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# Molecularly imprinted electrodeposition o-aminothiophenol sensor for selective and sensitive determination of amantadine in animal-derived foods

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ABSTRACT

A novel molecularly imprinted electrochemical sensor was successfully fabricated for detection of amantadine (AM) residue in animal-derived foods. This molecularly imprinted film was prepared by electrodepositing *o*-aminothiophenol (*o*-AT) on a gold electrode surface by cyclic voltammetry (CV). A series of parameters, including template/monomer ratio, CV scanning cycle number, and immersion time, were optimized in detail for controlling the performance of this imprinted sensor. The fabricated sensor exhibited remarkable characteristics of high selectivity, sensitivity, and reproducibility, and long-term stability for AM detection. The imprinting factor for AM achieved to 2.33 and the selectivity factor for three structural analogues achieved to 6.20, 5.29 and 3.95. Under optimal experimental conditions, good linearity was observed between the current response and AM concentration, ranging from $4.0 \times 10^{-7}$ mmol $L^{-1}$ to $8.0 \times 10^{-6}$ mmol $L^{-1}$, with a detection limit of $3.06 \times 10^{-9}$ mmol $L^{-1}$ ($S/N = 3$). Satisfactory results for the measurement of real samples were also obtained using the proposed sensor, and were consistent with those derived from typical high-performance liquid chromatography-tandem mass spectrometry with a high correlation coefficient ($R^2 > 0.99$). These results demonstrate that the proposed sensor could serve as a valuable tool for accurate and reliable detection of AM residue in animal-derived foods.
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## 1. Introduction

Amantadine (AM) is used pharmacologically as a glutaminergic receptor antagonist, and is therapeutically administered for treatment of both influenza and Parkinson's disease [1–3]. This compound contains a stable tricyclic amine in its molecular structure and can inhibit viral replication by blocking channel activity of the M2 proton channel, which is critical in the virus life cycle [4,5]. In recent years, with the worldwide outbreak of avian influenza, enhanced dependence of the breeding industry on AM has resulted in disordered expansion of its dosage and scope, leading to emergence of new strains that pose danger to public health, such as drug-resistant variants [6], as well as side effects including jitteriness, anxiety, nightmares, and, occasionally, hallucinations [7]. Since 2005, AM has been banned as an antiviral agent in poultry farming in many countries including the USA and China, owing to the potential resistance for human beings [8]. Nevertheless, this antiviral drug is still illegally used for the treatment of avian influenza, especially in chicken farming in China [9,10]. Therefore, to improve food quality and reduce the potential hazardous effects of AM to human health, it is of great significance to establish a selective, sensitive, and low-cost method to detect AM residue in animal-derived foods.

Currently, the methods for AM residue detection in animal-derived foods are mainly based on instrumental analysis and immunoaffinity. Instrumental analysis methods, including high-performance liquid chromatography (HPLC) [11,12], HPLC-tandem mass spectrometry (MS/MS) [13], gas chromatography (GC) [14], GC–MS [15], capillary electrophoresis [16], micellar electrokinetic chromatography [17], and spectrophotometric [18–21] and potentiometric methods [22,23], are all accurate, precise, and repeatable, but are expensive and require use of complicated instruments. More importantly, these instrumental methods usually require time-consuming and selective pretreatment steps for sample purification. Alternatively, biological analysis [24] based on

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antigen-antibody reaction shows good specificity, but the whole reaction process still heavily relies on the detection conditions because of the poor stability of biological materials. In this study, we aimed to efficiently combine the advantages of the instrumental and biological analysis methods to develop a simple, inexpensive, accurate, selective, and sensitive method for AM residue detection in animal-derived foods.

Miniaturized sensors with advantages of low cost, high sensitivity, and fast response have attracted considerable attention in the field of residual-drug testing. Biosensors have the drawbacks of instability and poor reproducibility due to the particularity of biological materials; therefore, choosing synthetic counterparts to replace a biological receptor as the recognition element of sensors has gradually become a primary focus of many studies [25]. Molecularly imprinted polymers (MIPs) with high affinity and selectivity are widely used as synthetic counterparts, owing to their several advantages of chemical and mechanical stability, low cost, and ease of preparation [26,27]. Depositing an MIP directly on the electrode surface using an electrochemical method has many benefits such as simple preparation, easy control of the film thickness, and high reproducibility of identical polymer films [28,29].

In the present work, we attempted to analyze the features of a molecularly imprinted electrodeposition sensor for the selective and sensitive detection of AM in animal-derived foods. This is the first example of the detection of AM by an electrodeposited MIP electrochemical sensor. First, self-assembly of a functional monomer, *o*-aminothiophenol (*o*-AT), was used as the connection medium between the MIP and surface of a gold (Au) electrode, and then the molecularly imprinted poly-*o*-AT film was electrodeposited on the Au electrode surface with AM as the template molecule. After elution of the AM template, the template entrapped in the polymer was removed to release the imprinted sites in the film. The present sensor provides a simple, inexpensive, accurate, specific, and sensitive electrochemical method for detecting AM residue in animal-derived foods.

