

ELECTRIC PROPERTIES IN COMMODITY– SCIENCE EVALUATION
OF HONEY *

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Abstract. The honey used for the study was honeydew honey obtained in 2010 from the region of the Świętokrzyskie Mountains. Dielectric properties of strained honey were determined: relative electric permittivity ϵ_r (–) and dielectric loss coefficient $\text{tg } \delta$ (–). The effect of water content in the honey on its electric properties was studied by analysing samples of honey with water content in the range of 17.6-24.4% (9 measurement points). Also tested was the effect of overheating of honey sample, to temperatures of 70 and 90°C, on the electric and dielectric properties under analysis (the sample was placed in a controlled climate chamber for a period of 24 hours). In addition, the values of the electric properties obtained for the honeydew honey were compared with those for a product obtained through bee-feeding with inverted sugar syrup (Apiinvert). Based on analysis of the results obtained it was concluded that assays of electric permittivity and dielectric loss coefficient of honey permit the estimation of its quality. In particular, the values of the two parameters, and especially the dielectric loss coefficient, change notably as a result of honey overheating in the process of its de-crystallisation. Increase in water content causes an increase in the values of both the dielectric loss coefficient and the electric permittivity. Particularly notable differences can be observed at water content above 21%. The electric properties studied differentiate honeydew honey from a product produced by bees as a result of their feeding with inverted sugar syrup.

Key words: honey, honey quality, dielectric properties

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INTRODUCTION

The adulteration of honey is an important economic and social problem. The decisions made by the producers (intentional or unintentional) may be a source of unjustified profits, while the consumer sustains a loss by purchasing a product of sub-standard value. Honey is a product that is often adulterated. The adulteration of honey starts already at the stage of bee feeding, through the acquisition of unripe honey (honey should ripen in the beehive), or the addition of syrups to ripe honey. As a result of those practices, deterioration of honey quality can take place both at the producer's and during the confectioning. This does not necessarily mean that the honey sold is unhealthy or unnatural, but the consumer is being misled.

The adulteration of honey can be effected through the production of honey by bees from substrates other than nectar or honeydew. Contemporary industry produces sugar syrups with composition similar to that of honey, and due to the discoloration of the syrup in the course of production and the possibility of controlling the ratio of fructose to glucose there are possibilities of adulteration both through the addition of specially prepared syrups to honey and through bee feeding with various kinds of syrups, molasses, artificial honey etc. On the market there appear honeys which, though meeting the required parameters of chemical analysis, do not meet quality requirements. According to Pidek (2001), the contemporary industry produces sugar syrups whose chemical composition is close to that of honey, e.g. from maize. The addition of sugar can be detected with isotope methods which are used in the USA and Canada, and accepted by the Association of Analytical Communities (AOAC) (Wierzchowski 2008). Adulteration of honey consisting in the addition of maize, cane or beet sugar is detected through analysis of oligosaccharides formed during the hydrolysis of sugar (Cordella *et al.* 2005, Martin *et al.* 1996, Targoński and Stój 2005).

Another method of adulteration of honey is the declaration of false origin of raw materials, consisting in the placement of false information on the place of their origin on the label or giving false information on the kind of nectar from which the honey was produced. The quality of honey can be significantly affected by admixtures of honeys from outside of the EU. The criterion of authenticity of the product is the agreement of information provided on the label with the true contents of the container. The problem here is the problem faced by the producers, of determining what kind of honey is produced, honeys from various floral sources differ significantly in price. To detect those irregularities a variety of methods are applied, including microscopy, chromatography, spectrometry, or differential scanning calorimetry (Tuszyński and Czernicka 2008, Tomaszewska-Gras and Kijowski 2010).

Confirmation of authenticity is therefore difficult, labour-consuming, and requires the application of many different analytical techniques. Moreover, all the methods usually require mathematical-statistical interpretation of the analysis of results for accurate identification of differences in the material tested. Due to the multitude of factors affecting the quality of honey, the methods applied for its determination include multivariate analysis, discriminant factor analysis, cluster analysis and, in the most recent research, artificial neural networks. The EU Commission indicated a need of conducting research that will permit more accurate identification of the product (Pidek 2001).

