Voltammetric Sensor Based On Poly Aspartic Acid/Gold Nanoparticles Modified Glassy Carbon Electrode For The Determination Of Vanillylmandelic Acid

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Abstract:

Vanillyl mandelic acid (VMA) is an important chemical intermediate and end-stage product of catecholamine metabolism in human body. It's determination in body fluids is important to diagnose various neurological disorders. For this reason, an electrochemical sensor based on poly aspartic acid/ gold nanoparticles modified glassy carbon electrode (Poly (Asp)-AuNPs/GCE) was developed for the effective analysis of VMA. This modified film offers stable, reproducible and selective determination of VMA. The experimental parameters needed for the effective determination of VMA was optimized and found that it give best results in 0.1 M acetate buffer solution at pH 7. The increase in peak current with concentration was found to be linear and two linear ranges were obtained from $4.1x10^{-6}$ M to $3.1x10^{-5}$ M and $9.1x10^{-5}$ M to $4.1x10^{-5}$ M. The sensor was successfully applied for the determination of VMA in artificial blood serum and urine.

Keywords: Vanillyl mandelic acid, poly aspartic acid, gold nanoparticles, voltammetric sensor, glassy carbon electrode.

1. Introduction

Vanillyl mandelic acid (dl-4-Hydroxy-3-methoxymandelic acid) is a chemical intermediate in the synthesis of artificial vanilla flavorings and is an end-stage metabolite of the catecholamines (dopamine,epinephrine and norepinephrine). Urinary VMA is elevated in patients with tumors that secrete catecholamines. These urinalysis tests are used to diagnose an adrenal gland tumor called pheochromocytoma, a tumor of catecholamine-secreting chromaffin cells. These tests may also to diagnose neuroblastomas, and to monitor treatment of these conditions. Norepinephrine is metabolised into normetanephrine and VMA. These hormones are released into the blood during times of physical or emotional stress. Development of Vanillyl mandelic acid is important and it can be done using a reported procedure of modification of glassy carbon electrode using poly Aspartic acid/ Au Nanoparticles modification.

2) Experimental

2.1 Reagents

All chemicals are of analytical grade and used without further purification. Vanillyl Mandelic acid was purchased from Sigma Aldrich. Both the monomer Aspartic acid and tetrachloro auric acid were obtained from Spectrochem Pvt. Ltd.

2.2 Apparatus

Electrochemical experiments were performed on CHI6023D electrochemical analyser (CH Instruments Inc. USA). A three electrode setup was used. Poly Aspartic acid/AuNPs modified GCE was used as the working electrode. Pt wire and Ag/AgCl electrodes were used as the counter and reference electrodes respectively.

2.3 Fabrication of Poly Aspartic acid/AuNPs/ GCE

The glassy carbon electrode was polished, cleaned and dried. Then the electrode was continuously CV scanned from –1.5 to 2.0 V at 100 $mV \cdot s^{-1}$ for 30 cycles in 10^{-3} M aspartic acid aqueous solution to form poly aspartic acid film on the electrode surface. It was washed and immersed into 0.1 M KNO_3 containing 0.4 $g \cdot L^{-1}$ $HAuCl_4$, electrodeposition from HAuCl4 was conducted for 60 s at –0.2 V.

3 Results and Discussion

3.1 Optimization studies

To select the supporting electrolyte for studies, the electrochemical response of VMA on poly (Aspartic acid)- Nano gold modified GCE was studied in 0.1 M concentration of acetate buffer, citrate buffer, phosphate buffer, NaOH, HCl, H_2SO_4, NaCl, KCl, Perchloric acid were studied and better response with lowest oxidation potential obtained for acetate buffer. From pH study, better response was obtained for acetate buffer of pH 7. Number of cycles were optimized to 10. Hence further studies were done by 20 number of cycles.

3.2 Comparison of oxidation of VMA on bare GCE and PAA-AuNPs modified GCE

$3x10^{-5}$M Vanillyl mandelic acid get oxidised on bare GCE at a potential of 0.592V with a current of 1.221×10^{-6}A while the same concentration of VMA on Polyaspartic acid/ AuNPs modified GCE get oxidised at a lower potential of 0.584V with a current of 3.556×10^{-6} A. A 3fold increase in current was obtained. Overlay of 3×10^{-5} M VMA is given in figure 1.

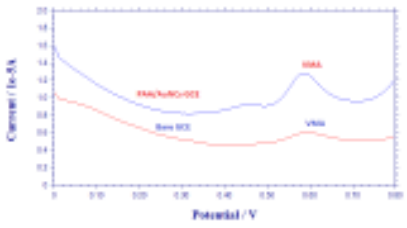


Fig.1: Overlay of 3×10^{-5} M VMA on bare and PAA/ nano Au modified GCE taken in acetate buffer.