## 2. Experimental section

### 2.1. Reagents and instruments

The imprinting AM template and other analytes, including rimantadine (RT), 1-chloroadamantane (CMT), and adamantine (AMT) (Scheme 1), were purchased from Sigma-Aldrich (St. Louis, MO, USA). The polymeric monomer *o*-AT and the supporting electrolyte tetrabutylammonium perchlorate (analytical grade), used for the synthesis reaction, were also obtained from Sigma-Aldrich (St. Louis, MO, USA). Potassium ferricyanide ($K_3[Fe(CN)_6]$), methanol, HCl, trichloroacetic acid (TCA), ammonium hydroxide, isopropanol, $H_2O_2$, $H_2SO_4$, and other chemicals used in the experiments were purchased from Tianjin No. 1 Chemical Reagent Factory (Tianjin, China) and were of at least analytical grade. Double-distilled water (18.2 MΩ cm) was prepared using a water purification system (Labconco, Kansas City, USA).

Stock solutions of the individual analytes were prepared by dissolving 6.0 mg of analyte in 10.0 mL of methanol (molar concentration: AM: 4.0 mmol $L^{-1}$, RT: 3.3 mmol $L^{-1}$, CMT: 3.5 mmol $L^{-1}$, AMT: 4.4 mmol $L^{-1}$) and stored at 4 °C in the dark. The corresponding working solutions were obtained by diluting the individual stock solutions with methanol to the required concentrations.

All electrochemical experiments were performed at room temperature, with a Lanlike 2006 electrochemical workstation (Tianjin Lanlike Chemical and Electronic High Technology Co., Ltd., China) connected to a personal computer. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were carried out with a three-electrode system consisting of a saturated calomel electrode as a reference electrode, a platinum wire as an auxiliary electrode, and the differently modified Au electrodes as working electrodes. HPLC–MS/MS (Agilent LC 1200; MS 6410, USA) was used for validation of the obtained experimental results.

### 2.2. Preparation of molecularly imprinted electrodeposited electrodes

Prior to modification, the surface of the Au electrode was polished carefully with metallographic abrasive paper (0.50 μm) and alumina slurry (0.05 μm). It was then immersed in "Piranha" solution (30% $H_2O_2$:98% $H_2SO_4$ = 1:3, v/v; caution: this solution causes strong oxidation and should not be mixed with an organic solvent) for 5 min, followed by rinsing thoroughly with double-distilled water to remove external contaminants. Then, the electrode was electrochemically activated in 0.05 mol $L^{-1}$ $H_2SO_4$ by CV scanning from −0.2 V to +1.0 V until a stable electrochemical response was obtained, and then dried in air.

The preparation process of the AM-imprinted film on the Au electrode is shown in Scheme 2. First, the pretreated electrode was immersed in 50 mL of the electropolymerization solution, which contained methanol, 50 mmol $L^{-1}$ of *o*-AT, 10 mmol $L^{-1}$ of AM, 5 mmol $L^{-1}$ of tetrabutylammonium perchlorate, and 10 mmol $L^{-1}$ of HCl, overnight to allow *o*-AT self-assembly. Prior to use, the electropolymerization solution was bubbled with nitrogen gas for about 10 min to remove oxygen. The electrode was placed in the electropolymerization solution at −0.8 V for 10 min to allow for monolayer formation. Then, the AM MIPs were produced via electrodeposition by CV scanning for 25 cycles in the potential range from +0.2 V to +1.4 V at a scan rate of 50 mV $s^{-1}$ in the above-mentioned solution. Subsequently, the modified electrode was treated with HCl (1.0 mol $L^{-1}$) at a potential of +0.8 V for 10 min so that the AM would protonate, making it easy to remove. Finally, the modified electrode was ultrasonicated in methanol and double-distilled water for 10 min twice to remove the template molecule, and was dried with nitrogen for further use.

For comparison, a non-imprinted (NIP) electrode was fabricated under the same experimental conditions, but in the absence of the template molecule AM.

### 2.3. Electrochemical measurement

The CV and DPV methods were used to characterize the electrochemical behavior of the MIP and NIP films on the electrode surface. The CV experiment was carried out in a 1.0 mmol $L^{-1}$ $K_3[Fe(CN)_6]$ solution containing 0.2 mol $L^{-1}$ $KNO_3$, and the scanning potential range was from +0.6 V to −0.2 V at a scan rate of 100 mV $s^{-1}$. The DPV measurement was performed in the scanning range from +1.0 V to +0.2 V. The potential increment, pulse amplitude, pulse width, pulse period, and quiet time were 0.01 V, 0.4 V, 0.5 s, 0.4 s, and 1 s, respectively. Prior to electrochemical measurement, the tested electrode was immersed in 0.1 mol $L^{-1}$ $KNO_3$ containing either AM or its structural analogs for 5 min under stirring. After each measurement, the template-entrapped electrode was scanned to reach +0.80 V, and was then held at this potential for the purpose of removing either the AM molecules or structural analogs in the polymer to be used for subsequent analyses.

### 2.4. Sample pretreatment

Five different sample matrices (chicken muscle, chicken liver, pork, beef, and mutton) obtained from a local market were chosen to confirm the performance of the MIP-modified electrode. The sample pretreatment process was as follows: crushed samples (2.0 g) were accurately weighted, placed into a 50-mL centrifuge tube. Three levels of AM (0.030, 0.060, 0.090 μg $g^{-1}$) were spiked

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