However, once we know where and from what nectar the honey has been produced, the next factor that has a significant effect on its quality is temperature to which it is exposed in the process of confectioning – overheating of honey causes that it loses its biological properties. The exposure of honey to the effect of high temperature can also cause an increase in the content of HMF (Majewska *et al.* 2010) and a decrease in the level of proline and a drop in the diastase value (Śliwińska and Bazylak 2011).

Also important for honey quality is its content of water and its water activity. The two parameters are correlated with each other (Bakier 2006), though their relations are not identical for various kinds of honey. Until now, both the Polish and the EU requirements concern only the content of water in honey. In accordance with the Polish Standard, water content in ripe honey cannot exceed 20%. Most honeys have water content within the range of 17-18%, and even 13-15% of water (certain polyfloral nectar honeys and honeydew honeys). Osmophilic yeasts contained in honey, which cause fermentation, become active in honeys with water content above 18%. Increase of water content by 1% causes a five-fold increase of the amount of yeasts, which may be provoked by honey preservation with chemical agents. There is no evidence that such honeys appear on the Polish market, but methods of this type are used outside of the EU.

The Polish quality requirements concerning bee honey are somewhat different from the EU directives, but the differences are not significant (Council Directive 2001/110/EC, Szczęsna 2003). In spite of announcements (Szczęsna 2003), the Polish Standard (PN-88/A-77626) that has not been in force since 2003, has not been replaced with a new one. The only legislative action has been the Regulation of the Minister of Agriculture and Development of Rural Areas, of 2009, concerning analytical methods for the estimation of honey quality. Among the electric parameters that could characterise honey, both the Polish and the EU requirements include only the specific electric conductivity of 20% solution of honey and in terms of the values required the Polish regulations are in compliance with the EU ones.

Methods used so far for the estimation of the quality and authenticity of honey based on its conductivity and time and labour consuming – they require the prepa-

ration of water solutions of honey. The development of modern microprocessor-controlled measurement instruments creates the possibility of studies on the design and construction of a meter which, on the basis of analysis of several electric properties of honeys, would permit rapid and accurate estimation of their quality.

The objective of the study presented here was the estimation of suitability of analyses of electric properties of honey in its commodity-science evaluation, and in particular of the content of water in honey and honey overheating in the process of confectioning, as well as the determination of the possibility of applying electric methods for the detection of instances of honey adulteration through bee feeding with inverted sugar syrup.

MATERIAL AND METHOD

The honey used for the study was coniferous honeydew honey obtained in 2010 from the region of the Świętokrzyskie Mountains.

The measurements of electric properties of honey were conducted with the use of an impedance analyser FLUCK PM6304 with adjustable frequency. The tests were conducted within the frequency range from 100 Hz to 10 kHz. The dielectric properties assayed for strained honey were the relative electric permittivity ϵ_r (-) and the dielectric loss coefficient $\text{tg } \delta$ (-). The relative electric permittivity was calculated by dividing the measured electric capacity of a dish with honey by the electric capacity of the empty system of electrodes. Samples of honey were placed in a controlled climate chamber (WEISS WK 111 340) with controlled humidity of 40% and temperature of 40°C for a period of time sufficient for the stabilisation of measurement conditions and during the measurement. That choice of parameters ensured that all samples tested had liquid form and their liquidity was maintained throughout all the measurements performed on the samples of honey. The honey samples were placed in the space between the electrodes of a cylindrical condenser made of copper. In the course of the measurements no changes were observed in the appearance of the electrodes, so we can assume that no chemical reactions took place between the honey and the surface of the capacitor plates that would have an effect on the results obtained.

The effect of water content in honey (17.6-24.4% – 9 measurement points) on its electric properties was determined. Water content in the honey was increased by adding distilled water and, after mixing, assayed with a digital refractometer PAL-22S.

