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Investigation of apples' aging by electric impedance spectroscopy

T. Yovcheva[1], E. Vozáry[2], I. Bodurov[3*], A. Viraneva[1], M. Marudova[1], G. Exner[1]

[1]*Plovdiv University "Paisii Hilendarski", 24 "Tsar Asen" str., 4000 Plovdiv, Bulgaria*
[2]*Corvinus University of Budapest, 14-16 "Somlói" str., H-1118 Budapest, Hungary*
[3]*Institute of Optical Materials and Technologies "Acad. J. Malinowski", Bulgarian Academy of Sciences, "Acad. G. Bonchev" str., block 109, 1113 Sofia, Bulgaria*

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Electric impedance spectroscopy, as a fast and non-invasive method, was used to monitor apples' properties during aging. This method provides information about the physical properties of apples which are closely related to the chemical ones. Two different analytical techniques for assessment of the changes of apples' properties during aging time were proposed. The first one is based on a single measurement in the low frequency range (around 100 Hz) and the other one - on Argand plot. According to our results, the observed changes in the electric impedance spectroscopy spectra can be attributed to the changes in the relative moisture content of the apples. The apoplastic and simplistic resistances and relaxation times were derived by modeling the apples' behaviour with equivalent circuit scheme.

Keywords: Apples aging, Dielectric properties, Impedance spectroscopy

INTRODUCTION

One of today's challenges in food physics field is to establish an exact relationship between the engineering properties of food and the food product quality. The best solution would be to find some fast and non-destructive methods, which can undoubtedly show the food quality.

The electrical properties of food are believed to be sensitive to the food quality and could be used to follow the structural properties changes. Some recent attempts have been made to prove the applicability of such approach [1-6].

We focus our attention on Electrical impedance spectroscopy (EIS), as one of the methods for rapid determination of the electric properties of food. In EIS, alternating voltage is applied to the sample, causing polarization and relaxation in it. This leads to changes in the amplitude and the phase of the alternating current signal and hence the changes in the sample' impedance (Z) can be determined. The impedance is a complex quantity, consisting of real (R) and imaginary (X) parts. At *a priori* known frequency, one defines single values of Z. If one varies the frequency in a certain interval, spectral dependence of Z could be obtained.

The aim of the present work is to find out whether appropriate EIS parameters sensitive to the changes in the apples' properties during 21 days aging, at room temperature, exist and to propose some applicable techniques for their monitoring.

MATERIALS AND METHODS

Idared apples were supplied from a local Hungarian market. They were stored at room temperature for period of 3 weeks. The mass of the apples was measured immediately after the apples were bought and each time just before the measurement (1st, 7th, 14th, and 21st day). The microbalance used, allowed accuracy ± 0,001 g of the measured values. Assuming initial moisture content of $w_0 = 89\ \%$ - wet basis [7] - and supposing that the soluble solid content (11%) remained unchanged during the entire storage period, the relative moisture content of the apples (dry basis) was calculated according to the equation:

$$w = \left(m - 0.11\, m_0\right) / \, 0.11\, m_0 \qquad (1)$$

where m_0 is the initial apple mass, expressed in kg; m is the apple mass at the time of the experiment (1st, 3th, 7th, 14th, and 21st day, respectively), expressed in kg.

For the sake of improving results reliability, each time the mass of 10 different apples (without any treatment) was measured and the standard deviation was calculated.

* To whom all correspondence should be sent:
E-mail: bodurov@uni-plovdiv.net

EIS measurements were performed on HP 4284A Precision LCR meter and HP 4285A Precision LCR meter, covering the frequency range from 30 Hz to 30 MHz. The voltage had a magnitude of 1 V for all measurements. The experimental values for impedance were corrected for stray admittance and residual impedance (open-short correction) [8]. Plate Ag/AgCl ECG electrodes (Fiab Spa) with a diameter of 10 mm were used, avoiding apples' injury.

For all measurements, cylindrical samples having initial length up to 46 mm and a diameter of 20 mm were cut from the equatorial part of the apples. Impedance magnitude ($|Z|$) and phase angle (θ) were measured at different frequencies. Consecutive shortening of the samples allowed us to gain $|Z|$ and θ dependences on the sample length (d).

