# DEGRADATION KINETIC MODELLING OF ASCORBIC ACID FROM ORANGE JUICE

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# THE AIM OF THIS STUDY

- To determine vitamin C in natural orange juices by spectrometric and voltammetric methods.
- To determine the kinetic and thermodynamics activation parameters for ascorbic acid degradation in orange juices over time and at different temperatures.

# PRACTICAL USES

- The kinetic and thermodynamic analysis of vitamin C degradation are very important because of its ubiquitous presence in food or biological systems and participation in biological processes as diverse as digestion, absorption, endocrinology, anti-carcinogenicity, collagen formation, cataract prevention and detoxification.
- The kinetic and thermodynamic parameters obtained can be used in any industrial situation by an appropriate modeling adaptation.
- Another reason for the importance of kinetics is that it provides evidence for the mechanisms of chemical processes that is of practical use in deciding what is the most effective way of causing a reaction to occur.

# SAMPLES

The analyzed samples were natural orange juices:

- SAMPLE 1 - COMMERCIAL ORANGES JUICE-WITH NO SUGAR ADDED,
- SAMPLE 2 -COMMERCIAL BLOOD SICILIAN ORANGES JUICE-WITH NO SUGAR ADDED,
- SAMPLE 3-COMMERCIAL ORANGES JUICE WITH SUGAR
- SAMPLE 4 - COMMERCIAL BLOOD ORANGES JUICE WITH SUGAR.

# METHODS


- Ascorbic acid in orange juices was determinate by UV-VIZ absorption spectrometry and differential pulse voltammetry (DPV) analysis with modified carbon-printed electrodes.
- Spectrometric analysis, the fruit juices were sonicated, then centrifuged at 5000 rpm for 10 min. The supernatant was filtered through filter paper. Metaphosphoric acid (20 g/L) was used for extraction. The extract was diluted with metaphosphoric acid. Blank was prepared by the same manner as except for the addition of fruit juice samples.
- The spectrometric method is based on the color reaction between potassium hexacyanoferrate and ascorbic acid in acid medium, when ascorbic acid has a reducing effect. The determinations were done at a wavelength of 700 nm using a UV-VIZ DR 3900 LANGE from ENGLAND spectrometer.
- The voltammetric method is based on the oxidation of ascorbic acid to dehydroascorbic acid. A conventional three-electrode potentiostatic system (stat400 bi-potentiostat) was used in order to carry out the electrochemical measurements. The three electrodes are integrated in the screen-printed electrodes, where working and counter electrodes are based on a carbon ink and the pseudo-reference electrode is made up of silver.

# RESULTS

Table 1. The content of AA mg/100 mL in studied samples

| Sample | The content of ascorbic acid mg AA/100 ml | |
|---|---|---|
| | Spectrometric method | Voltammetric method |
| 1 | 29.98±0.24 | 30.13±0.23 |
| 2 | 32.08±0.31 | 32.13±0.37 |
| 3 | 42.14±0.43 | 42.27±0.35 |
| 4 | 38.22±0.22 | 38.28±0.44 |

