



# Development of electrochemical method for the determination of olaquinox using multi-walled carbon nanotubes modified glassy carbon electrode

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## ABSTRACT

A simple and highly sensitive method for the electrochemical determination of olaquinox (OLA) was developed, which was carried out on the multi-walled carbon nanotubes (MWCNT) modified glassy carbon electrode (MWCNT/GCE) using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The results showed that MWCNT remarkably enhanced the reduction of OLA, which improved the cathodic peak current of OLA significantly. Under the optimum condition, the linear range for the calibration curve was 0.3–18.0  $\mu\text{g mL}^{-1}$  with a detection limit of 0.26  $\mu\text{g mL}^{-1}$ . The MWCNT/GCE showed a well reproducibility and the relative standard deviation (R.S.D.) was 3.5% ( $n=9$ ). And a great anti-interference ability of the MWCNT/GCE was also observed. Finally, the MWCNT/GCE was satisfactorily employed to analyze some synthetic and real water samples.

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## 1. Introduction

Olaquinox (OLA; 2-(*N*-2-hydroxyethylcarbonyl)-3-methyl-quinoxaline-*N*<sup>1</sup>,*N*<sup>4</sup>-dioxide) being a well known growth promoting and antibacterial agent was widely used to promote growth, to improve feed efficiency, and to control swine dysentery and bacterial enteritis in the swine industry during the last century. However, its severe phototoxicity, mutagenicity, genotoxicity and carcinogenicity have been demonstrated by large numbers of studies [1–11]. Due to its toxicities and food safety concerns, the Commission of the European Community forbade the usage of OLA as animal growth promoter in 1998 [12]. But OLA is still broadly used as feed additive for swine, poultry and aquatic products in some regions of the world, which has caused wide public concern. During the feeding process and metabolism of animals, OLA will be accumulated in water and soil, which will have potential negative effects on the ecological environment. Therefore, the development of a simple, sensitive, rapid, and reliable method for the on-line monitoring of OLA is of great importance.

Various analytical methods for OLA monitoring have been reported in the literature such as liquid chromatography, liquid chromatography–tandem mass spectrometry, liquid chromatography–electrospray-mass spectrometry [13–18], spectrophotometry [19–21] and single-sweep oscillopolarography [22].

The chromatographic method is a common method to test OLA, which has high accuracy and recovery, well reproducibility, and reliable ability of qualitative analysis, but the main problems encountered in using such methods are either the need for derivatization or the need for time-consuming extraction procedures and high cost. There were also some reports on the determination of OLA by spectrophotometry in the last century, but the background interference and low sensitivity restrict its application especially in the trace analysis of OLA. The electrochemical method has great potential for environmental monitoring because of its inherent advantages such as fast response speed, sensitivity, ease of miniaturization, low cost, simplicity, timesaving and *in vivo* real-time determination [23]. Especially single-sweep polarography and pulse voltammetry (DPV), have high sensitivity and excellent selectivity, make it possible to decrease the analysis time as compared to the time exhaustive chromatographic methods. The literature reported that the mercury film electrode was used in the determination of OLA by single-sweep oscillopolarography [22], and the detection limit was low (0.0026  $\mu\text{g mL}^{-1}$ ), but the mercury is so poisonous that can pose a great threat to the environment and human health. Therefore, building an environment-friendly electrochemical analysis method of OLA is urgently needed.

Carbon nanotubes (CNTs), ever since their discovery, have attracted extensive attention due to their unique physicochemical and electrical properties. Because of their ability to promote charge transfer reactions, CNTs are considered to be extremely superior electrode material and have been widely utilized for the modification of electrodes [24–27].

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However, literatures on the electrochemical techniques for OLA determination are limited. As far as we know, studies on the application of the multi-walled carbon nanotubes (MWCNT) modified glassy carbon electrode (MWCNT/GCE) for OLA determination has not been reported. The proposed method has advantages such as no time-consuming sample preparation step prior to OLA assay, high sensitivity, rapid response, good reproducibility, and low detection limit compared to other reported methods. In this paper, the electrochemical behavior of OLA on the MWCNT/GCE was studied. The conditions of OLA determination by difference pulse voltammetry (DPV) were optimized, the interference experiment was carried out, and some synthetic and actual water samples were determined by the proposed method. An attempt was made to build an electrochemical analysis method of OLA.

## 2. Materials and methods

### 2.1. Apparatus and chemicals

Cyclic voltammetry (CV) and DPV were performed using a CHI 660D electrochemical workstation (Chenhua Instrument Company of Shanghai, China) coupled with a conventional three-electrode cell. The working electrode was the MWCNT/GCE (3 mm diameter), the auxiliary electrode platinum wire, and the reference electrode saturated calomel electrode (SCE). A S-3C Model pH meter (Shanghai Precision Scientific Instrument Co., China) was used for measuring the pH of solutions.

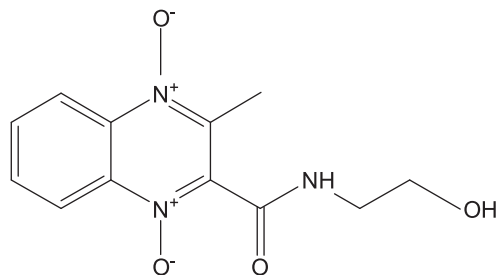
MWCNT (length 10–30  $\mu\text{m}$ ; specific surface area  $> 500 \text{ m}^2 \text{ g}^{-1}$ ; outer diameter  $< 8 \text{ nm}$ ; 95% purity) was purchased from Chengdu Organic Chemicals Co., Ltd., Chinese Academy of Sciences. The analytical standard OLA ( $\text{C}_{12}\text{H}_{13}\text{N}_3\text{O}_4$ ; MW 263.25; solubility at  $25^\circ\text{C}$ :  $5 \text{ mg mL}^{-1}$  in water; CAS no. 23696-28-8; 98.4% purity) was purchased from China Institute of Veterinary Drug Control (Beijing, China), and its molecular structure is shown in Scheme 1.