It is supposed [9] that the open-short corrected impedance (Z_m) values depend on electrode impedance (Z_e), tissue impedance (Z_t), and electrode distance (which equals the sample length - d) and the electrode impedance is independent of the place of the measurement. In such case:

$$Z_m = Z_e + d.Z_t \quad (2)$$

where Z_t is expressed in [Ω / mm] and Z_m is a complex number ($Z_m = R_m + jX_m$). R_m is the real and X_m is the imaginary parts of Z_m:

$$R_m = R_e + d.R_t \text{ and } X_m = X_e + d.X_t \quad (3)$$

In the present work, the open-short corrected experimental values ($|Z_m|$ and θ_m) were averaged over three consecutive measurements for one and the same d. R_m and X_m values for each d were calculated from those averaged values as follows:

$$R_m = |Z_m|.\cos\theta_m \quad \text{and}$$
$$X_m = |Z_m|.\sin\theta_m \quad (4)$$

The obtained values were drawn as R_m (or X_m) versus d dependences. With the help of linear regression, the values of R_e or X_e (as the intercept with R or X axis, at d = 0) and R_t or X_t (the linear slope) were derived for each sample and each frequency. The coefficient of determination was not lower than 0.98 for all plots. The final values for R_e, X_e, R_t, and X_t were obtain after a calculation of the average value of all measurements at identical conditions. Then after, Z_t and θ_t values were constructed from the averaged R_t and X_t, according to the equations:

$$|Z_t| = \sqrt{R_t^{\,2} + X_t^{\,2}} \text{ and } \theta_t = \arctan\frac{X_t}{R_t} \quad (5)$$

Further, the experimental results were modeled by the help of equivalent circuits' method, where the fruit tissue features could be described by means of electrical circuit scheme. The exact elements and connections of the scheme depend on the experimental findings. In this concern, one first constructs Argand plot, representing R_t versus X_t dependences. In the present investigations, the corresponding plots (Fig.1) consist of two arcs, which centers lie under the R_t-axis. Hence, as it was

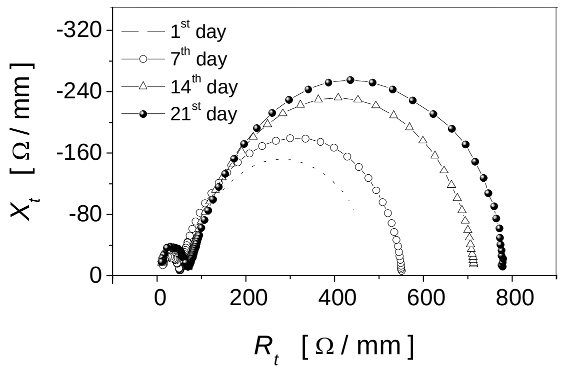

Fig. 1. Argand plot at different storage time.

pointed out in the literature [10], there is a distribution of the relaxation times rather than a single relaxation time. Following some previous works [10, 11], a model comprising of serial connection of two constant distributed circuit elements (CDCE) and one Ohmic resistance was built so that:

$$Z_t = R + \Delta R_1\left(1 + (j\omega\tau_1)^{\psi_1}\right)^{-1} + \Delta R_2\left(1 + (j\omega\tau_2)^{\psi_2}\right)^{-1} \quad (6)$$

where R – is an ohmic resistance, accounting for the resistance of the tissue at infinite high frequency; ΔR_1 , ΔR_2 - are the resistances of the first and second CDCE elements, respectively; τ_1, τ_2 - are the relaxation times, connected with each of the CDCE elements; ψ_1, ψ_2 - are parameters, which account for the relaxation time dispersion; $\omega = 2\pi f$, where f is the frequency. One gets R as the distance between the origin of the Argand plot and the intercept point of the R_t-axis with the high frequency arc, ΔR_1 and ΔR_2 correspond to the lengths of the chords appearing as cross-sectional points of the R_t-axis with the arcs at higher and lower frequencies, respectively. The relaxation times τ_1 and τ_2 are derived from the apex of the high and low frequencies arcs ($\omega_i.\tau_i = 1$), respectively.

ψ_1 and ψ_2 parameters (which vary from 0 to 1) describe the distributions of τ_1 and τ_2 relaxation times. When $\psi = 1$ a single relaxation time is observed, whereas at decreasing values of ψ, a broadening of the relaxation time distribution appears. The coefficients ψ_1 and ψ_2 were calculated ($\psi_i = 1 - \alpha_i / 90$, where α_i is the angle between the R_t-axis and the radius of the circle in the intercept point of the circle with the R_t-axis).

