KINETICS OF DEGRADATION OF ASCORBIC ACID BY CYCLIC VOLTAMMETRY METHOD

Article Highlights

- Reduced concentration of AA increases with the increase of temperature and storage time
- The kinetics of the oxidation reaction corresponds to the reaction of first order
- Substances present in peppers reduced degradation of AA

Abstract

Cyclic voltammetry was used to examine the kinetics of degradation of ascorbic acid (AA) at different temperatures. It has been shown that the reduction of the concentration of AA in all temperatures follow the kinetics of the first order reaction. The rate constant of the oxidation reaction increases with temperature as follows: $5 \times 10^{-5}$, $2 \times 10^{-4}$, $1 \times 10^{-3}$, and $3 \times 10^{-3}$ min$^{-1}$ at temperatures of 25, 35, 65 and 90 °C, respectively. The temperature dependence of the rate constant follows the Arrhenius equation, and the value of activation energy of the reaction degradation is 48.2 kJ mol$^{-1}$. The effect of storage time at a temperature of 90 °C on AA content in fresh juice of green peppers was investigated. It was shown that AA oxidation reaction in the juice is also the first order reaction, while the lower rate constant in relation to the pure AA ($5 \times 10^{-3}$ min$^{-1}$) indicates the influence of other substances present in the peppers.

Keywords: ascorbic acid, kinetics, cyclic voltammetry, green peppers.

The reduction of food quality with storage time is becoming an increasing problem because of the loss of nutrients and vitamins [1]. Vitamin C, known as AA, is a water soluble vitamin. It is a powerful antioxidant because of its reducing properties and is involved in many biological reactions in the human body [2]. Therefore, it is recognized as one of the most important vitamins and its recommended daily intake is 75-90 mg for an adult [3]. However, the human body is unable to synthesize vitamin C [4], and insufficient intake of this vitamin causes numerous abnormalities [2].

AA is very unstable and is readily oxidized under the influence of light, heat, oxygen [4] and storage time [5,6]. The mechanism of thermal degradation of AA is quite complex and not fully understood. In the presence of oxygen, AA easily oxidizes to dehydro-ascorbic acid (DHA) via its monoanion [7] and the rate at which DHA is formed is approximately first order with respect to the concentration of AA, oxygen and metal catalysts. Several authors indicate a negative effect of the oxygen on the quality of fruit juices, which is connected to the reduction of AA [8,9], increased browning [10] and the growth of aerobic bacteria [11]. However, while AA is readily oxidized to the DHA, the loss of its vitamin properties occurs after hydrolysis of DHA to form 2,3-diketogulonic acid [12]. Decarboxylation of diketogulonic acid may result in the formation of xylosone and 3-deoxypentaone. The first reaction product (xylosone) is further degraded to form reductones and ethylglyoxal, and 3-deoxypentaone degrades into furfural and 2-furancarboxylic acid [7]. These components may combine with amino acids to form brown pigments [12]. A number of studies suggest that the browning of juice during storage can be associated with the degradation of AA [13-15]. Limacher et al. [16] showed that the main product of heating the dry AA is furan, while we got smaller amounts of furan in the cooking under pressure. The most probable intermediates of AA degradation are 2-deoxyaldotereses, 2-furoic acid and 2-furaldehyde. The formation of furan as the main products of ther-
mal decomposition of AA during baking, cooking or pyrolysis, was confirmed in several studies [17-19].

The importance of vitamin C in human metabolism incited numerous studies to determine the content of this vitamin in fruits, vegetables and juices. They used primarily spectrophotometric [20-22], titrimetric and electrochemical methods [22-28]. A number of papers devoted to the quantitative determination of vitamin C in different samples of food and beverages by cyclic voltammetry indicated that this method has a number of advantages compared to other methods, being simple, inexpensive, accurate and selective.

The kinetics of degradation of vitamin C was also studied using titrimetric and spectrophotometric methods [29-35]. In the present study, we used cyclic voltammetry method to examine the kinetics of degradation of AA. The temperature and storage time were the varying parameters. The results showed that cyclic voltammetry presents a fast, simple, inexpensive and selective method of investigation of kinetics of AA degradation.

EXPERIMENTAL

All the cyclic voltammetric measurements were performed using a Potentiostat & Galvanostat Model 273 coupled with a Pentium IV personal computer. Pt disk (1 mm) sealed in a Teflon plate (2 mm) was used as working electrode. Pt foil, with the surface of 1 cm², was used as an auxiliary electrode, and a saturated calomel electrode (SCE) was the reference electrode.

