Voltammetric Determination of Tyramine on L-Aspartic Acid Polymerized Glassy Carbon Electrode

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Abstract:

Tyramine (TA) is an important biogenic amine that participates in various metabolic processes of living organisms and acts as quality markers of food. The excess concentration of TA causes various health issues that makes the determination of TA highly demanded. Herein, a selective electrochemical sensor has been developed for TA determination using L-Aspartic acid modified glassy carbon electrode. The simple modification of the electrode was performed through electropolymerization of L-Aspartic acid on the surface of GCE (L-Asp/GCE). The electrocatalytic activity of L-Asp/GCE on the electro oxidation of TA was investigated using square wave voltammetric technique. Under optimized conditions, the sensor enabled the quantification of TA in the range 6×10^{-6} M to 5×10^{-7} M and 3×10^{-5} M to 7×10^{-6} M. The mechanistic and the kinetic parameters has been determined. Good selectivity, sensitivity and reproducibility makes the sensor efficient for the determination of TA in artificial blood serum and urine.

Keywords: Tyramine, L-Aspartic acid, electrocatalytic, voltammetry

1. Introduction

Biogenic amines are naturally occurring nitrogenous compounds, formed due to the decarboxylation of proteinous amino acids [1,2]. Tyramine (TA), p-hydroxyphenyethylamine, one of the biogenic amines is the decarboxylation product of tyrosine [3]. It is found in various food products such as fish, chocolate, beer, cheese, ketchup etc. and it is considered as their quality indicator [4]. Consumption of TA containing food causes various health issues such as hypotension, headaches, increased blood pressure, and diarrhoea [4]. Hence, in diagnostic point of view, the development of a simple and accurate method for the determination of TA is highly demanded.

To date various method have been reported in literatures for the determination of TA. These include capillary electrophoresis, High performance liquid chromatography, quantitative polymerase chain reaction etc. [5]. Among them HPLC is widely used. Sophisticated instrument, lengthy procedure, use of excess solvent reduces its application in clinical diagnostic field. Herein, we have developed an electrochemical sensor for TA using L-aspartic acid modified glassy carbon electrode.

Materials and methods

All the chemicals used were of analytical grade. Millipore water was used for preparing solutions. Aspartic acid and tyramine were purchased from Spectrochem Pvt. Ltd, Mumbai and Tokyo chemical industry Co. Ltd respectively.

Cyclic voltammetry (CV), square wave voltammetry (SWV), linear sweep voltammetry (LSV), Impedence spectroscopy were done in CHI6017D electrochemical work station. L-aspartic acid modified glassy carbon electrode, Ag/ AgCl and platinum wire were used as the working electrode, reference electrode and counter electrode respectively.

Results and discussions

Fabrication of L-aspartic acid modified glassy carbon electrode ((L-Aspa)/GCE)

2×10^{-3} M L-Aspartic acid was used for fabricating the electrode using cyclic voltammetry (fig.1). It was done by scanning the potential between -0.8 V to 2 V at 0.1 Vs^{-1} for 40 segments.

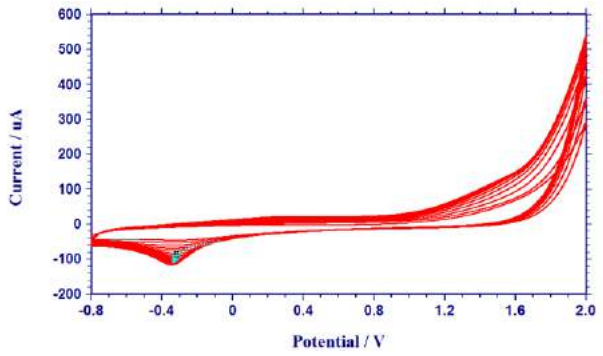


Fig. 1. Electropolymerization of L-Aspa on GCE

Voltammetric behaviour of TA on p(L-Aspa/)GCE

The electrochemical behaviour of 1×10^{-4} M TA on bare and modified glassy carbon electrode was noted. It is shown in fig.2. and was found that there is a fourfold increase in peak current on p(L-Aspa)/GCE.

Cyclic voltammogram of TA on p(L-Aspa)/GCE gave a single oxidation peak at forward scan suggesting that the electro oxidation of TA on L-Aspa / GCE is irreversible.