The derived values of R, ΔR_1 and ΔR_2 were then used to calculate the simplastic (intracellular), R_s, and apoplastic (extracellular), R_a, resistances [11]:

$$R_a = R + \Delta R_1 + \Delta R_2 \quad \text{and}$$
$$R_s = R\left[1 + R/\left(\Delta R_1 + \Delta R_2\right)\right] \qquad (7)$$

The last two equations were built on the supposition that at low frequencies the current may not pass the cell membranes but flows into apoplastic space and at high frequencies the current may pass the cell membranes and so the flow passed through both apoplastic and simplistic space [12].

RESULTS AND DISCUSSION

The moisture content values for different storage times, calculated from Eqn. 1, are shown in Fig.2. During the entire experimental time period, the moisture content decreases with storage time. In Fig. 3, the frequency dependencies of Z_t magnitude and θ_t (values obtained after Eqns.7-8) are presented. Since the uncertainty did not exceed 4 %, the confidence intervals are not presented in the figure.

As it is seen in Fig. 3A, the impedance magnitude values, Z_t, show considerable differences in the low frequency interval and the curves merge in the high frequency interval. The frequency dependencies of phase angles, θ_t, are very similar for all days of measurements (Fig. 3B). According to these results, Z_t magnitude values and Z_t frequency dependence are the EIS parameters, sensitive to the apples' quality changes. Since the main differences were observed in the low frequency interval (up to 400 Hz) one may choose to monitor the time changes of $|Z_t|$ at a single fixed frequency in this range. Comparing the results from Figs. 2-3, one might suppose that the changes in both dependencies could be connected and $|Z_t|$ increase could be attributed mainly to the moisture content decrease.

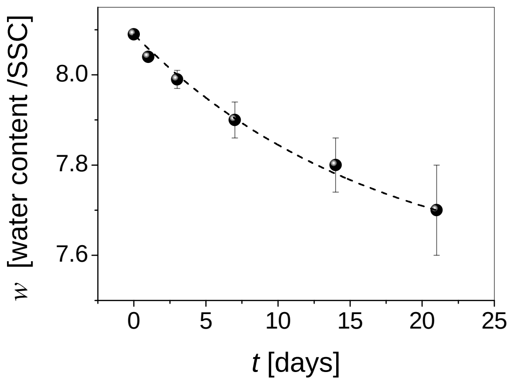

Fig. 2. Relative moisture content storage time dependence. The line is drawn only for eye guide.

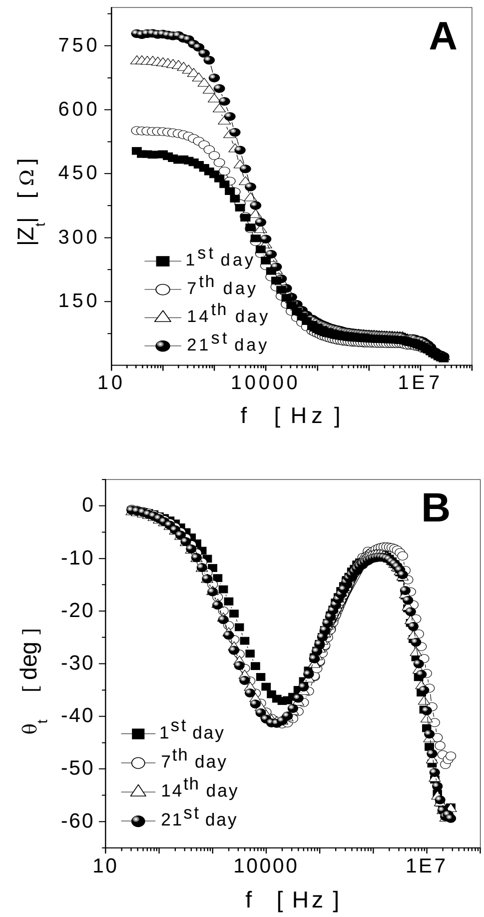

Fig. 3. Impedance magnitude, Z_t, (A) and phase angle, θ_t, (B) frequency dependencies for different storage times.

