse applications.

## 2. Experimental

### 2.1. Apparatus and chemicals

All electrochemical experiments including cyclic voltammetry (CV), square wave voltammetry (SWV) and other methods were performed using an Autolab Potentiostat/Galvanostat, Model 302 N. A conventional three-electrode system was used with a carbon paste working electrode (unmodified or modified), a saturated Ag/AgCl reference electrode and a Pt wire as the counter electrode. A magnetic stirrer (PAR-305) with a Teflon-coated magnet was used to provide the convective transport during the preconcentration step. The whole measurements were automated and controlled through the programming capacity of the apparatus. A pH-meter, Model 713, with a glass electrode (Metrohm, Swiss), was used to determine pH values of the solutions. The pharmaceutical samples (Citalopram hexal tablets from Hexal, Germany) were obtained from local drug stores.

All the chemicals were of analytical grade, or better purchased, and used as received. Unless otherwise stated, all the solutions were prepared with doubly distilled water (DDW). MWCNT (purity more than 95%) with outer diameter between 5 and 20 nm, inner diameter between 2 and 6 nm and tube length from 1 to 10  $\mu\text{m}$  was purchased from Plasmachem GmbH (Germany). Paraffin oil and graphite powder (mesh size < 100  $\mu\text{m}$ ) were obtained from Merck Company and used as received and n-octylpyridinium hexa-fluoro phosphate (OPFP) was purchased and used from Hangzhou Kemer Chemical Limited Company. Britton–Robinson (B–R) buffer was prepared in DDW and was used as supporting electrolyte. pH adjustments were performed with 0.01–1.0 mol L<sup>-1</sup> HCl or NaOH solutions.

### 2.2. Pretreatment of multi-walled carbon nanotube materials

A pre-treatment of the CNTs is usually necessary to eliminate graphitic nanoparticles, amorphous carbon, metallic impurities, and/or to improve the electron transfer properties and/or to allow further functionalization [46]. The pre-treatment consists of exposing the MCNTs to an acidic solution of sulfuric, nitric or hydrochloric acid, or mixture of these acids at room temperature, under refluxing or under sonication for different times [46,47]. Following one of the purification methodologies, 500 mg of MWCNT was heated at 400 °C using an air flow of 12 mL min<sup>-1</sup> (quartz tubular reactor of 14 mm diameter), for 1 h. To eliminate metal oxide catalysts, the heated processed amount of MWCNTs was dispersed in 60 mL of 6.0 mol L<sup>-1</sup> HCl for 4 h under ultrasonic agitation; filtered on a Whatman No. 42 filter paper and washed until the pH of the solution was neutral; and finally, dried.

### 2.3. Preparation of modified carbon paste electrode

The modified carbon paste electrode was prepared by mixing 75% (w/w) ZnO/MWCNT/graphite powder (8:14:53) with 25% (w/w) n-octyl-pyridinium hexa-fluoro phosphate (OPFP, as the binder) in a mortar and pestle. The mixture amount of 0.20 g was homogenized in a mortar for 30 min and the resulting composite was dispersed in dichloromethane (for more homogeneity of the electrode composite components leading to an increase in the reproducibility after each electrode surface polishing). The homogenized composite was stirred by a magnetic stirrer till the solvent evaporated completely. Then, the prepared modified composite was air dried for 24 h. Finally the homogenized paste was then inserted into a plastic needle-type capillary tube with a 1.5 mm diameter and a 5 cm length, using a 0.5 mm diameter copper wire connected to the measurement system.

### 2.4. Analytical procedure

The analysis of CIT using ASWV was carried out in a 25.0 mL aliquot (pH 5.0) using the following steps after purging with nitrogen for at

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