

P57: SELECTIVE VOLTAMMETRIC DETERMINATION OF ASCORBIC ACID (VITAMIN C) IN THE PRESENCE OF WATER SOLUBLE VITAMINS

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Abstract- Voltammetry has been considered as an important analytical technique applied to the identification and determination of trace concentrations of many biological molecules including ascorbic acid. In this study, ascorbic acid was determined by square wave voltammetry using carbon paste as working electrode modified by a film of a manganese(II) complex compound. Various factors, such as the effect of pH and some common instrumental parameters on the response characteristics of the modified electrode were investigated. From the calibration graph, the relationship between the peak height and ascorbic acid concentration within modified working electrode was investigated. The equation of the calibration graph was found to be: $I = 0.0550\gamma_{ac} + 0.155$ with $R^2 = 0.9998$, where I is the SWV current and γ_{ac} is the mass concentration of ascorbic acid. The LOD and LOQ for the developed method were determined to be 1.288 $\mu\text{g/L}$ and 3.903 $\mu\text{g/L}$, respectively. Several compounds, such as riboflavin and biotin, and ions, such as Fe and Cu, were tested and no one of them seemed to interfere with the analytic signal. The proposed procedure was successfully applied in the determination of ascorbic acid in Rosa canina hips.

1. INTRODUCTION

Voltammetric techniques have been considered important among the analytical techniques used for the identification and determination of trace concentrations of many biological compounds, such as ascorbic acid [1]. In this study, ascorbic acid was determined by square

wave voltammetry using a modified carbon paste as working electrode [2].

The mononuclear complex $[\text{Mn}(\text{thiophenyl-2-carboxylate})_2(\text{H}_3\text{tea})]$, where H_3tea = triethanolamine, has been synthesized and characterized in a previous work [3]. The complex was found to have a capped trigonal prism coordination geometry with the seven coordinate manganese atom of rather interesting and rare stereochemistry. Thereafter, an electrochemical study of the complex was performed at a carbon paste electrode with the techniques of cyclic voltammetry, differential pulse voltammetry and square wave voltammetry. The electrochemical results revealed that the manganese complex had a potential antioxidant and superoxide dismutase biomimetic actions. Therefore, the antioxidant capacity of manganese complex towards the most important oxidative agents was tested [4]. In addition, electrochemical experiments revealed that the complex forms a stable film onto the electrode surface and can be used for chemical modification of the working electrode. The modified electrode can be used in the analytical determination of vitamin C with excellent analytical features.

2. EXPERIMENTAL

2.1 Materials and Methods

Voltammetric measurements were performed using the potentiostat Autolab-Type III and the software GPES 4.9 (Eco Chemie, The Netherlands). All measurements were carried out in three-electrode system using a carbon paste

working electrode (CPE), a silver|silver chloride reference electrode (Ag|AgCl) and a platinum counter electrode.

After the preparation of the CPE electrode, the immobilization of the Mn(II) complex at the CPE electrode surface took place under stirring for 300 s at 0 V. The interaction of the Mn(II) complex modified CPE with ascorbic acid solution for 300 s. The square-wave (SWV) signal obtained after medium exchange and transfer voltammetry in the potential range from 1.2 to 0.0 V.

The rosa canina sample was purchased from the market. After being weighed, it was diluted 1: 100 with twice deionized water and remained in the ultrasonic bath for about 10 minutes. Filtration and a second dilution of 1:25 were then took place.

3. RESULTS AND DISCUSSION

The presence of the ascorbic acid improves the reduction signal of the manganese complex. Although, the presence of the modified electrode deteriorates the oxidation signal of ascorbic acid. For this reason the peak which indicates the reduction signal of the manganese complex was chosen for ascorbic acid determination. An influence of various factors, such as pH and some common instrumental parameters of the square wave voltammetry (step potential, amplitude, frequency) on the characteristics of the modified electrode were investigated. A linear voltammetric response for ascorbic acid was obtained with the equation of the calibration graph $I = 0.0550\gamma_{ac} + 0.155$ with $R^2 = 0.9998$, where I is the SWV current and γ_{ac} is the mass concentration of ascorbic acid. The LOD and LOQ for the developed method were determined to be 1.288 $\mu\text{g/L}$ and 3.903 $\mu\text{g/L}$, respectively. Several compounds (riboflavin, biotin, pyridoxal, niacin, pantothenic acid, thiamine, folic acid, caffeic acid, gallic acid, glucose, fructose) and ions of Fe, Cu, Al, Zn, Mg, Ni were tested and no one of them seemed to interfere with the analytical signal. The proposed procedure was successfully

applied in the determination of ascorbic acid in Rosa canina hips.

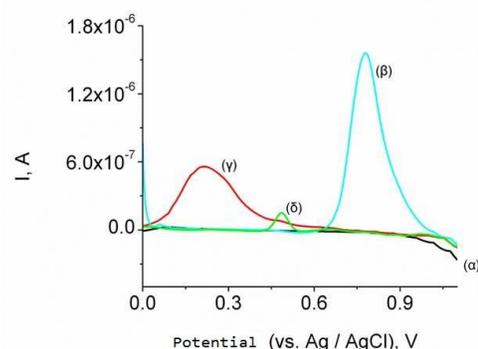


Figure 1. SW voltammograms of (α) CPE, (β) Mn-CPE, (γ) ascorbic acid at CPE, and (δ) ascorbic acid at Mn-CPE (oxidation).

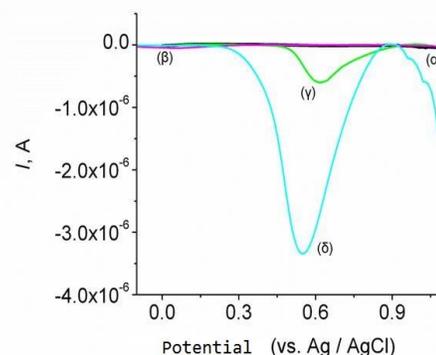


Figure 2. SW voltammograms of (α) CPE, (β) Mn-CPE, (γ) ascorbic acid at CPE, and (δ) ascorbic acid at Mn-CPE (reduction).

3.1 Analysis of rosa canina hips sample

The validated method was applied for the analysis of commercially available rosa canina hips sample. The method of standard addition has been used for this purpose. The equation of the calibration graph (figure 5) for the rosa canina hips extract was found to be $I = 5,83 \times 10^{-5} \gamma_{ac} + 1,53 \times 10^{-6}$ with $R^2 = 0.9998$. The concentration of ascorbic acid level found $4,84 \times 10^{-6} \pm 0,003 \text{ g/L}$. The analytical results are in good correlation with those which obtained from different methods.

Table 1. Optimization of parameters of the proposed procedure.

pH of ascorbic acid standard phosphate buffer solution	6.8
pH of ascorbic acid test phosphate buffer solution	5.4
Salt and its concentration in standard phosphate buffer solution	NaCl 0.01 mol/L
Salt and its concentration in test phosphate buffer solution	KBr 0.008 mol/L
Ionic strength of ascorbic acid standard phosphate buffer solution	0.05 mol/L
Ionic strength ascorbic acid test phosphate buffer solution	0.1 mol/L
Preconcentration time	300 s

4. CONCLUSIONS

The results showed that the modified working electrode with the $[\text{Mn}(\text{L})_2(\text{H}_3\text{tea})]$ complex compound improved significantly characteristics of the CPE. The proposed procedure proved to be simple, fast and low cost with a low detection limit and good selectivity regarding possible interferences. Finally, the proposed method was successfully applied to the ascorbic acid determination in rosa canina hips extract.

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