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A Simple Method for Determination of Nicotinic Acid in Urine Samples by using Differential Pulse Voltammetry and Carbon Paste Electrode

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Abstract- A new electrochemical method was introduced for nicotinic acid measurement in pharmaceutical samples. Electrochemical behavior of nicotinic acid was studied by cyclic voltammetry and differential pulse voltammetry on carbon paste electrode. Some important parameters affecting the electrode response to nicotinic acid was investigated and optimized. The optimal electroanalysis pH was found to be 2.2. Moreover, the optimal amount of binder used for carbon paste preparation was observed to be 27.50% of total mass of the paste composite. The peak current response versus nicotinic acid concentration was linear in the range of 5.0×10^{-5} to 3.0×10^{-3} M. The detection limit was calculated to be 3.1×10^{-5} M. The developed method was successfully used for determination of nicotinic acid in the urine samples.

Keywords- Nicotinic acid, Carbon paste electrode, Differential pulse voltammetry

1. INTRODUCTION

Nicotinic acid (niacin or pyridine-3-carboxylic acid, NA) is a water soluble B vitamin that there is in many foods including yeast, fish, milk, eggs, green vegetables and cereal grains,

and has many significant assignments in human and animal nutrition. In human body, nicotinic acid (NA) is transfigured into niacinamide, which is incorporated into two coenzymes: nicotinamide adenine dinucleotide and nicotinamide adenine dinucleotide phosphate. It is needed for lipid metabolism, tissue breathing and glycogenolysis [1] The shortage of NA and/or its precursor, tryptophan, results in pellagra, affecting the gastrointestinal tract, skin and central nervous system. High amount of NA may beget life-threatening poisonous reactions, thickening of the retina and raise the level of uric acid in the blood [2,3]. Thus, the determination of NA in biological samples, food, nutrient materials and pharmaceutical preparations has been a subject of growing interest due to the effect on human health. Different analytical methods including high-performance liquid chromatography (HPLC)[4-10], liquid chromatography-tandem mass spectrometry [11], ion chromatography [12], hydrophilic interaction chromatography with tandem mass spectrometry[13], micellar electrokinetic capillary chromatography [14], micellar liquid chromatographic [15], supercritical fluid chromatography [16], capillary electrophoresis [17,18], chromatographic low pressure flow injection system [19], drop-to-drop solvent microextraction coupled to matrix assisted laser desorption/ionization mass spectrometry[2] and enzyme sensor[20] have been developed for NA determination. Although, these methods are useful regarding the analytical aspects, but they suffer from some disadvantages such as the need for expensive and complicated instrument, complicated extraction process, long analysis time and poor sensitivity and selectivity.

Electrochemical methods can be a good alternative to spectroscopic methods due to their simplicity, sensitivity and low price. There are scarce electrochemical methodologies for the analysis of NA [21-25]. Nicotinic acid has a poor electroactivity on traditional electrodes and its reaction mechanism is complex, as described in several articles, being highly divergent. To the best of our knowledge, the determination of this compound using a carbon paste electrode (CPE) has not been exploited.

Nowadays, carbon paste electrodes (CPEs) are the most popular electrochemical or bioelectrochemical sensors in wide applications. The CPE was invented by Ralph Norman Adams from the University of Kansas in 1958. Due to its unique properties including a large potential window on both anodic and the cathodic regions, the simplicity of its preparation and modification, low cost and low capacitive current the CPE represents one of the most frequent types of working electrodes [26]. Previous studies have pointed out that NA could not create significant signal at carbon paste electrode without modification of carbon paste electrode. However, in this study we made the unmodified carbon paste electrode to create a significant response to nicotinic acid. This achieved by precisely adjustment of electroanalysis pH as well as the binder content, used for the preparation of the carbon paste electrode. Differential pulse voltammetry (DPV) was used as the determination technique.

The effects of some parameters were investigated. The analytical application of the proposed technique was successfully used for the determination of NA in the urine sample.

2. EXPERIMENTAL

2.1. Chemicals

Nicotinic acid and n-eicosane were supplied by Sigma–Aldrich (Munich, Germany), and used as received. Graphite powder was purchased from Fluka (Buchs, Switzerland). Other chemicals were of analytical grade and were purchased from Merck (Darmstadt, Germany) and used without further purification. The voltammetric measurements were performed in a mixture of KCl and HCl.

