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Enzyme-free amperometric method for rapid determination of histamine by using surface oxide regeneration behavior of copper electrode

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ABSTRACT

This work demonstrated a novel amperometric method to measure the concentration of histamine directly without using any enzymatic reaction or a complicated derivation scheme. Based on the strong chelating property between histamine and cupric (II) ions, cupric oxide would be dissolved by the histamine and a cupric-histamine complex would be formed on the electrode surface, subsequently, an oxidative current resulted from the regeneration of the surface cupric oxide was used to reflect the concentration of the histamine in the sample. Under the optimal conditions with operating potential at 200 mV in a 100 mM phosphate buffer, pH 10.0, containing 50 mM acetate, a suitable dynamic range of histamine from 1 to 750 μM with a sensitivity of 15 nA/μM (R = 0.999) and a detection limit of 0.33 μM was achieved on a typical FIA system. Subsequently, the performance of this scheme was integrated with high-performance liquid chromatography as an electrochemical detector. In optimal conditions, the linear range is estimated from 10 to 2500 μM (0.5–125 nmol per injection), which is an adequate range for the determination of the freshness quality of a seafood. Finally, the feasibility of this scheme in real sample application was demonstrated by evaluating the histamine level in a fresh saury fish and a defrost one, respectively.

1. Introduction

Fish is considered as an idea nutrition source for developing infants and children due to its high quality of protein, vitamins and minerals. However, since a dead fish loses its protection to bacterias and microorganisms, the propagation of these spoiled microorganisms makes this ingredient release unpleasant flavors, and toxic with time [1]. Therefore, the freshness value of fish becomes an important factor to evaluate the safety of this ingredient. In literatures, a number of index including total volatile basic nitrogen, K value, biologic amines and histamine have been proposed [2]. Among them, histamine level has been proposed as a significant index to evaluate the freshness of fish. Generally, the ingested histamine would be metabolized by diamineoxidase (DAO) and histamine-N-methyltransferase to maintain its plasma concentration around ng/mL, otherwise, several symptoms, including tachycardia, headache, flushing, urticaria, pruritus, bronchospasm and cardiac arrest would be caused by the high blood histamine level [3]. Because its potential risk to human health, the European Union established Commission Regulation No. 2073/2005 to limit histamine cannot exceed 200 ppm [4], in addition, the Food and Drug Administration (FDA) has also set a toxic and a caution level of histamine in fishes at 500 and 50 ppm, respectively [5].

In the determination of histamine in foodstuff or biological samples, most studies adopt optical detectors such as UV–vis and fluorescence to determine the histamine, and uses capillary electrophoresis or high performance liquid chromatography (HPLC) to isolate the histamine from the matrix [6,7]. However, histamine possesses a poor property to absorb or emit photons, a post- or pre-column labeling is required to obtain a suitable sensitivity of these methods [8,9]. Although the strategy of derivatization is a routine scheme in the analytical chemistry, it requires a tedious and time consuming process to tag a chromophore with the analyte. Mass spectrometer (MS) provides another sensitive route in the determination of the histamine [10], however, in order to keep the cleanliness of the vacuum system, the flow rate of an HPLC/MS combination is limited below 200 μL/min and requires a complicate interface design to further reduce the flow rate during ionization

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[11]. In contrast to the complicated interface design of an HPLC/MS, an electrochemical detector is another choice in an HPLC study due to its high sensitivity and simple interface. Unfortunately, the electrochemical property of histamine is also poor and requires an extreme overpotential to obtain an adequate sensitivity in real applications. In literatures, direct oxidation of histamine has been reported to exceed 1.2 V, and serious problems, including unstable response due to electrode surface fouling and the interference from most antioxidants need be further considered [12,13]. Further investigations utilized several metals based modified electrodes such as gold nanoparticle coupled with a pulsed amperometric scheme [14] and a nickel film modified electrode [15] to perform the direct determination of the histamine. However, the operational potential of these schemes is over than 0.7 V, which still suffer from the problem of antioxidants. In order to overcome the disadvantage of high detection potential in direct oxidation of the histamine, the strategy of immobilization of several histamine relevant enzymes such as monoamine oxidase and diamine oxidase has been modified on the electrode surface and measuring its enzymatic product, hydrogen peroxide, to reflect the histamine level in the sample. In literature, various hydrogen peroxide sensitive modifiers such as manganese dioxide [16] and ceria–polyaniline [17] have been used to participate in the histamine determination. However, both of the monoamine oxidase and the diamine oxidase are not specific to the histamine only, several amine based analytes such as catecholamines and polyamines have been also reported as a suitable substrate for these enzymes [18,19]. The low specificity of these enzymes indicates their relevant sensors may require an extra separation scheme to promote the analytical performance. Another challenge of these enzymatic sensors is their stability in a flow system. The immobilization scheme should compromise the enzymatic activity with its erosion stability of the running buffer. In literature, a histamine specific enzyme couples with a flow injection scheme has been reported by Takagi and Shikata who extracted a histamine specific dehydrogenase from *Nocardioides simplex* [20], and this enzyme was further immobilized on an Osmium (4,4-dimethylbipyridine) modified electrode. Although this method possesses a good correlation with an HPLC in the determination of the histamine, a tailing peak due to a bulky enzyme layer and a complicate process in enzyme purification are two major drawbacks for this application.

