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Determination of histamine in fish muscle at multi-walled carbon nanotubes coated conducting polymer modified glassy carbon electrode

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ABSTRACT

Glassy carbon electrode was modified with multi-walled carbon nanotubes, electropolymerized 4-amino-3-hydroxynaphthalene sulfonic acid, and their layer-by-layer composite. The electrodes were used to study the oxidation of an important fish spoilage indicator, histamine. Enhanced current responses and lower peak potentials were observed for histamine oxidation at modified electrodes compared to the bare electrode. Among the modified electrodes, a better catalytic response was observed using the multi-walled carbon nanotubes coated polymer modified glassy carbon electrode. This composite electrode was employed for the analytical determination of histamine after experimental parameters were optimized. Under optimum conditions, the oxidation peak current increased linearly with the concentration of histamine over the range of 1.0×10^{-7} to 1.0×10^{-4} M. The calculated limit of detection (3σ) and limit of quantitation (10σ) were 7.62×10^{-8} M and 2.54×10^{-7} M, respectively. The electrode showed excellent repeatability (2.80%) and reproducibility (4.60%) for measurements at 10.0×10^{-6} M histamine. The method was also successfully applied for the determination of histamine in fish muscle extract and spiked sample recovery results were in the range of 96.6–102.9%.

1. Introduction

Histamine (Fig. 1) is a biologically active compound playing important roles in a number of normal and abnormal physiological processes [1]. It is found in all human tissues acting as a chemical mediator in inflammation, gastric acid secretion and neural modulation [2,3]. Histamine also occurs exogenously in food supply produced by the decarboxylation of the essential amino acid, histidine, by bacterial action during food processing and storage [4,5]. Histamine poisoning is a food-borne chemical intoxication resulting from the ingestion of foodstuffs that contain high levels of histamine [1]. The symptoms of the poisoning include headache, nausea, vomiting, diarrhea, itching, oral burning sensation, red rash, and hypotension, usually resolved by taking antihistaminic drugs [6].

Histamine content in food is commonly regarded as one of the biomarkers in food quality monitoring during production, storage and transportation [3,5]. As a result, the United States Food and Drug Administration (FDA) has established 50 ppm of histamine as the chemical index for fish spoilage [7]. Based on the assessment of poisoning cases, the guidance levels suggested for histamine content in seafood are: for safe consumption <50 ppm; possibly toxic 50–200 ppm; probably toxic 200–1000 ppm and toxic and unsafe for human consumption >1000 ppm [6,8]. Therefore, the analytical determination of histamine is an important topic in clinical and food chemistry.

As a result, several analytical methods including high performance liquid chromatography (HPLC) [9–12], liquid chromatography (LC) [13,14], capillary electrophoresis (CE) [15,16], gas chromatography–mass spectrometry (GC–MS) [17,18], fluorometry [19], gas chromatography (GC) [20] and liquid chromatography–mass spectrometry (LC–MS) [21,22] have been reported. However, these techniques often suffer from limitations such as need for sample pre-treatment, necessity of derivatization, long analysis time and high cost of operation.

On the other hand, electrochemical methods offer a promising alternative due to their simplicity, precision, rapid response and low cost of instrumentation. In this regard, histamine has been detected amperometrically by enzyme based biosensors using

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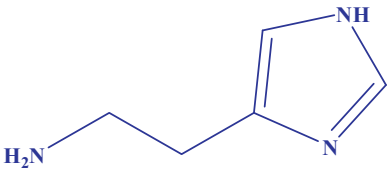

Fig. 1. Chemical structure of histamine.

immobilized amine oxidase [8,13,23–25], methylamine dehydrogenase [26] and quenohemoprotein amine dehydrogenase [2]. These biosensors have serious limitations with respect to substrate specificity and interference from molecular oxygen [27]. Despite major advantages offered by conventional modified electrodes, only few reports are available for histamine determinations which include: boron doped diamond (BDD) [5] and glassy carbon electrode modified with gold nanoparticles [28], nickel [3] and thin mercury films [4].

In recent years, conducting polymer modified electrodes have attracted much attention due to their good stability, reproducibility, homogeneity in electrodeposition, strong adherence to electrode surfaces and their available active sites [29]. Studies on poly(4-amino-3-hydroxynaphthalene sulfonic acid) modified glassy carbon electrode [*p*-(AHNSA)/GCE] have demonstrated improved electrochemical behavior for the oxidations of nicotine [30], quinine [31], and caffeine [32].

Similarly, multi-walled carbon nanotubes (MWCNTs) have also been used as novel materials in electrochemical sensor applications. Their unique properties including high chemical and thermal stability, high elasticity, and high tensile strength make them suitable to be used as electrode modifiers [33]. Recently, the electrochemical behavior and analytical determination of berberine [34], epinephrine [35], and paracetamol [36] at multi-walled carbon nanotubes modified glassy carbon electrode (MWCNTs/GCE) have been reported. The use of composite modified electrodes involving conducting polymers and carbon nanotubes for electroanalytical applications has also been reported to increase the catalytic role of both materials [37]. In this work, a multi-walled carbon nanotubes coated poly(4-amino-3-hydroxynaphthalene sulfonic acid) modified glassy carbon electrode [MWCNTs/*p*-(AHNSA)/GCE] is developed for the analytical determination of histamine. To the best of our knowledge, the composite use of MWCNTs and *p*-(AHNSA) for any similar applications was not reported previously.