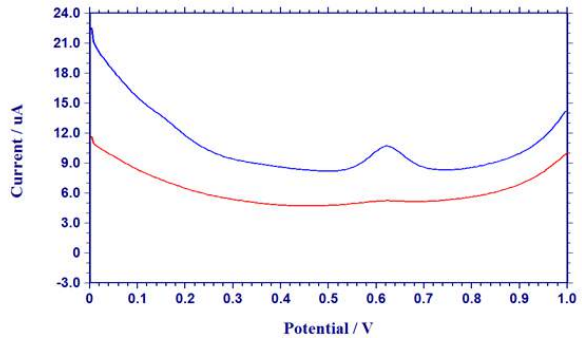


Fig. 2. Square wave voltammogram of TA on bare and modified GCE

Characterization of p(L-aspa)/GCE

The surface characterization of bare and modified electrode was carried by comparing the SEM images of bare and modified electrode. It was found that the smooth and uniform of surface of bare GCE was changed to a rough surface upon modification.

Surface area of bare and modified electrode was determined using 2mM $k_3Fe(CN)_6$. It was calculated using the Randles Sevick equation.

$$I = 2.69 \times 10^5 A\, n^{\frac{3}{2}} D^{\frac{1}{2}} C$$

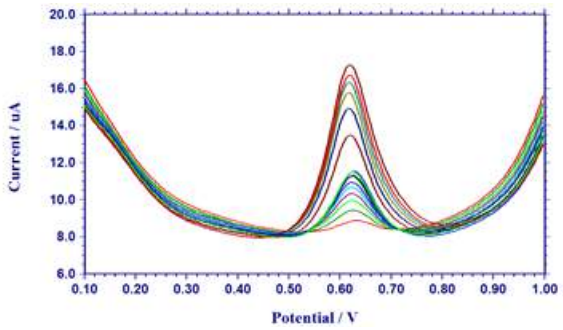
For bare and p(L-Aspa)/GCE , the surface area was calculated to be 0.0512 cm^2 and 0.09084 cm^2 respectively. The increase in surface area is an additional proof for the modification of L-aspartic acid on GCE.

Optimization of sensor parameters

Different sensor parameters were optimized for the effective quantification of TA. Of the different supporting electrolytes maximum peak current was obtained for 0.1 M PBS of pH 7. The number of scan cycles of electropolymerization of L-aspartic acid is optimized to be 20 cycles. Further studies were carried out under these conditions.

Sensor performance

Under optimized conditions, the anodic peak current was increased linearly with the concentration of TA. The quantification of TA was possible within the ranges 6×10^{-6} M to 5×10^{-7} M and 3×10^{-5} M to 7×10^{-6} M.



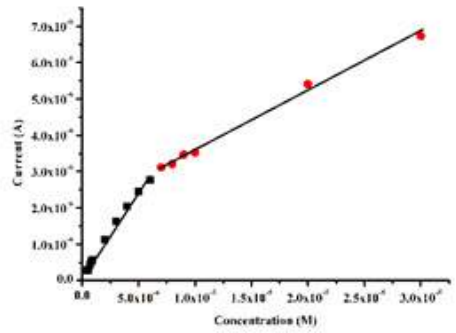


Fig.3 Overlay of SWVs for the oxidation of TA at various concentrations and calibration plot

Interference study

The selectivity of the proposed sensor was examined by studying the effects produced by various foreign species at different concentration ratios, on the determination of 1×10^{-4} M TA. NaCl, KCl, L-Dopa, glucose were did not interfered the analysis when present at ten times higher than TA. It was found that dopamine, histamine, tyrosine, epinephrine, ascorbic acid and uric acid were interfered the analysis at 1:1 concentration ratio.

Application study

The performance of the proposed sensor was analysed by quantifying the amount of TA in artificial blood serum and urine samples. Recoveries and RSD values were calculated. Satisfied recovery and RSD values shows the reliability of the proposed sensor towards the determination TA in physiological fluids.

Conclusion

Voltammetric determination of TA was carried out using p(L-Aspa)/GCE modified glassy carbon electrode. The different sensor parameters were optimized. Under optimized conditions, the sensor enabled the quantification of TA within the concentration range 6×10^{-6} M to 5×10^{-7}M and 3×10^{-5} M to 7×10^{-6} M. The mechanistic and the kinetic parameters has been determined. Good selectivity, sensitivity and reproducibility makes the sensor efficient for the determination of TA in artificial blood serum and urine.

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