2.2. Apparatus

Electrochemical data was obtained with a three-electrode system using a potentiostat/galvanostat model PGSTAT302, Metrohm. The CPE was used as a working electrode. A platinum wire and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively.

2.3. Preparation of the sensors

Certain amount of graphite and paraffin were mixed with a stainless steel spatula. The obtained paste was used to fill a hole (2.00 mm in diameter, 3 mm in depth) at the end of an electrode body, the excess of solidified material was removed with the aid of a paper sheet. The electrode can be reused after each experiment by moving the electrode surface on a paper sheet in order to extrude a thin layer of the electrode surface.

2.4. Differential pulse voltammetry measurements

The electrode was placed in the electrochemical cell containing 10 mL of KCl (0.1 M), HCl (0.01 M) and NA. Differential pulse voltammetry was then performed, applying the potential range of -0.8 to -1.4 V, step potential of 20 mV, modulation amplitude of 100 mV, modulation time of 0.05s and interval time of 0.1 s.

3. RESULTS AND DISCUSSION

3.1. Electrochemical behavior of nicotinic acid by cyclic voltammetry and differential pulse voltammetry on carbon paste electrode

Electrochemical characteristic of NA at CPE was examined by cyclic voltammetry (Fig. 1(I)). Cyclic voltammetry was performed in an electrochemical cell containing 10 ml of KCl

(0.1 M), HCl (0.01 M) and 1 mM of NA with a scan rate of 200 mV/s. As it is seen, a reduction peak is appeared in potential of -1.2V *vs.* Ag/AgCl. Also, DPV was performed in the same conditions (Fig. 1(II)). As it is clear, the current response of nicotinic acid is increased considerably using DPV procedure, compared to the response obtained by cyclic voltammetry. Thus, DPV was chosen as the analytical technique for nicotinic acid determination.

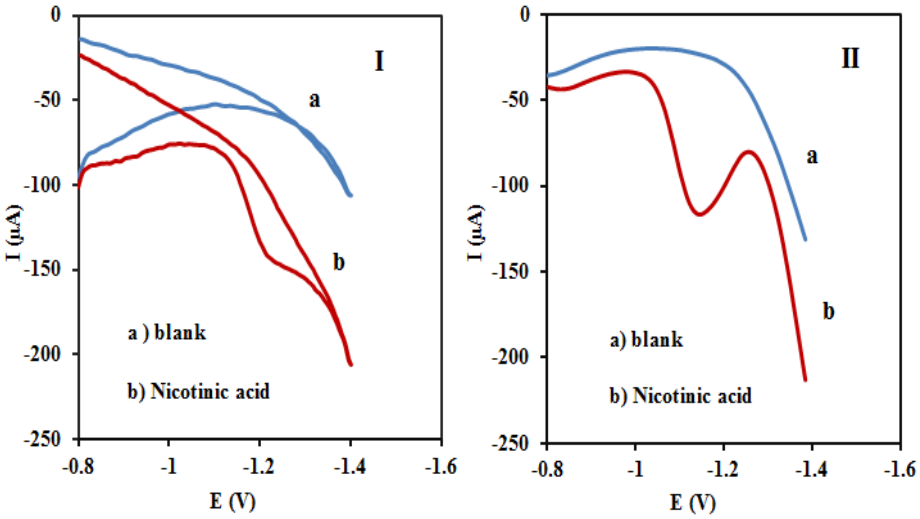

Fig. 1. Cyclic voltammograms (I) and differential pulse voltammograms (II) recorded for 1 mM of nicotinic acid in 10 ml of electrolyte solution containing of KCl (0.1 M) and HCl (0.01 M)

Cyclic voltammetry condition: step potential=5 mV, scan rate=200 mV/s. Differential pulse voltammetry condition: step potential=20 mV, modulation amplitude=100 mV, modulation time=0.05 s, interval time=0.1 s. Composition of electrode: graphite (0.145 g) and parafin (0.055 g).

3.2. Optimization of electrode composition

In order to find the best composition for CPE electrode, the amount of paraphine content of the paste electrode was changed, while the conditions of voltammetric determination was fixed. The obtained voltammetric responses were used for the conclusion. The results are shown in the Fig. 2. It can be seen that 27.5% of the binder is an optimum amount, capable to create the highest signal.