It was also tested how overheating affects the studied electric and dielectric properties of honey – comparison was made for results for 3 groups of samples (each group composed of 3 samples – replicates) de-crystallised at temperatures of 40°C, 70°C and 90°C (samples were placed in the controlled climate chamber

at selected temperature for a period of 24 hours, the honey was in a sealed container to avoid water evaporation). The measurements were made after the samples cooled to the temperature of 40°C. In the paper we present only the results for the boundary conditions, i.e. 40°C and 90°C.

A comparison was also made of the values of the studied electric properties of honeydew honey with those of a product obtained through bee feeding with inverted sugar syrup (Apiinvert). The honeydew honey was chosen for the comparison due to its price, and thus the highest potential profit for the dishonest producer.

RESULTS AND DISCUSSION

Increase of water content caused an increase in both the dielectric loss coefficient and in electric permittivity (Figs.1 and 2) for all electromagnetic field frequencies applied in the tests. Particularly distinct differences, nearly double for the dielectric loss coefficient and five-fold for the electric permittivity, can be observed at water content increase above 23%.

A notably stronger effect of water content on the relative electric permittivity was observed for the frequency of 1 kHz. The value of the dielectric loss coefficient of honey determined for that frequency (1 kHz) clearly stabilised for water content levels above the permissible limit, while the value of electric permittivity increased rapidly after that value was exceeded. Therefore, the possibility of definitive determination of the permissible water content in honey by means of the electric properties should probably be sought close to that value of frequency.

The next cycle of tests provided an answer to the question whether measurement of the electric properties of honey can detect if the honey had been overheated. Figures 3 and 4 present the relations of the relative electric permittivity and the dielectric loss coefficient on the frequency of the electromagnetic field obtained for non-overheated honey, de-crystallised for 24 hours at temperature of 40°C, and for overheated honey, de-crystallised for 24 hours at temperature of 90°C. The relations were determined for mean values from 3 replicates. The dielectric loss coefficient in particular is a property that distinctly indicates the occurrence of overheating of honey in the process of its de-crystallisation.

Samples of honeys de-crystallised at temperatures of up to 42°C not only have different values of the parameter measured throughout the whole range of frequencies, but also the characteristic points of the graphs analysed (maxima) appear at notably different frequencies. The relative electric permittivity varies considerably for the tested samples within the electromagnetic field frequency range of 100 Hz-1.5 kHz – the differences in values are from four- to two-fold.

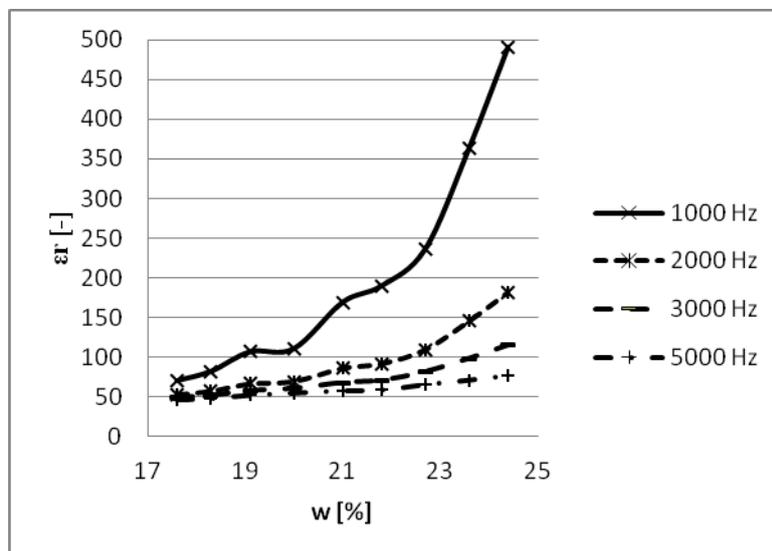


Fig. 1. Relative electric permittivity versus water content in honey at various electromagnetic field frequency

