

Article

Preliminary Studies on the Use of an Electrical Method to Assess the Quality of Honey and Distinguish Its Botanical Origin

Aleksandra Wilczyńska ¹, Joanna Katarzyna Banach ^{2,*}, Natalia Żak ¹ and Małgorzata Grzywińska-Rapca ³

¹ Department of Quality Management, Gdynia Maritime University, 81-225 Gdynia, Poland; a.wilczynska@wzsj.umg.edu.pl (A.W.); n.zak@wzsj.umg.edu.pl (N.Ż.)

² Institute of Management and Quality Sciences, Faculty of Economics, University of Warmia and Mazury in Olsztyn, 10-719 Olsztyn, Poland

³ Department of Market and Consumption, Institute of Economics and Finance, Faculty of Economics, University of Warmia and Mazury in Olsztyn, 10-719 Olsztyn, Poland; malgo@uwm.edu.pl

* Correspondence: katarzyna.banach@uwm.edu.pl

Abstract: This study aimed to determine the possibility of deploying an innovative electrical method and to establish the usefulness of conductivity and dielectric parameters for assessing the quality of Polish honeys, as well as for distinguishing their botanical origin. An attempt was also made to determine which standard physicochemical parameter could be replaced by conductivity and dielectric parameters. The experimental material consisted of seven varieties of honey (linden, rapeseed, buckwheat, goldenrod, phacelia, multifloral, acacia), obtained from beekeepers from northern Poland. Their quality was assessed based on their physicochemical parameters, biological activity, and color. Electrical parameters were measured using a measuring system consisting of an LCR meter, and own-construction sensor. Conductivity (Z, G) and dielectric (Cs, Cp) parameters were measured. Statistical analysis of the results of measurements of electrical parameters of the seven types of honey tested allowed classifying them in terms of their conductivity properties into two groups of single-flower honeys and one group of multi-flower honeys. This proves the feasibility of identifying their botanical origin using the electrical method, which is characterized by non-invasiveness, measurement speed, and high sensitivity. The usefulness of parameters Z and G in replacing quality parameters was confirmed mainly for single-flower honeys: buckwheat, linden, rapeseed, and phacelia.

Keywords: honey quality attributes; conductivity and dielectric parameters; botanical origin



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1. Introduction

Honey is a natural product produced by bees defined as follows: “the natural sweet substance produced by *Apis mellifera* bees from the nectar of plants or from secretions of living parts of plants or excretions of plant-sucking insects on the living parts of plants, which the bees collect, transform by combining with specific substances of their own, deposit, dehydrate, store and leave in honeycombs to ripen and mature” [1]. It contains over 180 components, including the following: fructose and glucose, water, sucrose, minerals, vitamins, proteins, and amino acids [2], in amounts dependent on the botanical origin of the honey (varietal origin of the forage—nectar or honeydew), environmental factors (temperature, season, sunlight, surroundings), and also beekeeper activities (method of running the apiary and honey collection) [3,4]. Its medicinal and nutritional properties are still the main determinant of consumer choice [5,6].

Honey is an expensive product, which is why it is often adulterated in terms of botanical and geographical origin, e.g., by mixing varieties of honeys from different countries. Other forms of adulteration include overheating to obtain a liquid consistency, addition of sugar syrups, and also incorrect classification and labeling of honey varieties [7–10].

The assessment of the quality and authenticity of honey may concern many aspects that are found in the literature on the subject. However, researchers around the world focus on three main problems in this respect:

1. quality—understood as a set of nutritional, physicochemical, sensory, and other characteristics typical of natural honey,
2. authenticity—i.e., ensuring that the honey is what it is considered and classified as (geographical origin, varietal origin, traces of adulteration),
3. safety—understood as meeting the parameters regarding the health safety of honey stipulated by law [8,11–13].

