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THE USE OF DIELECTRIC HONEY FEATURES FOR OVERHEATING DIAGNOSTICS

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During processing operations, honey can be exposed to excessive heat. That adversely affects the quality of product (its biological activity). The aim of this work was to test the possibilities of the use of dielectric properties (relative permittivity and dielectric loss coefficient) for honey overheating detection. Nine honey types obtained directly from beekeepers were investigated. Honey was heated at the temperatures 60, 70, 80, and 90 °C for 24 hours and then cooled down to 25–26 °C. At that temperature, dielectric properties of biological material under study were determined. In the frequency range 400 Hz to 4 kHz, the significant influence of thermal treatment temperature on both dielectric parameters was observed. Both dielectric parameters decrease as the heating temperature increases. The statistical analysis suggested that dielectric parameters can be used for distinguishing honey overheated from not overheated. Therefore, they can be potentially useful for honey quality assessment according to its overheating, e.g. in co-packing process. The proper frequency range for these parameters measurement is 1–4 kHz.

Keywords: dielectric properties, honey quality, honey overheating

Food processing operations have a significant effect on products quality. Food adulteration caused mostly by economic reasons is nowadays a constantly growing problem (Silvis et al., 2017). Therefore, quick and cheap methods of food quality assessment are developed and implemented instead of time-consuming methods based usually on chemical analyses.

Honey is a natural food produced by honey bees from the nectar of plants or from honeydew. Honey consists mainly of sugars but also of other minor compounds such as minerals, phenolic compounds, organic acids, amino acids, protein, vitamins, and enzymes (Saxena et al., 2010; Da Silva et al., 2016), and its positive influence on human health is well proven (Bogdanov et al., 2008; Kavapurayil et al., 2014). Packaging conditions, preservation methods, and storage time affect honey properties, therefore, only appropriately harvested, processed, and stored product retains its nutritional potential.

Normally, honey is not commercialized in its raw state. During the processing, it is commonly the subject of thermal treatment in two stages. The first stage comprises preheating at approx. 55 °C for honey liquefaction, straining, and clarification. The second stage is pasteurisation at approx. 80 °C to dissolve sugar crystals, inactivate spoilage microorganisms and undesirable enzymes, and facilitate packing (Escriche et al., 2014; Fauzi et al., 2014). Nevertheless, thermal treatment at the temperature above 40 °C results in adverse changes to honey properties such as brown turbidity, undesired flavour, or decrease of biological activity. The effect of heating up to 90 °C is decrease of total phenolic compounds and antioxidant activity (Kowalski, 2013; Chaikham & Prangthip, 2015). Honey type influences also the

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behaviour of diastase activity during thermal treatment. It was stated by SAMBORSKA and CZELEJEWSKA (2014) that honey diastase activity decreases with temperature increase in the 50–90 °C range differently in multifloral and rape honey. According to BABACAN and RAND (2007), the complete inactivation of amylase is the result of honey heated for 2 min at 71 °C or 8 min at 63 °C. Small reduction in invertase activity was the effect of honey thermal treatment at the temperature 45 °C (less than 20%). However, the pasteurisation process induces a decrease in invertase activity of about 90% (BONVEHI et al., 2000). In many papers, accumulation of 5-hydroxymethylfurfural (HMF) as a result of honey overheating is reported (CHAIKHAM et al., 2016). The increase in HMF content is also the effect of long storage time. TURHAN and co-workers (2008) suggest that the excessive HMF content might be related to primitive storage conditions rather than overheating. According to KARABOURNIOTI and ZERVALAKI (2001), the combination of HMF and invertase should be used in order to detect the honey exposure to heat. However, it is worth emphasizing that all chemical parameters mentioned above can only be tested by a specialist laboratory.

Some researchers stated that electrical properties can be used for food quality assessment (GUO et al., 2010; PENTOŚ et al., 2015; KARUPPUSWAMI et al., 2017; VALANTINA et al., 2017). GUO and co-workers (2011) found relationship between the temperature and honey dielectric properties in the frequency range from 10 to 4500 MHz. Similar results were reported by PASZKOWSKI and co-workers (2014) at the frequency below 2 MHz. Electrical honey properties seem to be promising as honey overheating indicators.

The aim of the present research was to determine the influence of thermal treatment temperature on honey electrical parameters: relative permittivity ε and dielectric loss coefficient tgδ in the frequency range from 10 Hz to 1 MHz.

