DIELECTRICAL PROPERTIES OF HUNGARIAN ACACIA HONEYS

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Abstract The statement of overheating of honey during the processing is very important in quality characterization of honey products. Four various Hungarian acacia honeys from different places were heated up to 35, 40, 50, 60, and 80 °C and were hold in water bath 0,5, 4 and 24 hours. The electrical impedance spectrum of honeys before and after heating were measured by precision LCR meters in frequency range from 30 Hz up to 30MHz at 1 V voltage with Ag/AgCl electrodes at room temperature (about 22 °C). The measured impedance spectra after open and short correction were approached with distributed circuit element in serial connection with a resistance. The parameters of this model were determined for honeys. Two parameters, the resistance and the relaxation time of model were decreased after heat treatment. After more detailed investigation these parameters can be used for detecting the earlier heating of honey products. The electrical permittivity and the loss factor also were determined in the frequency range from1 MHz up to 3 GHz.

Keywords: honey, heating, electrical permittivity, electrical impedance

Introduction

Honey is a natural sweet, viscous, fluid food. It is produced from the nectars of flowers by honeybees. It contains sugars, organic acids, various amino acids and biological active compounds: α-tocopherol, ascorbic acids and flavonoids (Turhan et al., 2008). The bee-honey is a natural food and does not allow the addition of any other substances (Diacu and Tantaveanu, 2007). The honey from beehive is processed by several operation among others thermal treatments. At first the honey is heated up to 55 °C for liquefaction and clarification and before packing is heated up to higher temperature for pasteurization (Subramanian et al. 2007). The heating can cause changes in the structure of proteins, can change, even can degrade the quality of honey

In consequence of heating the concentration of 5-hydroxymethylfurfural (HMF) can be increased (Turhan et al. 2008). The permissible HMF content can be maximum 40 mg/kg. Generally the detection of HMF content can be realized with chemical investigations, which are time-consuming and chemical-intensive.

The measurement of physical properties can be realizable in a short time and no chemicals needed. During the thermal processing the microcrystal structure of honey can change, the mobility of ions and charged groups can increase causing a decrease of electrical impedance of honey. The recrystallization of honey, the recovery to the original state is presumably relative long time – some weeks, months. On the bases of this supposition the aim of this work was to answer the question: can the electrical impedance spectrum, the parameter of spectrum or the electrical permittivity used for detecting the earlier heating of honey.

Materials and methods

Four acacia honeys - honey1 (from Kiskunsági Nemzeti Park), honey2 (from Örkény), honey3 (from Baracska) and honey4 (from Nagykáta) - were used in thermal processing. In each thermal processing a fresh (unprocessed) sample of 40 g was placed into a glass with cover. The glass was placed into the water bath of a thermostat – Thermo HAAKE DC10 - or into a laboratory drying oven – Venticell - for heating.

The temperature of thermostat was set 35, 40, 50, 60, and 80 °C and the sample were placed into the warm water for 0,5 hour or 4 hours. In experiment of 24 hours processing the glass with honey was placed into the laboratory drying oven of given temperature for 24 hours.

Electrical impedance spectrum of various honey samples was determined at room temperature before heating and after heating when the sample was cooled down for room temperature. Two Ag/AgCl electrodes (World Precise Instrument) one cm away from each other were inserted into the honey in 1 cm deep and the voltage between the two electrodes was 1 V. The magnitude and the phase angle of impedance were measured in frequency range from 30 Hz up to 1 MHz with a HP 4284A precision LCR meter and in frequency range from 75 kHz up to 30 MHz with a HP 4285A precision LCR meter. The measured spectra were open and short corrected – according to HP method – for eliminating the stray capacitance and inductance. The open and short corrected spectra were approached with a model consisting of serial connection of a resistance and a distributed element (Grimnes,and Martinsen, 2008):

$$R_0 + \frac{R_1}{1+(i\omega\tau)^{\psi}}, \qquad (1)$$

where R_0 and R are resistance, *i* is the imaginary unit, $\omega = 2\pi f$ is the angular frequency, f is the measuring frequency, τ is relaxation time and ψ is an exponent. The model parameters were determined the Solver function of Excel program.

The impedance measurement on one honey sample was repeated three times and each of the three spectra was approached with model (1) and the average and deviation of parameters were calculated.