The research methodology for assessing the quality of honey is strictly defined in legal acts [1,14,15]. The methodology for determining its physicochemical parameters and biological activity allows establishment of its quality and safety levels [2,4,11,12]. However, choosing the right research method and interpreting the results of quality parameters in terms of confirming the authenticity of honey is not easy. It should be remembered that honey is a unique product, the quality of which is influenced by many parameters. Given the above, researchers deploy a variety of non-standard and combined methods in order to achieve the best possible effect of assessing its quality and authenticity [14,16,17]. The methods developed thus far have proved viable in assessing the quality of honey, but the search is still underway for the chemical compound characteristics of a specific variety of honey. Unfortunately, the results of these works are still burdened with a margin of error [12,18,19]. Hence, it seemed justified to conduct further research aimed at developing a viable methodology for assessing the quality and confirming the authenticity of honey [17,20] that would reduce the number of measured parameters and be non-invasive [14,16–18].

Methods for assessing honey quality that take into account electrical parameters are becoming increasingly popular in scientific research. Honeys are considered dielectrics in terms of their electrical properties, which means that they generally do not conduct electricity and exhibit the ability to accumulate electric charge. The basic chemical components that determine the dielectric properties of honeys are water and sugars and organic compounds dissolved in it, which also affect the ionic conductivity and polarization of honey in the presence of an electric field. The contents of sugars (glucose and fructose) and organic acids affect the structure and mobility of ions, which is crucial for electrical permittivity [21–23].

The determination of dielectric properties of food materials provides data on the storage and dissipation of electromagnetic energy. This technology is widespread, time-saving, simple, highly sensitive, and non-destructive [24–26]. Researchers have already attempted to harness dielectric parameters to assess the quality and detect adulteration of food products, e.g., meat, fish, olive oil adulterated with vegetable oils, fats, flour, and honey [24–28]. Of course, these studies indicated many dependencies, e.g., on the contents of water [29,30], salt, or sucrose in the product [24]. A study conducted by Łuczycka's team showed a significant effect of the honey measurement temperature on the values of the dielectric loss coefficient [31]. Dielectric parameter measurements were also performed to determine the degree of honey adulteration with artificial invert as well as to check whether it was possible to detect whether honey was produced as a result of feeding bees with the invert. Additionally, this study indicated the viability of electrical permittivity in quick detection of honey adulterations and in their differentiation (nectar/honeydew)—three homogeneous groups were distinguished among the tested samples [32].

Electrical conductivity is one of the most frequently studied electrical parameters of honey. According to Duliu, Chelarescu, and Stihi [33], it can be used to differentiate honey varieties and detect contaminants in honey [33,34]. Impedance, on the other hand, is often applied in spectroscopic methods, which allows for the assessment of the chemical composition of honey and can be used to assess its stability and maturity [35] as well as to monitor the additives used—syrops [23]. Analysis of dielectric properties is also deployed

to distinguish honeys based on their chemical and mineral composition [36], as well as to assess their authenticity and adulteration [37].

The above-discussed and additionally presented in Table 1 possibilities of using electrical parameters and models to assess the quality of honey confirm their relevance and innovativeness. The indicated directions of their use testify to the relevance and innovativeness of the research conducted by the authors in developing a new and effective research tool.

Table 1. Examples of the use of electrical parameters and electrical models in international research on the quality, botanical identification, and detection of honey adulteration.

Parameter/Electrical Model	Application	Description	Literature
Impedance, conductivity	Differentiation of honey types	Electrical conductivity as an indicator of honey quality	[33,34]
Impedance	Distinguishing original honeys from honeys with added sugar	Impedance-based testing of primary honey	[38]
Dielectric parameters	Identification of honey adulterations (water, sweeteners) and their differentiation	Determination of the possibilities of using dielectric parameters and models to assess selected parameters of honey quality and freshness	[32,36,37,39,40]
Dielectric model	Evaluation of the influence of temperature and humidity on the properties of honey	Application of non-destructive measurement techniques to study dielectric properties.	[41]
Impedance spectroscopy based on neural networks	Identification of the origin of floral honey	The use of impedance spectroscopy and neural networks for rapid determination of honey floral origin	[42–45]
Impedance, resistance, Randles model	Identification of prior heating of honey	Using dielectric properties of Hungarian acacia honeys to assess their rate of heating	[46]
	Detecting honey adulteration with different types of syrup or rapeseed honey Assessment of chemical composition, stability, and maturity of honey	The rapid detection of honey adulteration by impedance spectroscopy	[23,35,47–49]
Impedance-based electronic tongue, Randles model	Distinguishing honey of various botanical origins	Sensing mechanism of an impedance-based electronic tongue for honey botanic origin discrimination	[50]