3.3 Probing VMA on modified electrode

Under optimized conditions, the sensor was found to show two linear ranges of VMA concentrations, one is in the range 4.1×10^{-6} M to 3×10^{-5} M (Ip= 0.06841 C- 6.310×10^{-8} (r^2= 0.975)) and the second one is in the range 9.1×10^{-5} M to 4.1×10^{-5} M (Ip = 0.0211C+ 1.8208×10^{-6} M (r^2= 0.963)) (Fig. 2).

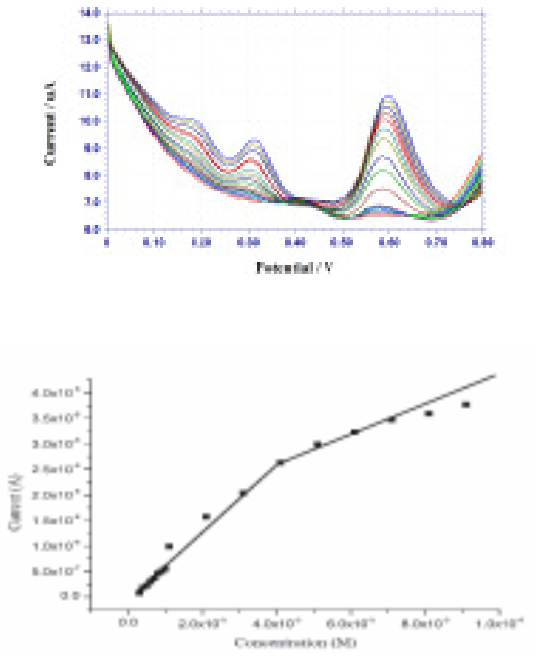
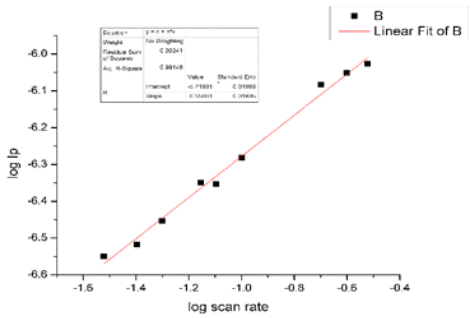


Figure 2 (a) Overlay of SWVs recorded in 0.1 M ABS 7 containing varying amount of VMA in the range 3×10^{-5} M to 4.1×10^{-6} M and 9.1×10^{-5} M to 4.1×10^{-5} M (b) Linear correlation graph between peak current and concentration of VMA (0.1 M ABS).

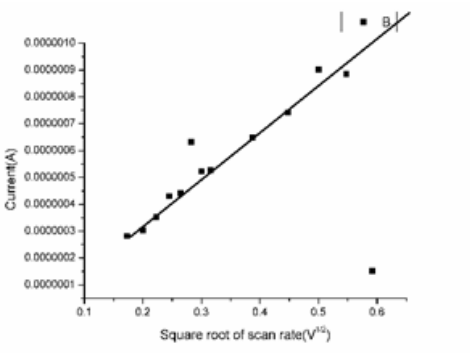
3.4 Kinetic Study

3.4.1 Scan rate study

Effect of scan rate on electro oxidation of VMA (3×10^{-5} M) on PAA/AuNPs modified GCE was studied using LSV at different scan rates. From CV it was obtained that the difference in peak potentials (E_{pa} and E_{pc}) was found to be 0.35. It shows a perfectly reversible electrochemical reaction. Figure 3 shows the linear plot of peak current versus square root of scan rate and this suggests a diffusion controlled process. The variation of log v Vs log Ip also shows a linear plot with slope is equal to 0.55 and this confirms a diffusion controlled process.



(a) Plot of log Scan rate Vs log Current



(b) Plot of square root of Scan rate Vs Current

3.5 Interference Study

Effect of various coexisting species on electrochemical oxidation of VMA on PAA/ AuNPs modified GCE was done by measuring the current for oxidation of different species with 1:1, 1:10, 1:100 molar concentration ratios with analyte (Table 1).

SPECIES	CONCENTRATION RATIO(ANALYTE: INTERFERENT)	SIGNAL CHENGE (%)
5-Hydroxy indole acetic acid	1:10	0.87
Dopamine	1:1	1.161
L Dopa	1:1	0.91
L Ascorbic acid	1:1	3.57
Uric acid	1:1	1.27
Homovanillic acid	1:1	4.87
Creatine	1:1	2.87
Creatinine	1:1	3.32
Norepinephrine Hydrochloride	10:1	7.5
Dextrose	1:1	0.426
NaCl	10:1	1.32
KCl	1:1	1.74

4 Conclusions

Poly aspartic acid/ nano Au modified GCE was fabricated and voltammetric sensing of vanillyl mandelic acid has done. Experimental parameters has been optimised. Interference study of co-existing species has also done.

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