The complex electrical permittivity also was determined with E4991A impedance analyser in frequency range from 1 MHz up to 3 GHz with 85070E Agilent coaxial measuring head and with the 85070D Agilent software:

$$\varepsilon = \varepsilon' + i\varepsilon'', \tag{2}$$

where ε' is the relative dielectric coefficient and ε'' is the dielectric loss.

Results

The all measured impedance spectra of honey samples – a typical spectrum can be seen on Fig.1 - were approached with model circuit (1) and the model parameters were determined.

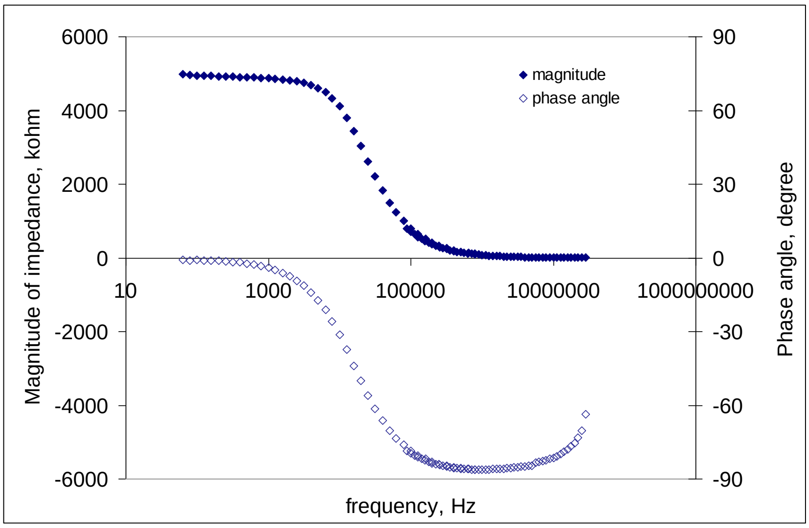

Figure 1. A typical measured impedance magnitude and phase angle spectrum of honey in the function of frequency

The result of curve fitting can be seen on Fig. 2. The spectra of all investigated honey samples were very similar to each other and all of them can be approached well with circuit model (1).

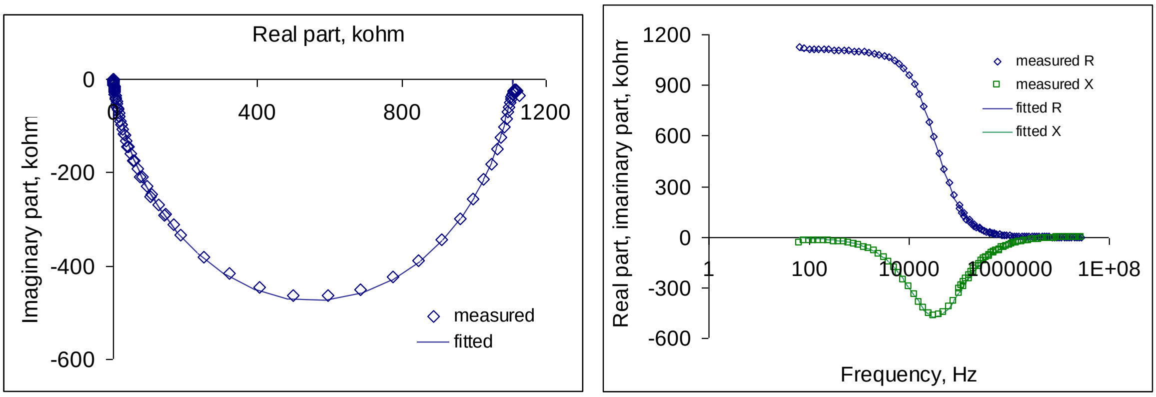

Figure 2. Measured and fitted real and imaginary part of a typical honey impedance on the complex plane and in the function of frequency