Therefore, the aim of our study was to determine the possibility of using an innovative electrical method (RCC electric model, adopted in the LCR meter + measurement sensor of own construction) and to identify the usefulness of conductivity and dielectric parameters for assessing the quality of Polish varietal honeys, as well as for distinguishing their botanical origin (varieties). An attempt was also made to determine which standard physicochemical parameter measurements used thus far, especially those performed using destructive methods, could be replaced by the measurement of conductivity and dielectric parameters.

2. Materials and Methods

Providing botanical and geographical confirmation of honey is a very difficult task. Therefore, the number of samples must be selected in a way that is characteristic for a given variety, but also has characteristic features. In the case of a product such as honey, this is often problematic. Therefore, this study included honey samples that had a number of

quality descriptors (physicochemical features) characteristic of a given sample. The essence of these features then determined the experimental study, which was aimed at proving the validity of the assumed thesis. The experimental material consisted of 7 varieties of honey (linden—3 samples, rape—2 samples, buckwheat—2 samples, goldenrod—2 samples, phacelia—2 samples, multifloral—3 samples, acacia—2 samples) with different botanical compositions. The research material came from 2020 to 2022 directly from beekeepers from the northern part of Poland. The samples were stored in tightly closed individual packages—250 mL glass jars with “Twist off” lids, at a temperature of 16 to 20 °C.

2.1. Physicochemical Analysis

The quality of honey was assessed based on reference methods provided in respective legal acts (content of the following: water, reducing sugars, 5-HMF; diastase number; conductivity level; and acidity) [51] and developed by research teams and implemented for the assessment of honey quality (capability for scavenging DPPH radicals [52], total number of free radicals TP [53], and color parameters in the CIE Lab system [54]). All analyses were performed in 3 parallel replicates, and respective results are given as the mean of 3 replicates.

2.1.1. Ability to Scavenge Free DPPH Radicals

The procedure described by Turkmen et al. [52] with some modifications was used to determine the scavenging activity of honey against the 1,1-diphenyl-2-picrylhydrazyl radical (DPPH). A 2 g honey sample was dissolved in 10 mL of distilled water. Then, 0.75 mL of the solution was mixed with 2.25 mL of a 0.1 mmol/L methanolic solution of DPPH radical. A sample with distilled water instead of the honey solution served as the control. After mixing the reaction mixtures, they were incubated in the dark at room temperature for 60 min. Absorbance was measured at $\lambda = 517$ nm against methanol using a Unicam UV–VIS spectrophotometer. Antiradical activity was expressed as the percentage of DPPH radical inhibition and was calculated from Equation (1):

$$AA[\%] = (ABS_{contr} - ABS_{sample}) / ABS_{contr} \times 100\% \quad (1)$$

2.1.2. Total Phenolic Content (TP)

The total phenolic content of honeys was determined using the method of Meda et al. [53]. To this end, the honey solution (0.5 mL, concentration of 1 g/10 mL) was mixed with 2.5 mL of a 0.2 mol/L Folin–Ciocalteu reagent solution and 2 mL of a sodium carbonate solution (75 g/L). Then, the reaction mixture was incubated in the dark and at room temperature for 2 h. Afterwards, its absorbance was measured at $\lambda = 760$ nm using a UV–VIS spectrophotometer. The standard curve was plotted for gallic acid in a concentration range from 0 to 200 mg/L. Total phenolic content was expressed as gallic acid equivalents in mg/100 g of honey sample (mg GAE/100 g).

2.1.3. Color Parameters

Color parameters (L^* , a^* , b^*) were measured in the CIE system using a Minolta CR-400 Chroma-meter (Konica-Minolta, Osaka, Japan) with illuminant D65 and a 2° standard observer. The instrument was calibrated with a white reference tile [54].