Values are means, n=3

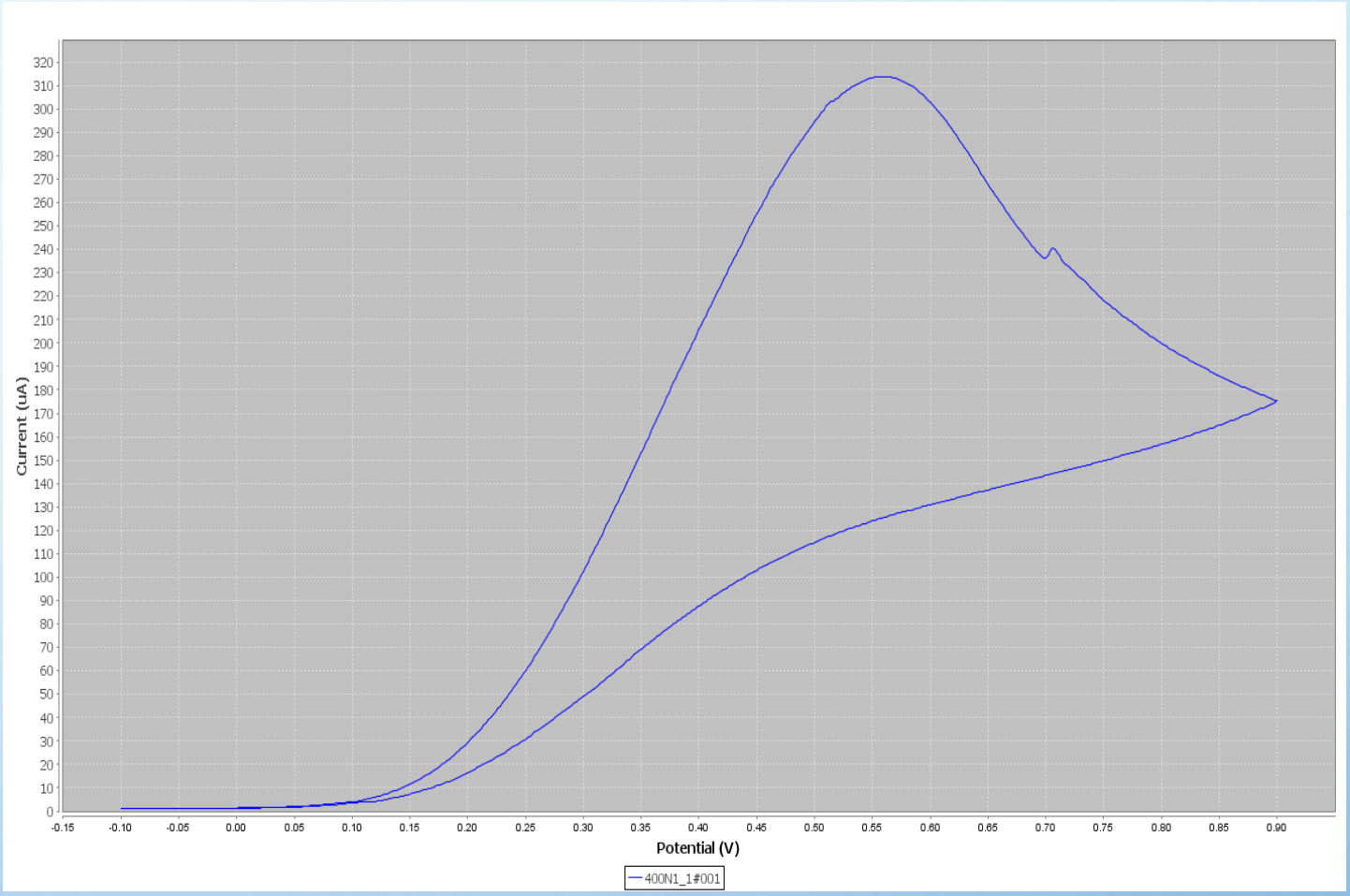



Fig. 1. The cyclic voltammogram obtained for the ascorbic acid solution

# RESULTS

Table 2. Rate equations and the correlation coefficients

| Sample | Temperature | Zero-order kinetic model | | First-order kinetic model | |
|---|---|---|---|---|---|
| | | Rate equation | $R^2$ | Rate equation | $R^2$ |
| 1 | 277 K | y = -0.4406x+30.605 | 0.9979 | y = -0.0164x+0.0062 | 0.9998 |
| 2 | | y = -0.3797x+32.607 | 0.9919 | y = - 0.0132x+0.007 | 0.9998 |
| 3 | | y = -0.3734x+42.692 | 0.9979 | y = -0.0094x+0.0027 | 0.9999 |
| 4 | | y= -0.3374x+38.599 | 0.9995 | y= - 0.0089x+0.0007 | 0.9997 |
| 1 | 295 K | y= -0.553x+30.657 | 0.9992 | y = -0.0006x-0.0011 | 0.9998 |
| 2 | | y= -0.52x+32.674 | 0.9994 | y = -0.0006x+0.0027 | 0.9998 |
| 3 | | y= -0.537x+42.815 | 0.9998 | y = -0.0004+0.0009 | 0.9999 |
| 4 | | y= -0.525x+38.829 | 0.9989 | y= - 0.0005x+0.0021 | 0.9993 |

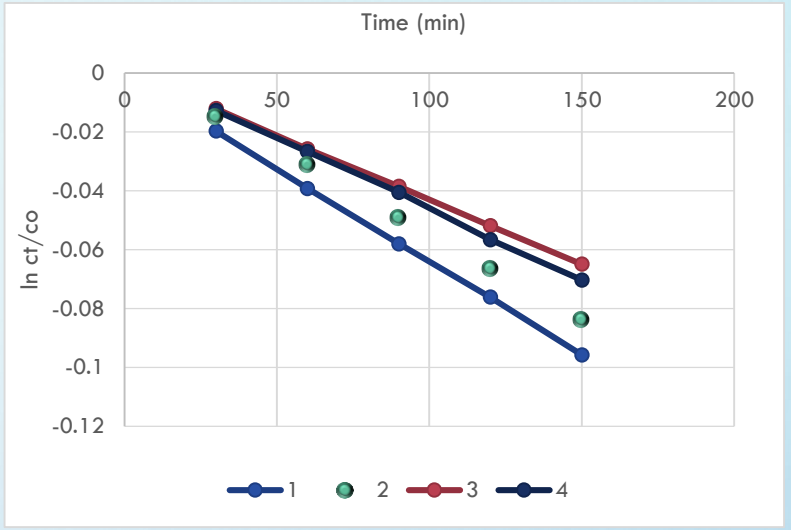
first-order kinetic models $\ln C - \ln C_0 = - k_1 t$