Argand plots at different storage times (Fig. 1) allows one to gain information about the apples' properties change. Each of the plots consists of two arcs. As it can be seen, the arc at higher frequencies (left side) remains almost unchanged during the experimental period, but the arc radius at lower frequencies (right side) increases with storage time. The apex of the arc (the place of the minimum value of X_t) moves to higher R_t values. Hence, the latter arc is the sensitive one and could be used for apples' properties monitoring.

The processes, taking place during storage time, can be investigated by an exact calculation of all model parameters. The results are listed in Table 1. The parameters connected with the first arc (ΔR_1, τ_1, and ψ_1) do not show any clear tendency with increasing storage time. τ_1 values are very small, in order of nanoseconds, but they still cannot be attributed to an electron polarizability (which is in order of 10^{-16} s [10]). One can assume that the discussed arc appears as an electrical response from the tissue, which has been damaged during the cutting procedure [6]. The second arc properties show very clear storage time dependence. The values of ΔR_2 increase with time. τ_2 values also increase with time. One can suggest that when the moisture content decreases, the processes of relaxation take longer time. It is also to be expected, as it is well known that the water plays crucial role in all processes in the biomaterials. The τ_2 values are in order of microseconds, which corresponds to dipole relaxation process in ionic biomaterial [12]. Simplastic resistance (R_s in Table 1) does not change with storage time, whereas the apoplastic resistance (R_a in Table 1) increases. Hence, the inner structure of the apple cells is not disturbed and water losses originate from the extracellular space.

Table 1. Model parameters, derived from the equivalent electrical circuit model

Day	R [Ω/mm]	ΔR_1 [Ω/mm]	ΔR_2 [Ω/mm]	ψ_1	ψ_2	τ_1 [nsec]	τ_2 [μsec]	R_s [Ω/mm]	R_a [Ω/mm]
1	5	58	449	0.84	0.50	32	33	5	512
7	8	45	516	0.83	0.51	12	41	8	569
14	6	65	656	0.81	0.54	15	46	6	727
21	3	75	737	0.80	0.51	13	50	3	815

CONCLUSIONS

The results show that EIS could be used for monitoring apples' properties during storage. This can be done either by measuring the magnitude of the impedance at one or several fixed low frequencies (from 100 to 400 Hz) or by measuring the impedance spectra in the range from 30 Hz to 30 MHz. In the latter case the parameter, which may be monitored, is the arc radius in Argand plot.

EIS method also allows calculation of structural parameters such as relaxation times of the processes in the structure, as well as simplistic and apoplastic resistances. In the present investigation, Argand plot consists of two arcs. The parameters of the higher frequency arc (radius and relaxation time) do not depend on the storage time. The parameters of the lower frequency arc are sensitive to the storage time. Relaxation time of this arc is in order of microseconds and increases with storage time. The arc radius also increases. Apoplastic resistance increases with storage time whereas simplastic resistance remains constant during the entire experimental storage period.

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ИЗСЛЕДВАНЕ СТАРЕЕНЕТО НА ЯБЪЛКИ С ЕЛЕКТРИЧНА ИМПЕДАНСНА СПЕКТРОСКОПИЯ

Т. Йовчева[1], Е. Возари[2], И. Бодуров[3], А. Виранева[1], М. Марудова[1], Г. Екснер[1]

[1]*Пловдивски университет „П. Хилендарски", ул. Цар Асен 24, 4000 Пловдив, България*
[2]*Корвинус Университет Будапеща, ул. Сомлои 14-16, H-1118 Будапеща, Унгария*
[3]*Институт по оптически материали и технологии, БАН, ул. „Акад. Георги Бончев", блок 109, 1113 София, България*

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(Резюме)

Елекричната импедансна спектроскопия, като бърз и недестуктивен метод, е използвана за проследяване на свойствата на ябълките при стареене. Този метод дава инфорация за физичните свойства на ябълките, които са тясно свързани с химичните. Две различни аналитични техники за проследяване на промените в свойствата на ябълките са предложени. Едната се базира на единично измерване в нискочестотния диапазон (около 100 Hz), а втората е основана на Argand диаграмата. Получените резултати показаха, че наблюдаваните промени в импедансните спектри се дължат на промяна във влажността на ябълките. Апопластичното и симпластичното съпротивления, както и времената на релаксация бяха получени чрез моделиране с еквивалентна електрична верига.