1. Materials and methods

1.1. Materials

Honey samples harvested in the year 2011 from May to September, derived directly from beekeepers located in Lower Silesia region (Poland), were used for this study. A total of nine samples were analysed: linden flower (*Tilia* spp.), rapeseed (*Brassica napus* L.), phacelia (*Phacelia tanacetifolia* Benth.), buckwheat (*Fagopyrum esculentum* Moench), heather (*Calluna vulgaris* L.), willow (*Salix* spp.), multiflower, and honeydew. For the verification of honey types, a pollen analysis was accomplished in an accredited laboratory (Bee Products Quality Testing Laboratory in Puławy, Poland). Pollen analysis was conducted according to harmonized methods of melissopalynology, particularly according to Polish Standard PN-88/A-77626, paragraph 5.3.18. Additionally, the classification of honey sample as the honeydew honey was based on the value of conductivity of 20% honey aqueous solution (electrical conductivity higher than 0.8 mS•cm^{-1} is required for honeydew honey). The percentage content of pollen in honey samples is detailed in Table 1.

Honey samples were fresh, without a thermal treatment or improper storage. The water content of honey samples was determined by the refractometric method with the use of refractometer PAL-22S (dedicated to honey water content measurement). The water content of honey samples varied from 14.2% to 17.2%. Samples were stored at the temperature of 10–12 ºC until analysis. In Table 2, the selected chemical properties of honey samples are presented. These properties were measured with the use of the methods compiled by the International Honey Commission (BOGDANOV et al., 1997).

Table 1. The percentage concentration of pollen in honey samples (only pollen content exceeding 10% is presented)

Honey sample	Brassica napus	Phacelia	Brassicaceae	Fagopyrum	Salix	Trifolium	Solidago	Calluna	Echium	Tilia	Prunus
Rapeseed	74.43										
Phacelia		80.64									
Buckwheat			43.84	13.31	13.45						
Honeydew			24.48			16.12					
Multiflower		32.42	16.44				23.22				
Heather				10.67				73.39			
Willow					84.83						
Linden flower			27.82						21.46	30.84	
Multiflower	65.51										20.26

Table 2. Chemical characteristics of honey samples

Honey sample	Glucose content (g/100 g)	Fructose content (g/100 g)	HMF (Hydroxy-methylfurfural) content (mg kg^{-1})	Diastase activity (Schade units)	Proline (mg/100 g)
Rapeseed	40.5	35.6	16.8	33.0	42.3
Phacelia	40.4	31.8	12.6	16.8	37.9
Buckwheat	39.3	33.2	15.0	65.8	44.4
Honeydew	37.9	32.3	19.9	21.8	53.3
Multiflower	38.5	33.7	25.5	35.2	41.4
Heather	38.2	30.0	4.2	69.3	45.1
Willow	39.5	34.1	15.0	18.6	33.0
Linden flower	39.9	29.3	3.6	21.6	30.3
Multiflower	36.5	29.3	5.2	18.9	20.3

1.2. Heating procedure

For the experiment, honey samples were thermally treated for 24 hours in climatic chamber at temperatures 60, 70, 80, and 90 °C. As a reference, honey samples heated to temperature 26 ºC were analysed. After thermal treatment, samples were cooled down to 25–26 °C (in the climatic chamber, in which the further measurements were taken). Both honey heating and cooling were conducted at the air humidity of 40%. Measurement of honey dielectric parameters was conducted directly after the cooling procedure (in less than one hour).

1.3. Determination of honey dielectric parameters

Measurements of honey impedance have been taken with the ATLAS 0441 HIA apparatus (impedance analyzer) and cylindrical electrode system. The impedance was represented as real and imaginary parts:

$$Z = ReZ + j \cdot ImZ \tag{1}$$

where Z is complex impedance, ReZ is the real part of impedance, and ImZ is the imaginary part of impedance.

The frequency range was set as 10–10^6 Hz, measurement voltage was set as 100 mV. The measurements were conducted with 5 measurement points per decade on a logarithmic scale (26 measurement points in the whole frequency range). As the result, an arithmetic mean of three consecutive measurements was taken. Based on impedance values, relative permittivity ε (-) and dielectric loss coefficient tgδ (-) were calculated as follows:

$$\text{tg}\delta = \frac{ReZ}{\text{ImZ}}, \tag{2}$$

$$\varepsilon = \frac{\text{C}}{C_{\text{p}}} \tag{3}$$

where C is capacitance of capacitor (cylindrical electrode) with honey sample (F), C_p is capacitance of empty capacitor (F). The capacitance C was calculated according to the following equation:

$$C = \frac{B}{\omega} = \frac{B}{2 \cdot \Pi \cdot f} = \frac{\frac{-ImZ}{(ReZ^2 + ImZ^2)}}{2 \cdot \Pi \cdot f} \tag{4}$$

where B is susceptance (S), ω is angular frequency (rad s^{-1}).

