COMPARISON BETWEEN THE PERFORMANCES OF PLATINUM AND CARBON PASTE ELECTRODES FOR VOLTAMMETRIC VITAMIN C DETERMINATION

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Abstract. Voltammetric and amperometric methods allow fast, sensitive and selective ascorbic acid determination, requiring little or no sample preparation. Voltammetry at various electrodes was used to assess the ascorbic acid content in different media. For differential pulse voltammetry, the oxidation peak of ascorbic acid occurs at about 470 mV on a carbon paste working electrode and at about 530 mV (vs. SCE) on a Pt strip working electrode. A linear dependence between the current intensity measured for the peak height and ascorbic acid concentration was obtained between 0.31 and 20 mM on a Pt working electrode and between 0.07 and 20 mM on a carbon paste electrode. Lower detection limits were obtained with a carbon paste working electrode.

Keywords: voltammetry, ascorbic acid, Pt electrode, carbon paste electrode

1. Introduction

Ascorbic acid is the most common electroactive biological compound and one of the most often encountered water-soluble vitamins. It is important in forming collagen; it helps in the absorption of iron and maintains capillaries, bones, and teeth. Ascorbic acid is known for its reductive properties (antioxidant activity) [1]. Hence, it represents an important quality indicator that contributes to the antioxidant properties of food [2]. Analytical methods for ascorbic acid assessment imply titration with dichlorophenol indophenol [3], potassium iodate [4] or bromate [5], chromatographic [6] or fluorimetric techniques [7].

Electrochemical (amperometric and voltammetric) methods allow sensitive and selective ascorbic acid determination in various media [8-12].

The use of a carbon nanotube/ferritin film in the construction of an amperometric biosensor allows the determination of ascorbic acid with a sensitivity of 767 μA/mg (for a 1 mmole L^{-1} vitamin C solution) [8]. An amperometric biosensor was developed for ascorbic acid determination in fruit juices, by immobilizing ascorbate oxidase on a nylon membrane, which was fixed on a Clark-type transducer [9].

Voltammetric methods combine the advantages of rapidity and procedure simplicity, with sensitivity and selectivity, for ascorbic acid determination without the necessity of separating the analyte from the matrix [1, 10-12].

Simultaneous determination of ascorbic acid and dopamine was possible at the surface of electrodes modified with self-assembled gold nanoparticle films [10]. The electrochemical oxidation and selective determination of ascorbic acid in pharmaceutical dosage forms and in some Rosa species was investigated by cyclic, differential pulse and square-wave voltammetry [1]. Differential pulse voltammetry at a glassy carbon electrode was applied to quantitative determination of ascorbic acid in tablet dosage form and in some fruit juices [11]. The simultaneous assessment of ascorbic acid and acetaminophen was investigated by differential pulse voltammetry and cyclic voltammetry, performed on a boron-doped diamond electrode. Relative standard deviations of 2-3% and low detection limits (10^{-6} moles L^{-1} order of magnitude) were obtained [12].

This study aims at investigating the ascorbic acid determination by differential pulse voltammetry and cyclic voltammetry at Pt strip and carbon paste working electrodes. The developed method was applied to ascorbic acid content assessment in juices.

2. Materials and methods

Reagents and instrumentation: potentiostat-galvanostat KSP, laboratory made by Professor Slawomir Kalinowski, University Warmia and Mazury (Olsztyn), as well as the respective softs, Differential Pulse Voltammetry and Cyclic Voltammetry. A Pt strip electrode (Radelkis 30 mm^2 surface) and then a carbon paste electrode

were used as working electrodes. The reference electrode was a saturated calomel electrode (SCE). The counter electrode was a Pt strip (Radelkis 30 mm^2 surface).

Ascorbic acid (Merck, ACS ISO, biochemical grade), KCl (Chimopar, Bucharest, Romania). Standard solutions of ascorbic acid with concentrations ranging between 0.05 and 20 mM were obtained by diluting the 0.1 M vitamin C stock solution with the respective volumes of 0.10 moles L^{-1} KCl (electrolyte) solution.