The measurements were performed in solutions with ascorbic acid concentration of 10 mmol dm⁻³ obtained by dissolving the appropriate amount of pure acid (Merck) in distilled water. The solutions were thermostated at the appropriate temperature (25, 35, 65 and 90 °C), and at specified time intervals the amounts of 25 ml were taken, cooled to room temperature, and the I-E curves were recorded. In all experiments, KCl (Merck) was used at a concentration of 0.34 mol dm⁻³ as an auxiliary electrolyte.

The calibration curve was obtained by recording the voltammograms of AA solutions in the concentration range 2-10 mmol dm⁻³, obtained by successive dilution of the stock solution (10 mmol dm⁻³).

The pepper juice obtained by squeezing fresh green pepper was then filtered and thermostated at 90 °C. I-E curves were recorded in the same way as in the case of pure AA.

RESULTS AND DISCUSSION

Figure 1a shows the I-E curves obtained in the AA solutions with the concentration range of 2-10 mmol dm⁻³, with the addition of 0.34 mol dm⁻³ of KCl solution as an auxiliary electrolyte. The anodic peaks at 0.45 V versus SCE is attributed to the oxidation of AA to DHA, in accordance with literature data [23-28].

Based on Figure 1a, a calibration curve was drawn to show the dependence of the current density of the anodic current peak on the concentration (Figure 1b). The anodic peaks at 0.45 V were found to vary linearly with ascorbic acid concentrations. The high value of the regression coefficient (R² = 0.9968) confirms the validity and legitimacy of cyclic voltammetry for quantitative determination of AA in different samples.

The kinetics of the degradation reactions of AA at different temperatures are shown in Figure 2. Figure 2 shows a decrease in oxidation current peak of solution with time of storage at all investigation temperatures. Also, at high temperatures,
shorter period of time is required for the reduction of the concentration of AA during storage compared to the time at the room temperature. Thus, for example, at 90 °C the reduction in the concentration of AA after 120 min is 33%, and after 300 min it is 70%. At room temperature, the ascorbic acid degradation occurs much more slowly: after 6 days the reduction of the concentration is 32% and after 12 days, the percentage is 56%. This fact indicates the significant impact of heat on the stability of AA.

During storage the solution of AA visually changes colour: a colourless solution became yellow, and the colour became more intensive with time. The change in the colour of the solution is accompanied by the change in voltammograms. Namely, on the voltammograms shown in Figure 2, the presence of the second anodic peak current is observed after a certain storage time of AA solution. According to the literature data, the change of the colour of the solution, or the presence of second current peak may be explained by the further oxidation of DHA, namely the formation of furan-type compounds, resulting from thermal degradation of AA under aerobic conditions [9-19].

The dependences of \( \ln \left( \frac{c}{c_0} \right) \) as a function of time (Figure 3) have high values of \( R^2 \), indicating that the kinetics of the degradation of AA at all tested temperatures can be described by first-order kinetic model:

\[
\frac{dc}{d\tau} = kc^n
\]
where $c$ is the concentration, $k$ is the rate constant, and $n$ is the order of reaction. The degradation reaction is first order if $n = 1$, and by integration of Eq. (1) one obtains the equation of the first order reaction as follows:

$$\ln \left( \frac{c}{c_0} \right) = -k \tau$$

(2)

The dependence of $\ln \left( \frac{c}{c_0} \right)$ as a function of time is the curve whose slope determines the rate constant of the investigation reaction, where $c_0$ and $c_\tau$ are the concentrations of ascorbic acid at the beginning of the reaction and after time $\tau$, respectively.

The dependence of reaction rate constant on the temperature is given by the Arrhenius equation:

$$k = A_0 \exp \left( \frac{-E_a}{RT} \right)$$

(3)

where $E_a$ is the activation energy, $R$ is the universal gas constant, $T$ is temperature and $A_0$ is a constant.

The first-order degradation reaction of AA is in accordance with the works of other authors [30-34,36-38].

From the slope of the straight line, the values of the rate constants of the oxidation reaction at different temperatures were calculated. The half-life of the reaction ($\tau_{1/2}$), i.e., the time required to reduce the concentration of AA in half compared to the initial value is calculated based on the value of the rate constant as $0.693/k$ [31]. The calculated values of $k$ and $\tau_{1/2}$ at different temperatures are shown in Table 1. With the increase in temperature the rate constant of the reaction increases, while the reaction half-life decreases. Thus, a temperature rise of 25 to 90 °C can cause an increase of the rate constant of $5 \times 10^{-5}$ to $3 \times 10^{-3}$ min$^{-1}$, while the half-life of the reaction decreases from 231 h to 231 min within the same temperature range.