2. Materials and methods

2.1. Reagents and instruments

All chemicals were of analytical grade and were used as received without any further purification. All aqueous solutions were prepared with doubly distilled water. Histamine dihydrochloride, creatine and glycine were purchased from Sigma Chemical Co., St. Louis, USA. Histidine monohydrochloride, di-sodium hydrogen orthophosphate, sodium di-hydrogen orthophosphate, methionine and phenylalanine were supplied by BDH Chemicals Ltd., England. Multi-walled carbon nanotubes (>7.5% MWCNTs) and HPLC grade *N*,*N*-dimethyl formamide (DMF) were purchased from Sigma–Aldrich and Riedel-de Haen AG, respectively. Histamine stock solution of 50.0×10^{-3} M was prepared in doubly distilled water and was diluted using an appropriate buffer solution before measurements.

All electrochemical measurements were performed using CHI760D Electrochemical Workstation (CH Instruments, Austin, TX, USA). A conventional three electrode system was employed consisting of bare glassy carbon electrode (GCE) (3 mm in diameter), *p*-(AHNSA)/GCE, MWCNTs/GCE, or MWCNTs/*p*-(AHNSA)/GCE as the working electrode, silver/silver chloride (Ag/AgCl, KCl, saturated) as reference electrode and platinum wire as the auxiliary electrode. pH of buffer solutions were monitored using Jenway 3345 ion meter.

2.2. Preparation of the modified electrode

Before modification, the GCE was polished with 1.0, 0.3 and 0.05 micro size alumina powders on polishing cloth and rinsed with distilled water. The polymer film was then deposited on the polished GCE by electropolymerization of 2.0×10^{-3} M 4-amino-3-hydroxynaphthalene sulfonic acid (AHNSA) in 0.1 M HNO_3 solution. The electropolymerization was performed using cyclic voltammetry by scanning the potential from −0.8 V to +2.0 V for 15 cycles at 0.1 V s^{-1}. Then, the electrode was placed in monomer free 0.5 M H_2SO_4 solution and stabilized by sweeping the potential between −0.8 V and +0.8 V until a stable voltammogram was obtained. This *p*-(AHNSA)/GCE was coated with 10 μL of the MWCNTs suspension and allowed to dry at room temperature to prepare the MWCNTs/*p*-(AHNSA)/GCE. The MWCNTs suspension was prepared by dispersing 2 mg of MWCNTs in 2 mL of DMF and then immersed in an ultrasonic bath for 30 min. The polymer modified (*p*-(ANHSA)/GCE) and nanotubes modified electrodes (MWCNTs/GCE) were prepared in a similar procedure without the nanotubes coating and electropolymerization steps, respectively.

2.3. Sample preparation

The fish sample, originally from Lake Tana (near Bahir Dar, Amhara region, Ethiopia) was purchased from a local supermarket and was kept in a refrigerator until analysis. The sample extraction was based on previous reports with some modifications [25,38]. Briefly, fish muscle of 10.0 g was homogenized with 100 mL of 0.1 M phosphate buffer solution of pH 7.0. The homogenate was ultrasonicated for 10 min and filtered through a Whatman filter paper. 100 μL of this filtrate was transferred to a 10 mL volumetric flask and diluted to the mark with the same phosphate buffer solution to make the final determination.

3. Results and discussion

3.1. Electrochemical behavior of histamine

Cyclic voltammetry was used to study the oxidation of 1.0×10^{-3} M histamine in 0.1 M phosphate buffer solution (pH 7.0) at bare GCE, *p*-(AHNSA)/GCE, MWCNTs/GCE and the composite MWCNTs/*p*-(AHNSA)/GCE. In all the voltammograms (Fig. 2), a single oxidation peak was observed with no corresponding reduction peak in the reverse potential scan indicating the irreversibility of the electrode reaction. The oxidation peak is observed at +1.37 V at the bare electrode which shifted negatively by about 0.16 V at the modified electrodes. Moreover, both the *p*-(AHNSA)/GCE and MWCNTs/GCE showed significant enhancement in peak current responses of 13-fold and 34-fold of the bare electrode response, respectively. This indicates the electrocatalytic effect of the polymer and nanotube modifiers used for the oxidation of histamine. The higher performance of the polymer modified electrode can be explained by the existence of electrostatic interaction between the charges on the protonated histamine and the polymer film functional units. While, the catalytic effect of MWCNTs stems from the structure and unique properties they possess: such as large specific surface area, strong adsorptive ability and subtle electronic properties [33]. The result at the MWCNTs/*p*-(AHNSA)/GCE showed a further enhancement in the peak current response of about 40