Working procedure: a three-electrode cell was used, with working, counter and a reference electrodes; all measurements were performed at 295.5 K, using a 0.10 M KCl solution as supporting electrolyte. Before each determination, the Pt working electrode was cleaned by applying a -1.5 V potential pulse for 3 seconds. The potential was scanned from -100 to + 1000 mV.

3. Results and Discussions

3.1. Voltammetric studies performed at a Pt working electrode

In figure 1, several differential pulse voltammograms, obtained at a Pt working electrode, for different ascorbic acid concentrations, are presented. The peak corresponding to ascorbic acid oxidation appeared at 530 mV (versus SCE). The calibration graph (figure 2) shows a linear range obtained between 0.31 and 20 mM ascorbic acid ($y = 21.839\ x + 35.726$, $r^2 = 0.9940$, where y represents the value of the current intensity, from which the background value was substracted and x the analyte concentration). The value calculated for the relative standard deviation R.S.D. was 2.09% (c = 2.5 mM ascorbic acid; n = 10). The values obtained for the limit of detection and the limit of quantification were 0.087 mM and 0.29 mM respectively.

3.2. Voltammetric studies performed at a carbon paste working electrode

In figure 3 several differential pulse voltammograms, obtained with a carbon paste electrode for different ascorbic acid concentrations, are presented. The peak corresponding to ascorbic acid oxidation appeared at 470 mV (versus SCE). The calibration graph (figure 4) shows a linear range obtained between 0.07 and 20 mM ascorbic acid ($y = 3.4429x + 5.7334$, $r^2 = 0.9971$, where y represents the value of the current intensity, from which the background value was substracted and x represents the analyte concentration).

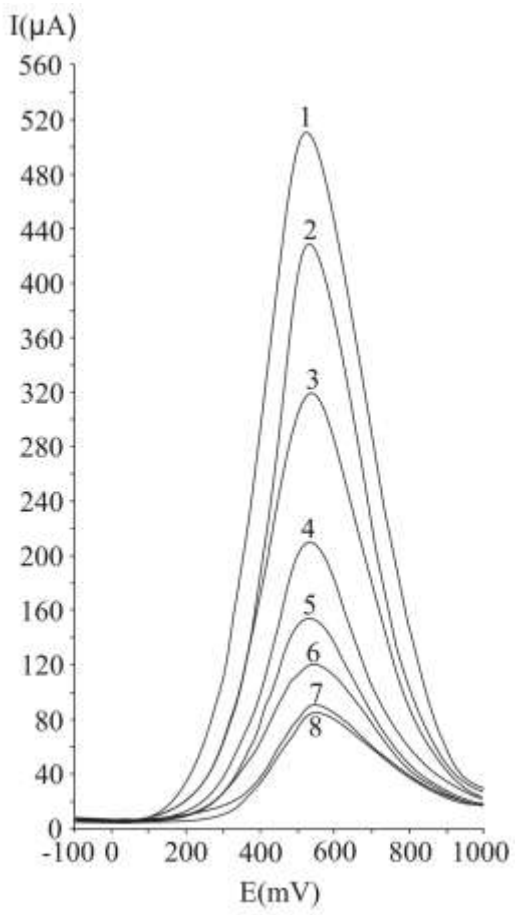

Figure 1. Differential pulse voltammograms obtained with a Pt working electrode for different ascorbic acid concentrations, expressed as mM: 20 (1), 15 (2), 10 (3), 5 (4), 2.5 (5), 1.25 (6), 0.625 (7) and 0.31 (8); experimental conditions: pulse amplitude 75 mV, pulse period 125 ms, potential scan rate 50 mV/s.