<table>
<thead>
<tr>
<th>$t$ / °C</th>
<th>$k$ / min$^{-1}$</th>
<th>$\tau_{1/2}$ / min</th>
<th>$R^2$</th>
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</tr>
<tr>
<td>90</td>
<td>$3 \times 10^{-3}$</td>
<td>231</td>
<td>0.998</td>
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</table>

Table 1. The kinetic parameters of the degradation reactions AA

Figure 4a shows cyclic voltammograms obtained at different concentrations of AA in Tafel coordinates $E = f(\log j)$. These data were used for drawing the dependency $\log j = f(\log c)$ (Figure 4b). The slope of this dependence is 1.113 and this confirms the previous observation that the kinetics of the AA degradation reaction can be described by a first-order kinetic model.
The Arrhenius plot of the AA degradation reaction is shown in Figure 5. The slope of the line leads to the value of activation energy of the reaction, which is 48.204 kJ mol\(^{-1}\).

Cyclic voltammograms obtained in fresh pepper juice with the addition of 0.34 mol dm\(^{-3}\) KCl on the Pt electrode at different times of storage at 90 °C are shown in Figure 6a. Based on the calibration curve (Figure 1a), the concentration of AA in the pepper juice is 5.38 mmol dm\(^{-3}\).

As well as in the pure AA, in the pepper juice the reduction of anode current peak corresponding to the oxidation of AA indicates a decrease of AA content in the juice over time. The straight-line dependence ln (\(c_\tau/c_0\)) as a function of storage time (Figure 6b) with \(R^2\) value of 0.998 indicates that the reaction kinetics can be described by the first-order kinetic model. From the obtained linear dependence the rate constant of the degradation reaction of AA in pepper juice is calculated (5\(\times\)10\(^{-3}\) min\(^{-1}\)), which corresponds to the half time of the reaction of 138.6 min.

The lower value of the rate constant of the oxidation reaction of AA in pepper juice in comparison to pure AA can be explained by the presence of various
substances in the juice, which stabilize AA, slowing its degradation [31,35].

CONCLUSION

The paper proposes a fast and simple method for examination of the kinetics of degradation of AA. The experimental studies in this paper have shown that the degradation of AA, whether pure or contained in the pepper juice, increases with the increase of temperature and storage time. The kinetics of the oxidation reaction in both cases corresponds to the reaction of first order and the rate constant of the oxidation reaction increases with temperature. The lower value of the rate constant in the case of pepper juice in comparison to pure AA indicates a significant effect of the substances present in the pepper on the stability of AA.

REFERENCES

ISPITIVANJE KINETIKE DEGRADACIJE
ASKORBINSKE KISELINE CIKLIČNOM
VOLTAMETRIJSKOM METODOM

U radu je predložena brza, jednostavna, jeftina i selektivna metoda ciklične voltametrije za ispitivanje kinetike degradacije askorbinske kiseline (AA) na različitim temperaturama. Pokazano je da smanjenje koncentracije AA na svim temperaturama prati kinetiku reakcije I reda. Izračunate vrijednosti konstante brzine ispitivane reakcije oksidacije rastu sa porastom temperature i iznose $5 \times 10^{-5}$; $2 \times 10^{-4}$; $1 \times 10^{-3}$ i $3 \times 10^{-3}$ min$^{-1}$ na temperaturama 25, 35, 65 i 90 °C, redom. Temperaturna zavisnost konstante brzine slijedi Arenjusovu jednačinu, a vrijednost aktivacione energije ispitivane reakcije degradacije iznosi 48,2 kJ mol$^{-1}$. Takođe je ispitana uticaj vremena stajanja na temperaturi od 90 °C na sadržaj AA u svježem soku zelene paprike. Pokazano je da je reakcija oksidacije AA u soku zapravo reakcija prvog reda, dok niža vrijednost konstante brzine u odnosu na čistu AA ($5 \times 10^{-3}$ min$^{-1}$) ukazuje na uticaj supstanci prisutnih u paprici na stabilnost AA.

Ključne reči: ascorbinska kiselina, kinetika, ciklična voltametrija, zelena paprika.