Recently, a ReO_2 modified electrode shows a dramatic catalytic oxidation behavior which could directly monitor the histamine at −0.1 V (Ag/AgCl, 3 M) in a flow injection system without using any enzyme [21]. Although this measurement did not suffer from biological interferences, a serious problem of peak tailing might limit its further application. In our previous studies, we have demonstrated a structure-specific based amperometric scheme on a copper electrode for direct determination of a series of electrochemical inactive analytes [22–25]. We found that this method is particularly useful in the determination of an electrochemically inactive molecule with multi-dentate groups, especially with amine or thiol functional groups that can form a complex with a cuprous or a cupric ion. It is found that the amine groups at α and π position of histamine can be used as a bi-dentate ligand for the cupric ion. Here, we extend our previous effort to develop an amperometric method for monitoring the histamine molecule itself. This simple method does not need a sophisticated operator and possesses a suitable dynamic range with an excellent stability in the determination of histamine. Finally, in order to demonstrate the feasibility of this method in real application, this sensor was also coupled with an HPLC to determine the histamine level in a saury fish. The detail experimental designs, analytical performances of the proposed scheme are also described in this study.

2. Experimental

2.1. Apparatus

Cyclic voltammetric experiments, electrochemical deposition, and thin-layer amperometric detection in the flow injection analysis (FIA) system were carried out with a CHI 750A electrochemical workstation from CH Instruments (Austin, TX, USA). The flow rate of the FIA system was controlled with a syringe pump (74900 series, Cole-Parmer Instrument Company, Illinois, USA). A GBC LC 1150 HPLC system (Gibco, Dandenong, Vic, Australia) with 50 μL sample loop was utilized in the HPLC analysis. A water durable ODS column (InertSustain, AQ-C18, GL Sciences, Japan) was adapted to perform the HPLC study.

2.2. Reagents

Histamine, L (+) -ascorbic acid, uric acid, dopamine, (±) -epinephrine, acetic acid, copper sulfate, thiourea, sulfuric acid, dextrin, cyclohaxanone, sodium dodecyl sulfate, succinic acid, malic acid, spermine, spermidine, putrescine, cadaverine, tryptamine, 2-phenylethylamine, tyramine agmatine, and 4-acetaminophenol (99.5%) were obtained from Sigma-Aldrich (St. Louis, USA). Deionized water was prepared by a Barnstead water purification system with a resistance of 18.3 MΩ-cm (Easypure Ro and Easypure UV/UF, Dubuque, IW, USA) was used to make up for all the buffer solutions.

2.3. Electrode preparation and preservation

The copper plating electrode was fabricated by electrochemical deposition of copper layer on a platinum electrode surface (Φ = 3 mm). The composition of this copper plating solution is 210 g/L copper sulfate, 60 g/L sulfuric, 120 ppm potassium chloride, 0.1 g/L thiourea and 0.01 g/L dextrin. Before deposition, this platinum electrode was electrochemical polished by scanning a potential range from 1.0 V to −0.2 V for 20 cycles in a 0.1 M H_2SO_4 solution. Subsequently, this platinum electrode was then transferred into the copper plating solution and a constant potential of−0.2 V was applied for 400 s. Before each study, the copper plating electrode was activated firstly by injection 500 μM histamine for 5 times to obtain a stable current response. When not using, this sensor was stored in a dry box containing nitrogen gas to maintain its activity.

2.4. Long-term electrolysis

A copper wire from a local supplier (Φ = 3 mm) was used for long-term electrolysis. A portion approximately 2 cm copper wire was immersed into a 50 mM phosphate buffer, (pH 10.0) that contained 10 mM histamine. A constant voltage of 0.2 V was applied and the absorption of this solution between 475 and 700 nm was measured every 30 min.

2.5. Real sample preparation and HPLC study

A fresh saury fish purchased from local market was used as the real sample. After homogenization, 10 mL pure water was added in the 4 g homogenous fish tissue and shacked for 5 min. This slurry was centrifuged with 6000 rpm and sequentially filtrated with 0.45, 0.25 and 0.1 μm filter, respectively. Subsequently, 10 mL buffer was added in 5 mL filtration, and this stock solution was used to evaluate the linearity of this scheme in the HPLC application. The mobile phase is prepared by mixing 0.05 M phosphate buffer and 0.05 M acetic acid and adjusts its pH to 6.0. An isocratic chromatography was achieved by continuously flowing the prepared running buffer

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