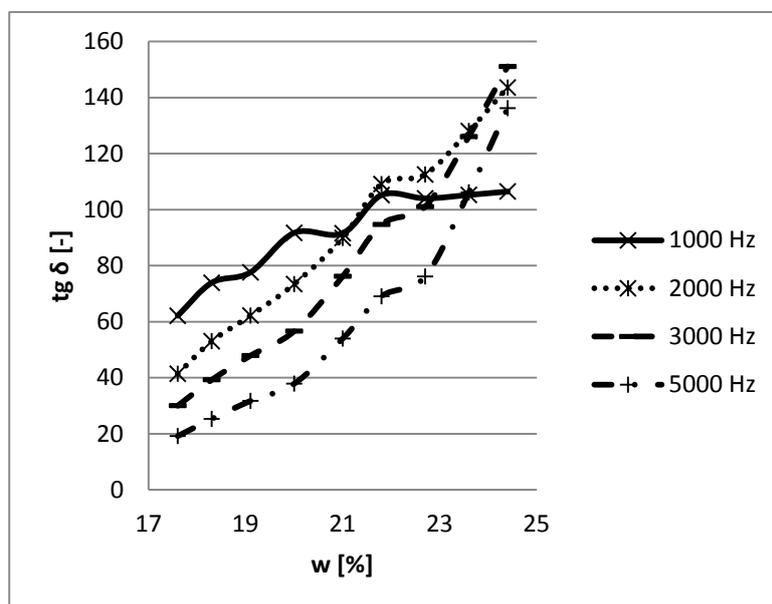


Fig. 2. Dielectric loss coefficient versus water content in honey at various electromagnetic field frequency

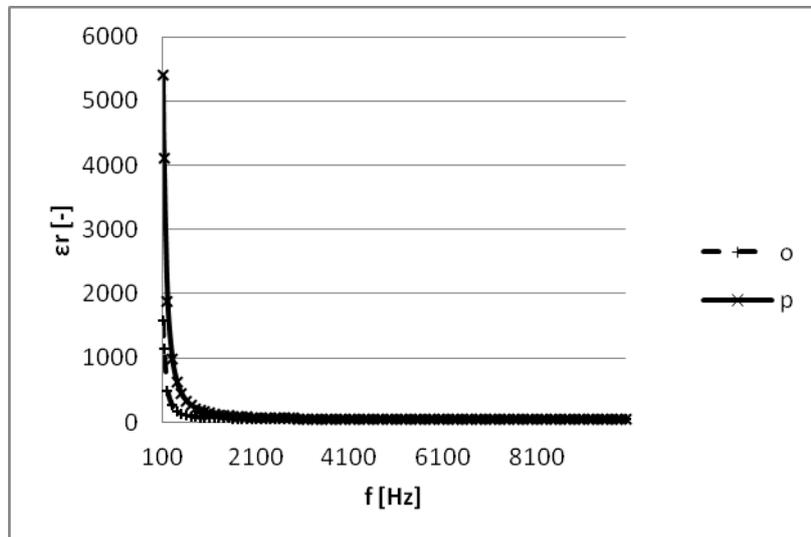


Fig. 3. Relative electric permittivity versus electromagnetic field frequency for honeydeew honey (o – honey de-crystallised at temperature of 40°C; p – honey overheated in the course of de-crystallisation)