The analytical reagent grade *N,N*-dimethylformamide (DMF) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All other chemicals were of analytical reagent grade and purchased from Shenyang Chemical Company, China. Ultrapure water used throughout experiments was purified using a Sartorius Arium 611 system (Sartorius, Göttingen, Germany).

A  $600.0 \text{ mg mL}^{-1}$  stock standard solution of OLA was prepared by dissolving 609.8 mg OLA in ultrapure water and diluting to the mark in a 250 mL brown volumetric flask, and was kept in the dark below  $4^\circ\text{C}$ . A  $3.0 \text{ mg mL}^{-1}$  MWCNT–DMF dispersion was prepared by dissolving 3.2 mg MWCNT in 1 mL DMF by ultrasonication for 60 min.

### 2.2. Construction of the MWCNT/GCE

The GCE was polished with three grades of  $\alpha\text{-Al}_2\text{O}_3$  slurries (1.0, 0.3 and  $0.05 \mu\text{m}$ ) respectively, followed by sonicated in



Scheme 1. Molecular structure of OLA.

anhydrous ethanol and ultrapure water after each stage of polishing successively. A  $23 \mu\text{L}$  drop of  $3 \text{ mg L}^{-1}$  MWCNT–DMF dispersion was coated on the surface of GCE, and then the solvent was evaporated under the infrared lamp to obtain the MWCNT/GCE.

### 2.3. Procedure for OLA analysis

The electrochemical behavior of OLA was studied by CV; the determination of OLA was performed by DPV. All the experiments were carried out in a conventional electrochemical cell holding  $5.00 \text{ mL } 0.06 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$  (pH 1.1) and certain amount of OLA at room temperature ( $25 \pm 1^\circ\text{C}$ ). Before OLA analysis, the experimental solution was deaerated by highly pure nitrogen for 10 min. The CV was recorded from  $-0.60$  to  $0.80 \text{ V}$  at a scan rate of  $0.1 \text{ V s}^{-1}$ ; the DPV was recorded from  $-0.60$  to  $0.80 \text{ V}$  (with an amplitude of  $50 \text{ mV}$  and a pulse period of  $0.5 \text{ s}$ ), and the cathodic peak current at  $-0.280 \text{ V}$  was chosen for the quantitative analysis of OLA.

### 2.4. Water samples

The real water samples were collected from two different rearing ponds in Yuhong Borough Shenyang City (real Sample 1 and Sample 2), one aquatic product market in Huanggu Borough Shenyang City (real Sample 3), the Xinkai River in Shenyang City (real Sample 4) and the North Canal in Shenyang City (real Sample 5). Four synthetic water samples were prepared by dissolving a certain amount of OLA and 20-fold common existing substances with ultrapure water. Suitable amounts of  $1.0 \text{ mol L}^{-1} \text{HCl}$  were added to adjust the pH of real samples to be 2 for storage. All above samples were stored at  $4^\circ\text{C}$  in low-density polyethylene (LDPE) bottles.

## 3. Results and discussion

### 3.1. Electrochemical behavior of OLA

The CVs of OLA on the bare GCE and the MWCNT/GCE in  $0.06 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$  (pH 1.1) are illustrated in Fig. 1. As can be seen, no visible signal was found on the bare GCE (Curve a) but two sharp and well-resolved reduction peaks at  $-0.225$  and  $-0.406 \text{ V}$  (Curve c; P1, P2) were found on the MWCNT/GCE,

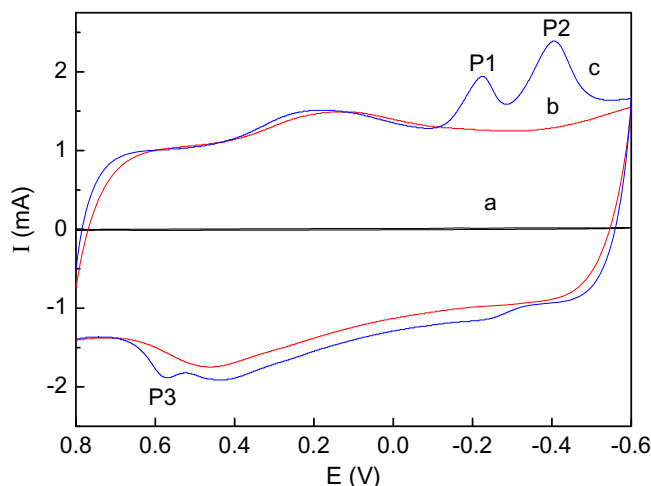


Fig. 1. CVs of OLA in  $0.06 \text{ mol L}^{-1} \text{pH } 1.1 \text{H}_2\text{SO}_4$  solution ( $C_{\text{OLA}}$ :  $5.9 \mu\text{g mL}^{-1}$ ; a: OLA on the bare GCE; b: blank on the MWCNT/GCE and c: OLA on the MWCNT/GCE). Scan rate  $0.1 \text{ V s}^{-1}$ , quiet time 2 s.

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