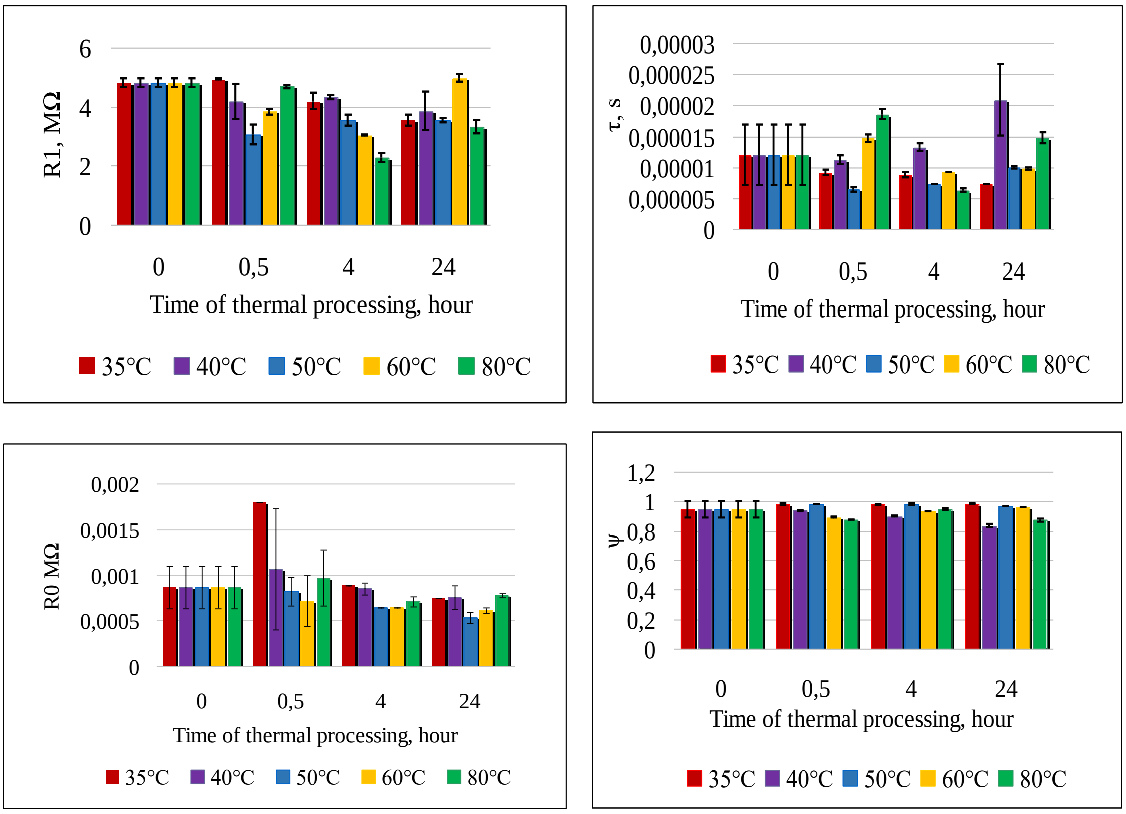

Figure 3. Model parameters of honey1 after various thermal processing

The model parameters in all experiments were determined for all honeys. Although all investigated honeys were acacia honey and their geographical origins are not far from each other the parameter values of untreated honeys (0 hour) are different as it can be seen on Fig. 3-6. The tendency of parameter changes after thermal processing also shows differences for the different honeys. The R_1 parameter showed decreasing tendency for all processed honeys as the time of heating is increased, but the individual R_1 values had a large spread.

The initial values of R_0 were different for the four honeys. The value of R_0 parameter also decreased as the time of thermal process was increased for honeys 1, 3 and 4, but not for honey2, for what this parameter increased. For all honeys there was a positive correlation (not shown) between the R_0 and R_1 parameters.

The initial (unheated) τ values were varied from $1{,}2*10^{-5}$ s up to $7{,}6*10^{-5}$ s. The relaxation time had also decreasing tendency for honeys except honey4 when the temperature and the time were increased in heating processes. There was a negative correlation between the R_0 and τ and between the R_1 and τ (not shown).