1.4. Statistical analysis

Correlations were established using Pearson's correlation coefficient (r). Dependence of honey dielectric features on the three factors, namely frequency, honey type, and thermal treatment temperature, were determined using three way analysis of variance (ANOVA) followed by Tukey's honestly significant difference (HSD) post hoc test, when the data followed a normal distribution. The distribution of data was evaluated by the Kolmogorov-Smirnov and Shapiro tests. A $p \leq 0.05$ was considered statistically significant. Statistical analyses were carried out with *Statistica v.10* environment (StatSoft, Poland).

2. Results and discussion

As is presented in Table 2, the HMF content, an indicator of the thermal treatment of honey samples, was found to be in the range of 3.6 mg kg^{-1} to 25.5 mg kg^{-1}, which is lower than the internationally recommended limit of 80 mg kg^{-1} (Codex Alimentarius Commission, 2001). In the analysed samples, the proline content varied from a minimum of 20.3 mg/100 g to a maximum of 53.3 mg/100 g. Only one sample (multiflower) did not comply with the recommended limit of minimum 25 mg/100 g according to Polish Standard PN-88/A-77626 "Honey". The diastase activity in honey samples was from 16.8 to 69.3 Schade units, which is in agreement with internationally recommended limit of minimum 8 Schade units (Codex Alimentarius Commission, 2001). In order to determine how physicochemical honey parameters are related to dielectric features, Pearson's correlation coefficients were calculated (Table 3). The values of dielectric parameters measured at the frequency of 1.1 kHz and at the temperature of 26 °C were used for calculations.

Generally, linear correlations between physicochemical and dielectric honey parameters are very low and statistically insignificant. Only correlation between relative permittivity and fructose content is relatively high (–0.81).

Table 3. Correlation coefficients between physicochemical and dielectric honey parameters

	Glucose content	Fructose content	HMF content	Diastase activity	Proline	Dielectric loss coefficient	Relative permittivity
Glucose content	1.00	0.23	–0.21	–0.37	–0.63	–0.56	–0.45
Fructose content	0.23	1.00	**0.75**	–0.12	0.17	–0.61	**–0.81**
HMF content	–0.21	**0.75**	1.00	–0.22	0.40	–0.51	–0.68
Diastase activity	–0.37	–0.12	–0.22	1.00	0.39	0.44	0.29
Proline	–0.63	0.17	0.40	0.39	1.00	0.27	0.03
Dielectric loss coefficient	–0.56	–0.61	–0.51	0.44	0.27	1.00	**0.93**
Relative permittivity	–0.45	**–0.81**	–0.68	0.29	0.03	**0.93**	1.00

Numbers in bold indicate statistically significant correlations ($P<0.05$).

The preliminary statistical analysis (ANOVA) revealed the significant influences of the temperature of thermal treatment, frequency, and honey type on dielectric loss coefficient tgδ. In the case of relative permittivity ε, results of the analysis of variance do not show the influence of thermal treatment temperature over the entire frequency range (Table 4).

Table 4. Results of ANOVA for dielectric loss coefficient tgδ and relative permittivity ε, for frequency 10 Hz –1 MHz

Source of variation	Degrees of freedom d.f.	ANOVA F-ratio	Significance level
Dielectric loss coefficient tgδ			
Type of honey	8	7.3355	0.0000
Temperature	5	5.3332	0.0000
Frequency	25	61.7180	0.0000
Relative permittivity ε			
Type of honey	8	4.1694	0.0000
Temperature	5	0.8633	0.5051
Frequency	25	5.9303	0.0000

The dependence between dielectric parameters of multiflower honey and a frequency is presented in Figure 1.

For further analysis, the frequency range of 400 Hz – 4 kHz was chosen. In this frequency range, the significant influence of thermal treatment temperature on both dielectric parameters was observed (Table 5).