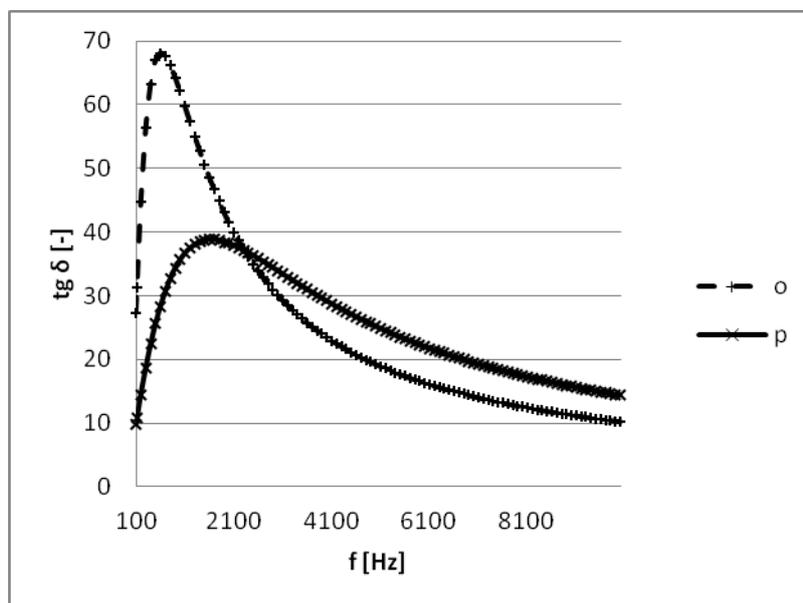


Fig. 4. Dielectric loss coefficient versus electromagnetic field frequency for honeydeew honey (o – honey de-crystallised at temperature of 40°C; p – honey overheated in the course of de-crystallisation)

The results obtained clearly indicate the possibility of detecting the phenomenon of overheating of honeys in the process of their liquefaction (e.g. for the purpose of confectioning) on the basis of determination of the electric properties of the honeys. The authors undertook further studies aimed at the identification of the character of changes in the electric properties with increase of the temperature of de-crystallisation of honey and of the duration of the process.

Comparison of values of electric properties of honeydew honey with those of a product obtained through inverted sugar syrup (Apiinvert) transformation by bees is presented in Figures 5 and 6.

The basic problem in studies of this type is the acquisition of product of transformed inverted syrup alone – small amounts can be obtained only in the period when bees do not make pollen fights, and then acquisition of transformed syrup is not favourable for bees.

Both the honeydew honey and that obtained from transformation of inverted sugar syrup by bees were ripe honeys (water content of 17.6-18%), so their water content had no significant effect on the values measured.

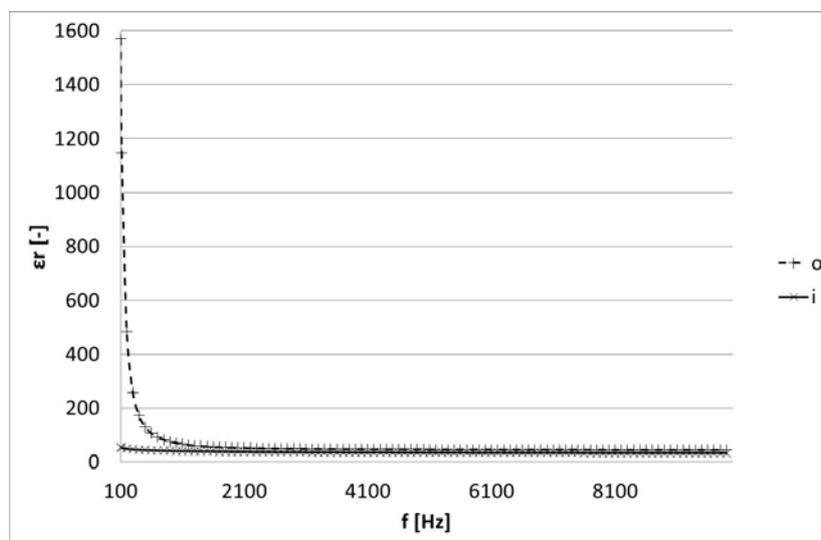


Fig. 5. Relative electric permittivity versus electromagnetic field frequency for honeydew honey (o) and inverted sugar syrup transformed by bees (x)