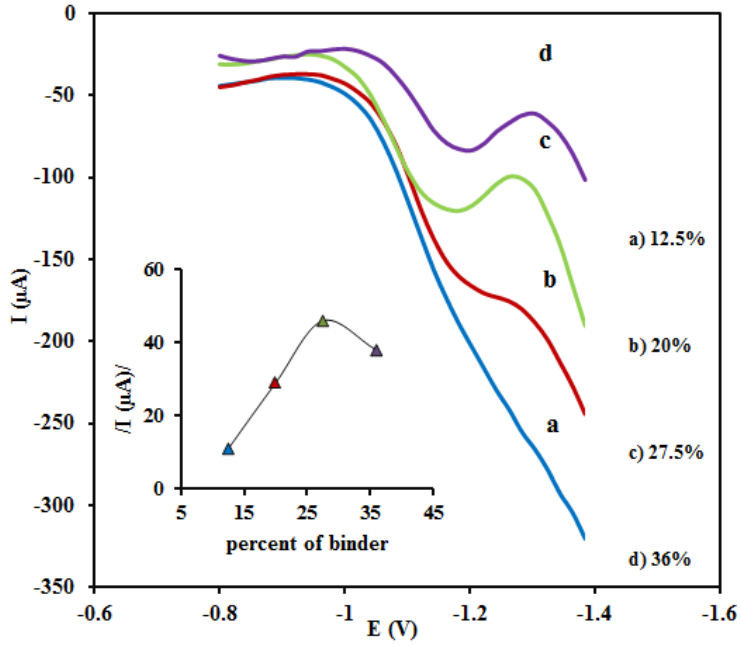

Fig. 2. Optimization of precent of binder in electrode composition

3.3. Optimization of pH of electrolyte solution

One of the most important parameters in determination of NA was found to be the pH of the electrolyte solution. For this purpose, voltammetric studies were performed in a solution of KCl (0.1 M), adjusted to various pH in the range of 1.5 to 5, by HCl solution. The results are shown in Fig. 3.

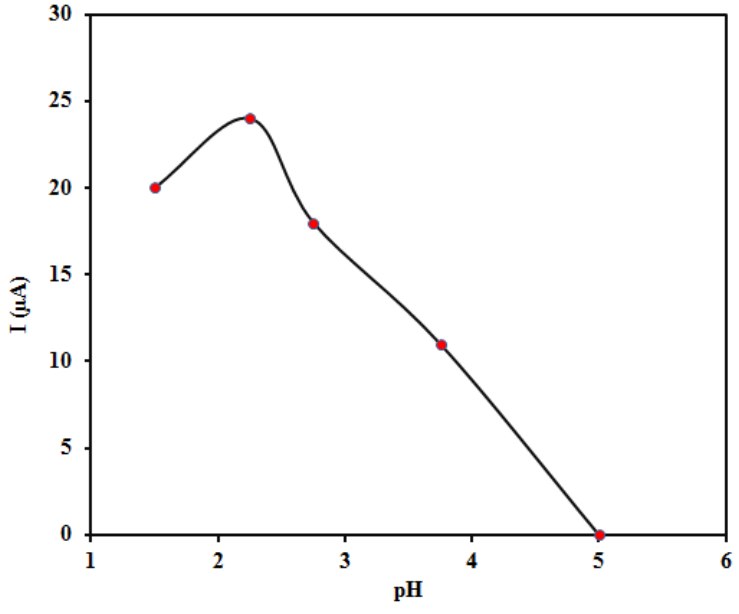

Fig. 3. Optimization of pH of electrolyte

The results represented in the figure suggest that the electrode response to nicotinic acid is extremely sensitive to pH value. As it is clear, the electrochemical signal of nicotinic acid is wholly disappeared at pH of 5; wheras, it meets a big value at highly acidic condition. Accordingthe curve, the highest reduction peak of NA is obtained in acidic pHs of 2.2, chosen as the optimal pH condition for NA electroanalysis.

3.3. Analytical characteristic of the method

The calibration curve of the developed method for nicotiinic acid determination is represented in Fig. 4. As shown, the calibration curve exhibits a linear relationship over NA concentration in the range of 5.0×10^{-5} to 3.0×10^{-3} M. Furthermore, based on 3S/N principal, a detection limit of 3.10×10^{-5} M was calculated for this determination method. Each point of the calibration graph is the average of three replications. Moreover, five separate determinations of NA by the same electrode resulted in an RSD%=1.1 (n=5). This can be considered as an indication for approriate repeatability of the method.