More detailed information than presented in Table 5 was provided by the Tukey’s HSD post-hoc tests and the analysis of interaction effects. The Tukey’s HSD post-hoc tests revealed that for dielectric parameters, significant difference between honey no thermally processed and honey heated up was observed ($p=0.000017$ for tgδ and $p\leq0.000040$ for ε). However, these parameters can be useful only for distinguishing honey overheated from not overheated, but not for distinguishing eg. honey overheated up to 60 °C from honey overheated up to 80 °C. The analysis of Tukey’s test results in the case of honey types suggests that some samples are similar according to tgδ, eg. willow and rapeseed (p=0.998) or buckwheat and rapeseed (p=0.749) and ε, e.g. honeydew and rapeseed (p=0.999) or buckwheat and rapeseed (p=0.946).

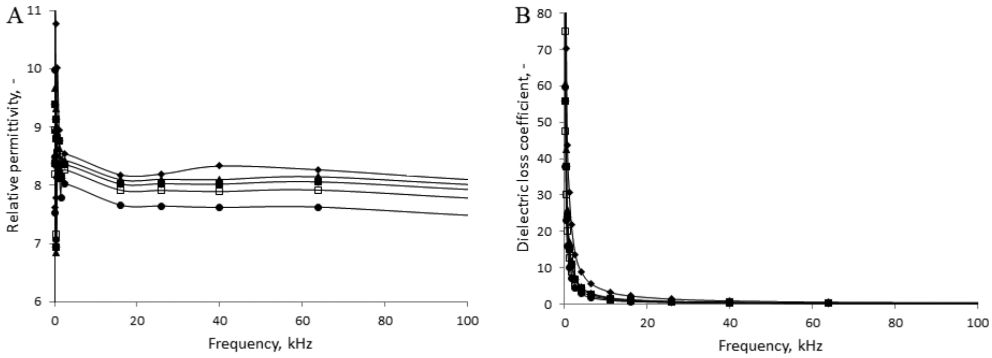

Fig. 1. Multiflower honey relative permittivity ε (A) and dielectric loss coefficient tgδ (B), as affected by frequency, for honey thermally treated at various temperatures (°C)
—◆— : 26; —▲— : 60; —■— : 70; —□— : 80; —●— : 90

Table 5. Results of ANOVA for dielectric loss coefficient tgδ and relative permittivity ε, for frequency 400 Hz - 4 kHz

Source of variation	Degrees of freedom d.f.	ANOVA F-ratio	Significance level
Dielectric loss coefficient tgδ			
Type of honey	8	120.9392	0.0000
Temperature	5	25.0750	0.0000
Frequency	5	72.1536	0.0000
Relative permittivity ε			
Type of honey	8	47.415	0.0000
Temperature	5	13.020	0.0000
Frequency	5	5.837	0.0000

The analysis of interaction effects revealed that in the case of dielectric loss coefficient, interaction effect frequency × thermal treatment (F=0.244 and p=0.999) as well as honey type × thermal treatment temperature (F=0.360 and p=0.998) are not statistically significant. It can be stated that tgδ can be useful for overheating detection when measured in the whole frequency range (400 Hz to 4 kHz) and for all honey types under study.

The presence of statistically significant interaction effect of honey type × thermal treatment temperature (F=3.324 and p=0.000000) for relative permittivity suggests that the use of these parameters for honey overheating detection can be difficult. This problem requires further analysis with the use of more honey samples.

The nature of the relationship between both tgδ and ε and frequency is similar for honey thermally treated at different temperatures (Fig. 2). More significant differences in tgδ and ε values between samples thermally treated at various temperatures are observed for lower frequencies. The value of tgδ as well as the range of tgδ values decrease as the frequency increases.

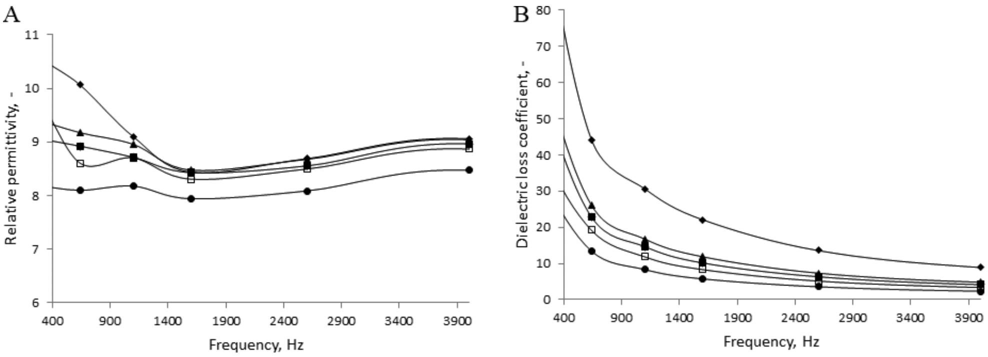

Fig. 2. Phacelia honey relative permittivity ε (A) and dielectric loss coefficient tgδ (B), as affected by frequency, for honey thermally treated at various temperatures (°C)
—◆— : 26; —▲— : 60; —■— : 70; —□— : 80; —●— : 90