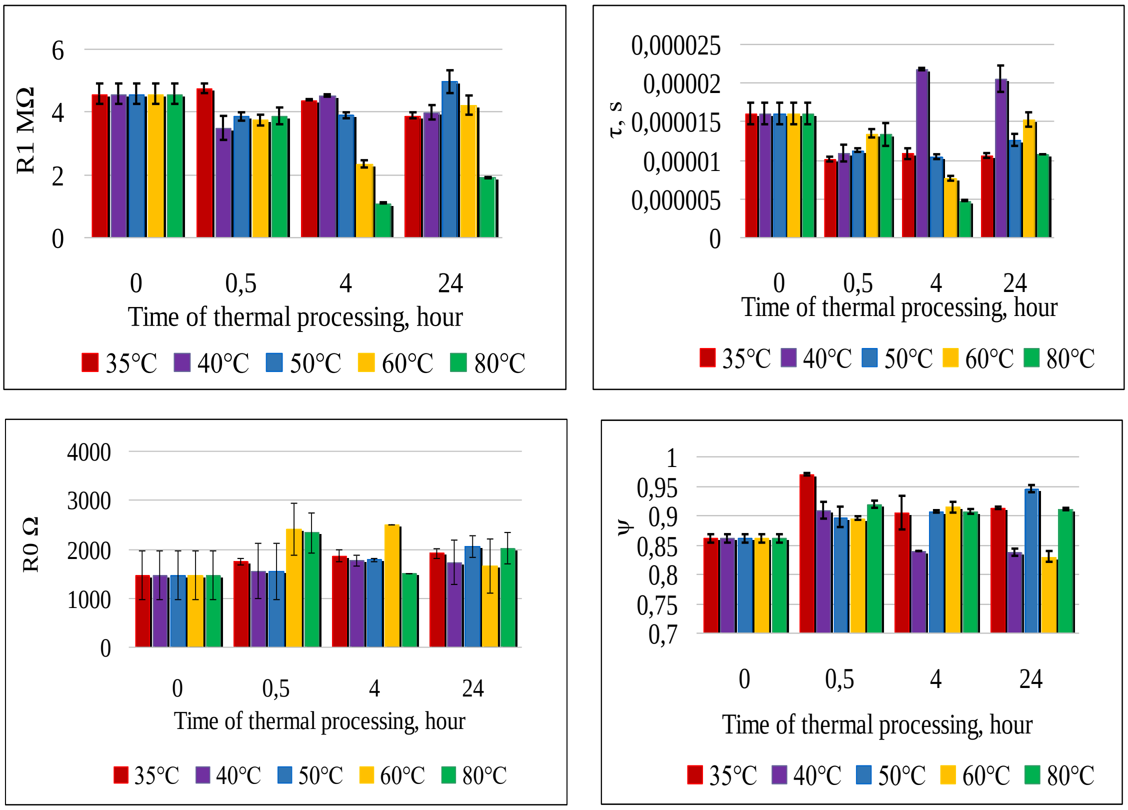

Figure 4. Model parameters of honey2 after various thermal processing

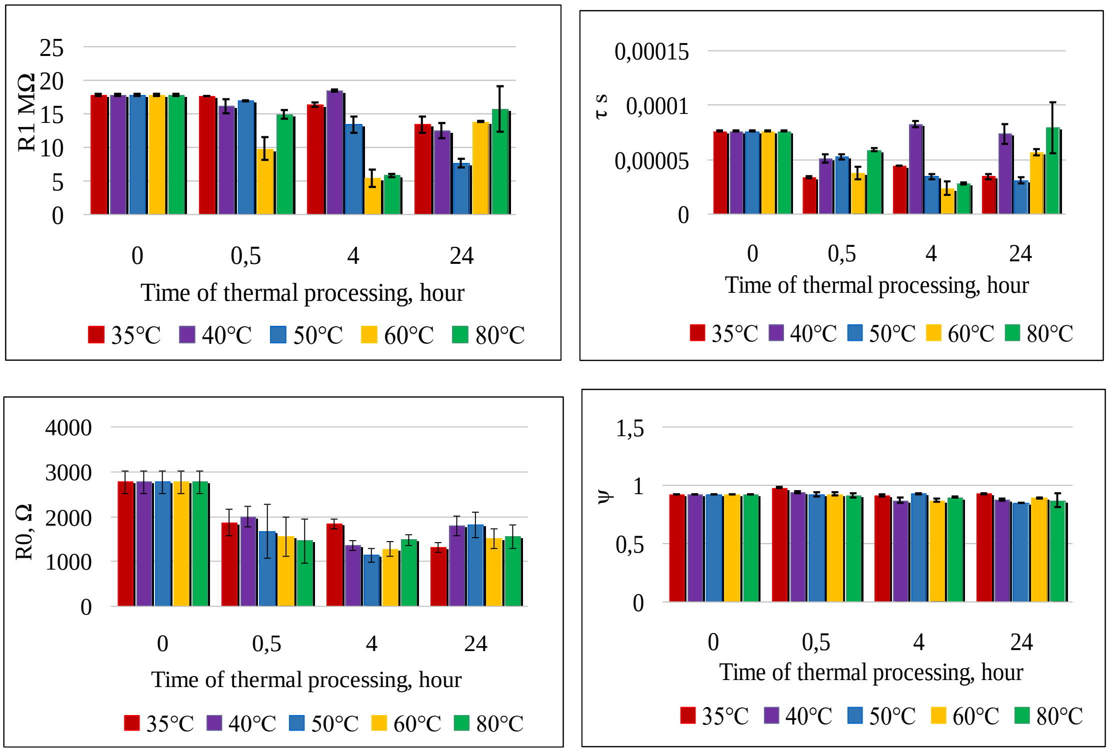

Figure 5. Model parameters of honey3 after various thermal processing

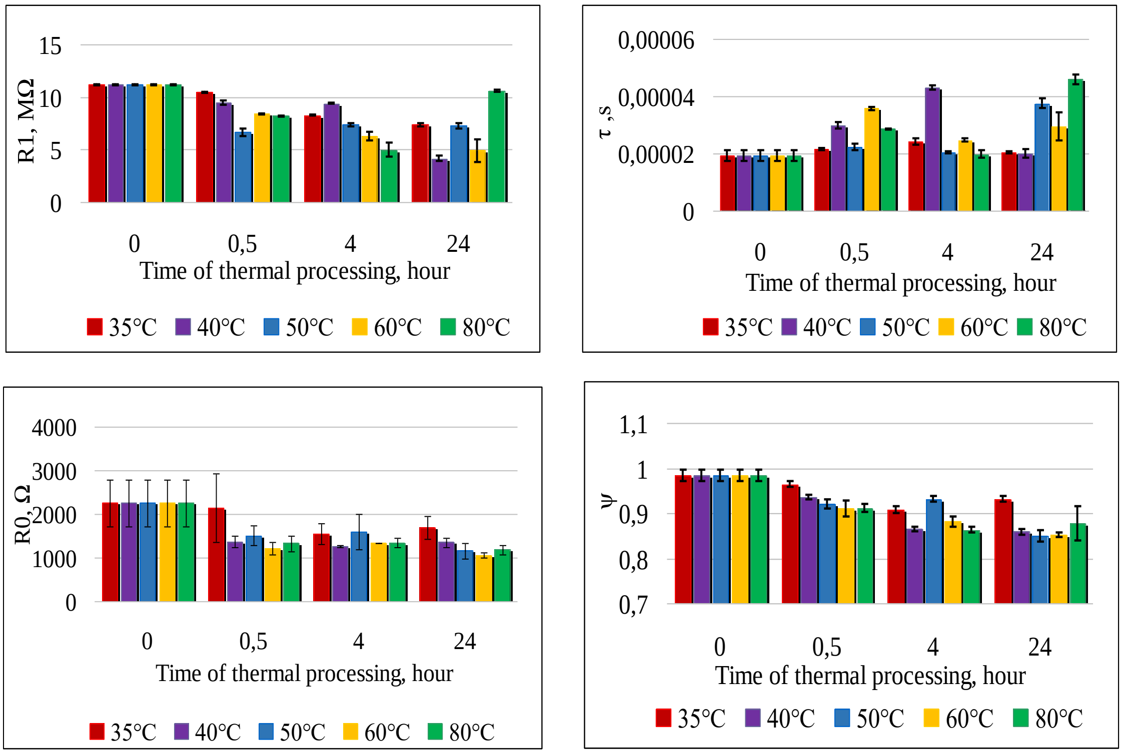

Figure6. Model parameters of honey4 after various thermal processing

The exponent ψ had various values for untreated honeys. This parameter had decreasing tendency at increasing time and temperature of processing for honey1, honey3 and honey4. The ψ values increased with increasing temperature and time of thermal processes for honey2.

The real and imaginary part of electrical permittivity of acacia honey1 (Fig, 6.A and B) has similar spectrum as it can be found in scientific literature (Guo et al., 2008, 2010). The other investigated honeys had similar spectra of dielectric coefficient and dielectric loss factor (not shown).

Generally both dielectric coefficient and dielectric loss increased after thermal processing. The changes were little and were not correlation of temperature and time of processing.