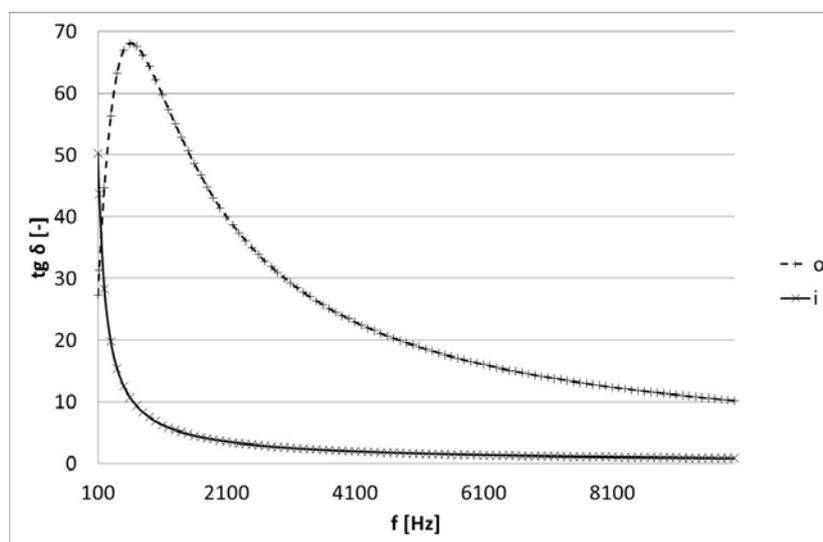


Fig. 6. Dielectric loss coefficient versus electromagnetic field frequency for honeydew honey (o) and inverted sugar syrup transformed by bees (i)

The product obtained through the transformation of inverted sugar syrup by bees has distinctly lower values of the relative electric permittivity throughout the whole range of electromagnetic field frequencies analysed. The curve of the dielectric loss coefficient versus frequency has a completely different shape for the product obtained by bees from the syrup than for the natural honey, and moreover for frequencies above 200 Hz the measured values of $\text{tg } \delta$ are distinctly lower than for the honeydew honey.

The results of this study can indicate suitability of the electric methods for the detection of adulteration of honey consisting in the feeding of bees with inverted sugar syrup during the period when they produce honey with the aim of increasing the amount of honey obtained for commercial purposes.

CONCLUSIONS

1. Determination of the electric permittivity and the dielectric loss coefficient of honey permits the estimation of its quality.
2. Both parameters, and the dielectric loss coefficient in particular, notably change their values as a result of overheating of honey in the process of its decrystallisation.

3. Increase of water content causes an increase in the values of the dielectric loss coefficient and the electric permittivity. Particularly distinct differences can be observed at water content levels above 21%.

4. The electric properties under study differentiate honeydew honey from a product produced by bees as a result of their feeding with inverted sugar syrup (Apiinvert).

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CECHY ELEKTRYCZNE W TOWAROZNAWCZEJ OCENIE MIODU*

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Streszczenie. Do badań użyto miód spadziowy iglasty pozyskany w 2010 roku w Górach Świętokrzyskich. Określono cechy dielektryczne patoki: przenikalność elektryczną względną ϵ_r (–) oraz współczynnik strat dielektrycznych $\tan \delta$ (–). Badano wpływ zawartości wody w miodzie na jego cechy elektryczne – analizie poddano próbki miodu o zawartości wody od 17,6 do 24,4% (9 punktów pomiarowych). Sprawdzone również, jak wpływa na analizowane cechy elektryczne i dielektryczne przegrzanie próbki miodu (próbkę umieszczano w komorze klimatyzacyjnej przez okres 24 godzin) do temperatury 70 i 90°C. Dodatkowo porównano wartości badanych cech elektrycznych miodu spadziowego z produktem pozyskanym w wyniku karmienia pszczoł inwertem. Na podstawie analizy uzyskanych wyników badań stwierdzono, że określenie dla miodu przenikalności elektrycznej oraz współczynnika strat dielektrycznych pozwala na ocenę jego jakości. W szczególności obydwa parametry, a głównie współczynnik strat dielektrycznych, zmieniają wyraźnie swoje wartości w wyniku przegrzania miodu w procesie jego dekrystalizacji. Wzrost zawartości wody powoduje wzrost zarówno współczynnika strat dielektrycznych jak i przenikalności elektrycznej. Szczególnie wyraźne różnice można zaobserwować przy zawartości wody powyżej 21%. Badane cechy elektryczne różnicują miód spadziowy od produktu wytworzonego przez pszczoły w wyniku karmienia ich inwertem.

Słowa kluczowe: miód, jakość miodu, cechy dielektryczne

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