Analogical results were obtained for dielectric parameters measured for other honey types under investigation.

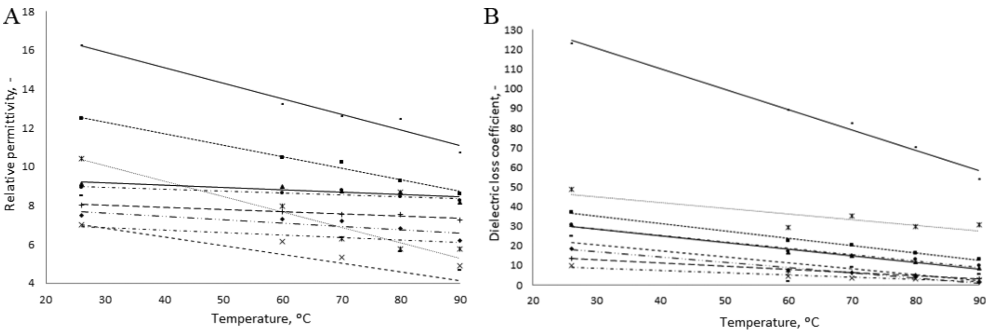

Fig. 3. Relative permittivity ε (A) and dielectric loss coefficient tgδ (B) measured at the frequency 1.1 kHz, as affected by thermal treatment temperature-tested honeys: 1: rape; 2: linden flower; 3: phacelia; 4: buckwheat; 5: honeydew; 6: multiflower (harvested in spring); 7: multiflower; 8: heather; 9: willow
● : 1 — —; ■ : 2 ·······; ▲ : 3 ——; × : 4 - - - - -; ×: 5 ——; ●: 6 - - - - -; ◆: 7 — —; • : 8 ——; ▬: 9 – – –

Dielectric loss coefficient tgδ and relative permittivity ε values decrease as the thermal treatment temperature increases (Fig. 3). Maximum values of tgδ and ε are observed when honey was not heated at all. In the case of tgδ these values are in average twice the tgδ values measured for honey overheated up to 90 ºC.

Correlation coefficient between dielectric honey parameters measured at the frequency 1.1 kHz and thermal treatment temperature equal r = –0.99 for dielectric loss coefficient tgδ and r = –0.93 for relative permittivity ε.

Dielectric features, in particular tgδ, are promising honey parameters for overheating detection. This is in agreement with our previous results, where significant relationship between HMF content and dielectric loss coefficient was found (PENTOŚ & ŁUCZYCKA, 2017).

It would be valuable to compare our findings with the results obtained by other authors referring honeys of other botanical and geographical origin. Unfortunately, to the best of authors' knowledge, no other scientific reports concerning the relative permittivity or dielectric loss coefficient measured at frequency below 1 MHz used as honey overheating indicator can be found in prior literature. Nevertheless, some authors pointed out the influence of honey thermal treatment temperature on its dielectric features. GUO and co-workers (2011) investigated temperature-dependent dielectric properties of yellow-locust and jujube honey in the frequency range from 10 to 4500 MHz. The strong influence of honey thermal treatment temperature on complex dielectric permittivity of acacia honey in the frequency range from 20 Hz to 2 MHz was reported by PASZKOWSKI and co-workers (2014). However, the maximum temperature of heating up was 35 °C, and overheating with negative impact on honey quality did not occur during experiments.

3. Conclusions

Values of relative permittivity ε and dielectric loss coefficient tgδ decrease with increasing thermal treatment temperature. This effect is particularly visible in the frequency range from 650 Hz to 4 kHz. Both these dielectric parameters, in particular dielectric loss coefficient, can be potentially used as honey overheating indicators. The proper frequency range for honey overheating assessment is 1–4 kHz. Measurement results at frequencies below 1 kHz can be incorrect due to specific behaviour of biological material placed in electromagnetic field.

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