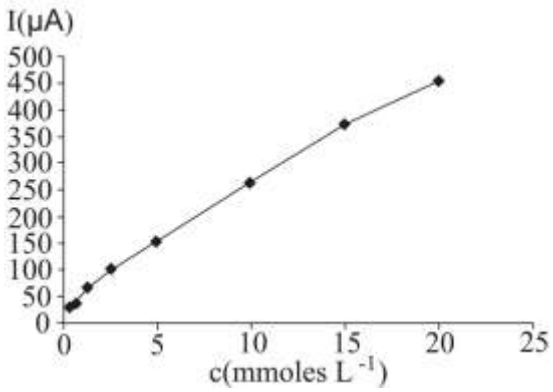

Figure 2. Calibration graph obtained at ascorbic acid determination by differential pulse voltammetry at a Pt working electrode for experimental conditions presented in figure 1

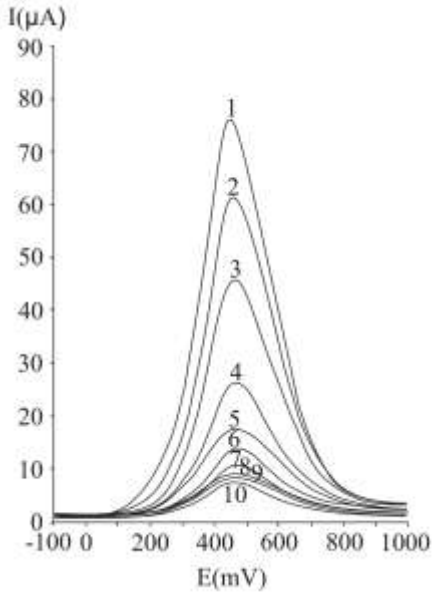

Figure 3. Differential pulse voltammograms obtained with a carbon paste working electrode for different ascorbic acid concentrations, expressed as mM: 20 (1), 15 (2), 10 (3), 5 (4), 2.5 (5), 1.25 (6), 0.625 (7), 0.31 (8) 0.15 (9) and 0.07 (10); experimental conditions: pulse amplitude 75 mV, pulse period 125 ms, potential scan rate 50 mV/s

The value calculated for R.S.D. was 2.35% (c = 2.5 mM ascorbic acid; n = 10). The limit of detection and the limit of quantification were 0.02 mM and 0.068 mM respectively.

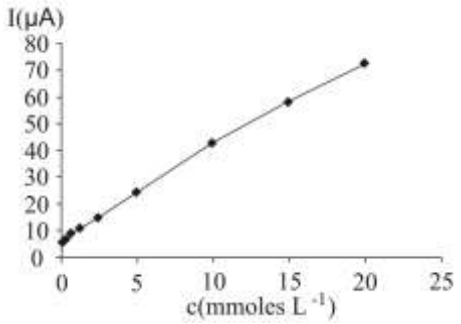

Figure 4. Calibration graph obtained obtained at ascorbic acid determination by differential pulse voltammetry at a carbon paste working electrode; for experimental conditions see Fig. 3.

2.3. Real sample analysis

The working procedure employed for standard ascorbic acid solutions was also applied to juices and soft drinks. The obtained results are presented in table 1.

The results obtained by the two methods (differential pulse and cyclic voltammetry) are in good agreement.

Table 1. Results obtained at ascorbic acid (AA) content (mg/100 mL juice) determination in natural juices and soft drinks by differential pulse voltammetry (DPV) and cyclic voltammetry (CV), performed at Pt strip and carbon paste working electrodes

Analysed product	AA concentration CV Pt electrode	AA concentration DPV Pt electrode	AA concentration CV Carbon paste electrode	AA concentration DPV Carbon paste electrode
Orange juice	39.25	41.24	39.40	40.68
Lemon juice	50.82	52.15	52.94	54.74
Prigat activ grapefruit	12.46	11.79	12.81	12.27
Prigat activ sour cherry	11.91	12.38	12.99	12.16

4. Conclusions

The developed voltammetric method for ascorbic acid determination is characterized by sensitivity, rapidity and reproducibility.

The limit of detection (LOD) and the limit of quantification (LOQ) obtained by differential pulse voltammetry were 0.087 mM and 0.29 mM respectively, when a Pt electrode was used. Lower values for LOD and LOQ were obtained when a carbon paste electrode was employed as working electrode: the limit of detection and the limit of quantification obtained by differential pulse voltammetry were 0.02 mM and 0.068 mM, respectively

Differential pulse voltammetry has turned out to be a technique characterized by sensitivity, rapidity, good specificity, reproducibility and can be applied with good results in food quality control.

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