C is the ascorbic acid concentration at time t

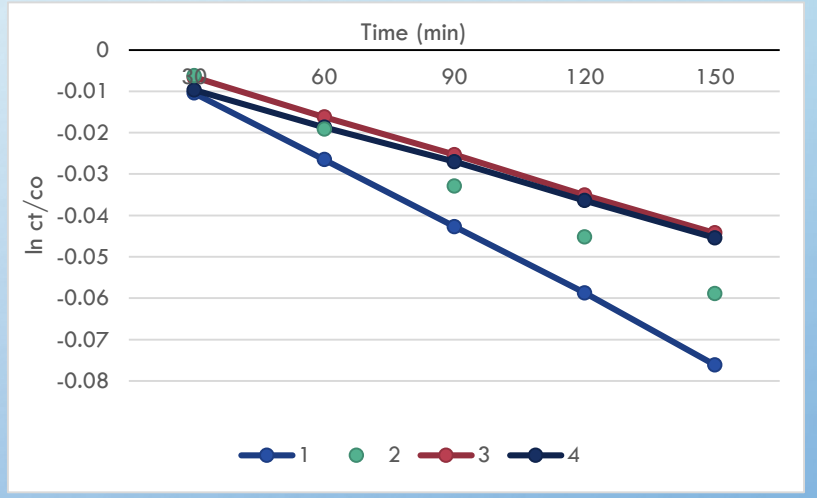
$C_0$ is the ascorbic acid concentration at time 0

$k_0$ and k are the ascorbic acid degradation rate constant for the zero order and for the first order

t is the storage time.




a)




b)

Fig. 2. The dependences of ln ct/co as a function of time at 277 K (a) and 295K (b)

# RESULTS

Table 3. Values of rate constant and half-life time for both studied temperatures

| Sample | Temperature | Rate constant k ($min^{-1}$) | $t_{1/2}$ (min) | Temperature | Rate constant k ($min^{-1}$) | $t_{1/2}$ (min) |
|---|---|---|---|---|---|---|
| 1 | 277 K | $5x10^{-4}$ | 1386 | 295 K | $6x10^{-4}$ | 1155 |
| 2 | | $4x10^{-4}$ | 1732.5 | | $5x10^{-4}$ | 1386 |
| 3 | | $3x10^{-4}$ | 2310 | | $4x10^{-4}$ | 1732.5 |
| 4 | | $2.97x10^{-4}$ | 2333 | | $4.5x10^{-4}$ | 1540 |

The first order rate constants were calculated from the slope of the straight line and the half-life time, $t_{1/2}$ was calculated from the rate constant as 0.693/k.

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$$

$$ln\frac{k}{T} = -\frac{\Delta H\#}{R}\cdot\frac{1}{T} + ln\frac{k_B}{h} + \frac{\Delta S\#}{R}$$

$k_B$ is the Boltzmann's constant ($1.381 \times 10^{-23}$ J/K); T is the absolute temperature in Kelvin (K); h is Planck's constant ($6.626 \times 10^{-34}$ Js); R is the ideal gas constant (8.314 $J \cdot mol^{-1}K^{-1}$).

Table 4. Values for activation energy, activation enthalpy, activation entropy and Gibbs free energy

| Sample | E $kJmol^{-1}$ | $\Delta H^{\#}$ $Jmol^{-1}$ | $\Delta S^{\#}$ $J \cdot mol^{-1}K^{-1}$ | $\Delta G^{\#}$ $kJmol^{-1}$ | |
|---|---|---|---|---|---|
| | | | | 277K | 295K |
| 1 | 7289.24 | -992.6 | -308.48 | 84456.36 | 90009 |
| 2 | 8422.80 | -1331.9 | -310.67 | 84723.69 | 90315.75 |
| 3 | 10856.64 | -1868.1 | -313.60 | 84999.1 | 90643.9 |
| 4 | 15689.54 | -2930.6 | -314.75 | 84255.15 | 89920.65 |

# CONCLUSIONS

- According to applied pair t-test, no statistically significant differences values of AA content determined by both methods ($t_{calculated} = 0.15 < t_{table} = 2.20$) were found. In the same time, $p = 0.87 > 0,05$ which means that differences are not significant, demonstrating that the two methods: spectrometric and voltammetric can be successfully applied for the determination of ascorbic acid in the analyzed samples.
- The reaction order was determined through integrated graphical analysis where the dependences of $\ln c_t/c_0$ as a function of time reveals the high values for $R^2$, indicating that the kinetics of the degradation of AA follows first order reaction at both studied temperatures.
- It was observed that the ascorbic acid loss was decreased when the samples were kept at the refrigerator. For sample 1 the loss of ascorbic acid was: 7.33% at 277K and 9.13% at 295K, sample 2: 5.73% at refrigerator at 8.03% at room temperature, sample 3: 4.33% at 277K and 6.29% at 295K and sample 4: 4.44% at refrigerator and 6.79% at room temperature.
- The rate constants were increased with the increase of storage temperature. Samples of blood orange juices reveal smaller values for rate constants and respectively half-life times than the orange juices.
- Activation energy ranged between 7289.24 $kJmol^{-1}$ and 15689.54 $kJmol^{-1}$.
- The highest values for activation enthalpy, activation entropy were obtained for orange juice with no sugar added.