Discussion

The decrease of R_1 and R_0 parameters after thermal processing supports that assumption during heating the microcrystal structure changes and the mobility and polarizability of charges and charged groups increase. Presumably the recrystallization after heating is a long process.

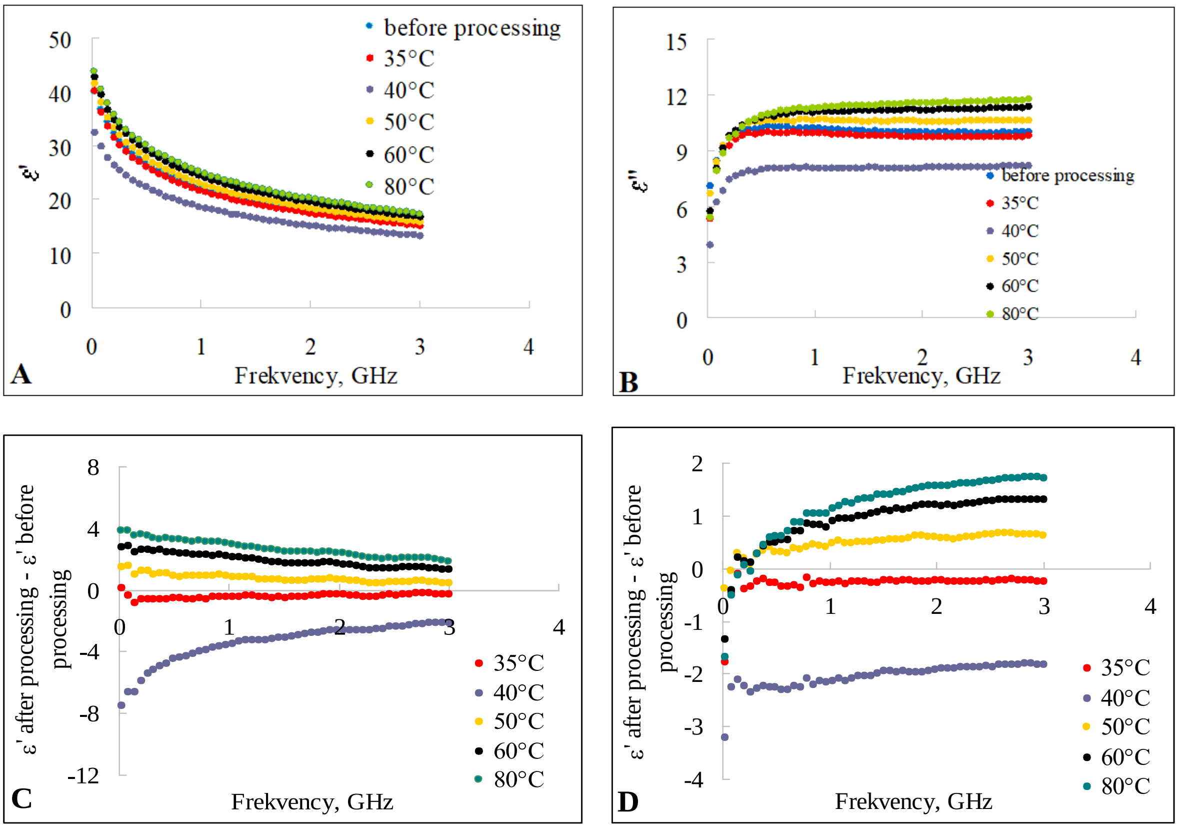

Figure 7. Dielectric coefficient (A) and dielectric loss (B) spectrum of honey1 before and after thermal processing and the difference spectra (C and D) of „after processing – before processing" at 0,5 hour processing.

The similar tendency in relaxation time decreasing after heating also can support the presence of charges and charged groups with higher internal energy. The decreasing ψ parameter also can show the more disordered structure.

The increase in ε' and ε'' also can reflect the increased conductivity and increased polarizability.

The outstanding values in decreasing or increasing tendency of impedance parameters can be caused by the fact, that the time period after thermal processes were various for the different samples. Some impedance spectra were measured right after heating when temperature of sample reached the room temperature and other spectra were measured a few days after the heat treatment.

Conclusions

Some impedance parameters – R_0, R_1 and τ - are able to indicate that the honey was earlier heated. But the impedance spectrum can be used for detecting earlier thermal processing in honey if the recrystallization process after heating of honey is well known.

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