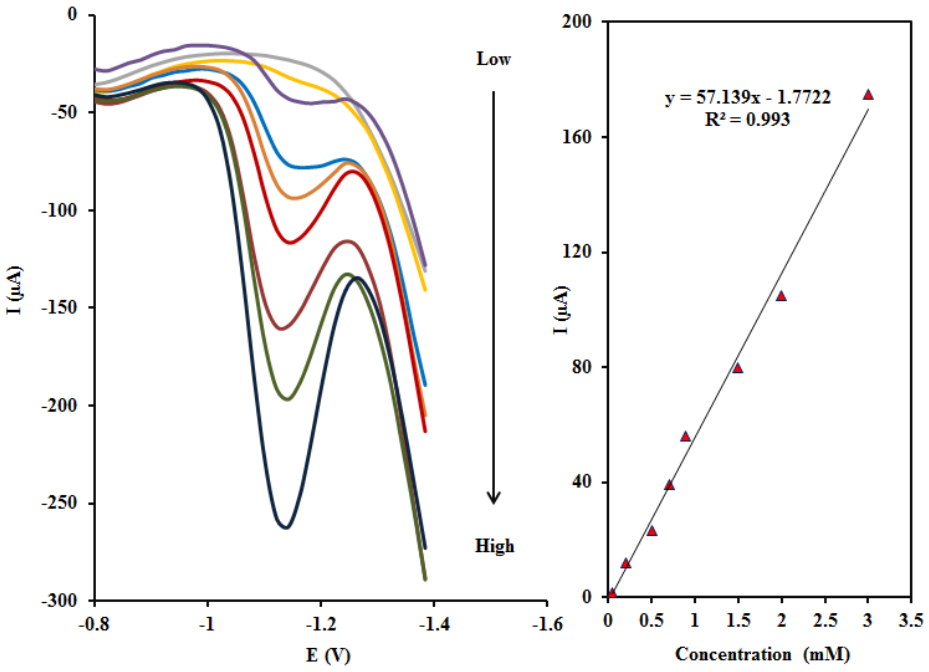

Fig. 4. Differential pulse voltammograms of nicotinic acid in different concentrations (0.05, 0.25, 0.50, 0.70, 0.90, 1.50, 2.00, 3.00 mM) and the calibration curve of the optimized electrode, plotted based on the depicted CV grams

3.4. Determination of nicotinic acid in urine by proposed sensor

The proposed electrode was utilized to determine NA in urine samples. To this aim, urine samples were firstly diluted five times by the electrolyte solution (KCL (0.1 M)+HCl (0.01 M)) and then the described DPV was executed to obtain the nicotinic acid related signal. The

obtained signal was used for NA concentration calculation based on the previously established calibration curve. Since, urine samples, tested with the method, resulted in no signal for NA, a determined amount of NA was spiked to the urine samples, followed by performing the developed determination procedure. The results obtained were summarized in table.1. According to the depicted data the method exhibits good capability for nicotinic acid determination in urine samples, regarding either recoveries or confidence limits obtained.

Table.1. Determination of nicotinic acid in urine samples using the proposed sensor

Sample	Added (mM)	Found (mM)	Recovery (%)
	0.2	0.196(±0.012)	98.1
Urine1	0.4	0.387(±0.006)	96.8
	0.6	0.575(±0.022)	95.8
	0.2	0.193(±0.015)	96.5
Urine2	0.4	0.376(±0.020)	94.0
	0.6	0.566(±0.024)	94.3

4. CONCLUSION

Direct electrochemical reduction of nicotinic acid has not already been reported at carbon paste electrodes**.** In this work, nicotinic acid was determined using simple carbon paste electrode and applying differential pulse voltammetry method. It was demonstrated that adjusting of electroanalysis pH and precisely control of binder amount in the paste electrode are very influential parameters to create a significant voltammetric signal for nicotinic acid at carbon paste electrode applying DPV. The main advantages of the proposed method are its simplicity, fastness, and cheapness. The proposed sensor was successfully used for the determination of NA in the urine samples.

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