2.1.4. 5-HMF

The determination of 5-HMF content consists of developing a color reaction of 5-HMF with barbituric acid and o-toluidine, followed by the photometric measurement of the resulting color. A 50 g measure of honey were transferred to a 50 mL volumetric flask and dissolved in distilled water, and then the flask was filled up with water. Next, 2 mL of the honey solution and 5 mL of o-toluidine solution were transferred to two test tubes using a pipette. A 1 mL measure of distilled water (blank sample) was added to one test tube and 1 mL of barbituric acid solution to the other. After 3–4 min, the absorbance of the exact

sample was measured against the blank sample at a wavelength of 550 nm. The content of 5-HMF (X) in mg per 100 g of honey was calculated using Equation (2):

$$G = 19.2 \times A/d \quad (2)$$

where

A—arithmetic mean of the read absorbance value,

D—thickness of the liquid layer in the cuvette [cm],

19.2—conversion factor [52].

2.1.5. Diastase Number (LD)

A blank sample was prepared by transferring 5.0 mL of acetate buffer to a test tube. A honey sample solution was prepared by weighing 1.00 g of honey and transferring it quantitatively using acetate buffer to a 100 mL volumetric flask, that was next filled up with phosphate buffer. The procedure was carried out within an hour. Then, 5.0 mL of the sample solution was transferred to a test tube and placed in a water bath at 40 °C; the test tube with the blank sample was also placed in a water bath at 40 °C. After approximately 15 min, starch conjugated with blue dye was added to both solutions. The solutions were mixed using a stirrer until the tablets dissolved (approximately 10 s), then they were transferred back to the water bath; then, after exactly 15 min, 1 mL of a sodium hydroxide solution was added (to stop the enzymatic reaction). The solutions were mixed using a stirrer for approximately 5 s and then immediately filtered through filter paper. Their absorbance was measured in 1 cm cuvettes at 620 nm, using water as reference; the absorbance for the blank solution was subtracted from the absorbance of the sample solution (ΔA_{620}); if the absorbance was greater than 1.0, the sample solution was diluted with water, and the dilution was taken into account when calculating the results.

For diastase number (LD) values in the range of 8–40, the LD value was determined using Equation (3):

$$LD = 28.2 \times \Delta A_{620} + 2.64 \quad (3)$$

where

ΔA_{620} —denotes the difference in absorbance of the tested honey solution and the blank sample, 28.2 and 2.64—denote constants that take into account the dependence between the diastatic activities of honey.

For the diastase number (LD) values in the range of 0–8, the LD value was determined using Equation (4):

$$LD = 35.2 \times \Delta A_{620} - 0.46 \quad (4)$$

where

ΔA_{620} —denotes the difference in absorbance of the tested honey solution and the blank sample, 35.2 and 0.46—denote constants that take into account the dependence between the diastatic activities of honey [52].

2.1.6. Acidity

The method of acidity determination consists of titrating organic acids contained in the aqueous extract of the tested honey with a sodium hydroxide solution in the presence of phenolphthalein. A 10 g measure of honey weighed exactly to 0.01 g was transferred quantitatively to a conical flask, to which 50 mL of distilled water was added. Then, titration was carried out with a 0.1-molar sodium hydroxide solution against phenolphthalein until a light pink color persisted for 30 s. The degree of acidity is the number of mL of a 1-molar NaOH solution needed to neutralize 100 g of honey. The value of mL of sodium hydroxide read from the burette is the acidity in degrees [51].

2.2. Electric Method

Electrical measurements of the honeys were carried out using our own measurement system, consisting of the following:

- (1) a measurement sensor (of own construction) and a glass tank (internal dimensions: $l = 88.80$ mm, $d = 49.20$ mm, $h = 76.20$ mm) equipped with two stainless steel plate electrodes (area 68 cm²), mounted on two opposite smaller walls of the container;
- (2) a stainless-steel tank equipped with a water jacket, which was coupled to a thermostat (PolyScience, Niles, IL, USA) with a water temperature of 40 ± 0.05 °C;
- (3) an E4980a LCR meter (Agilent, Santa Clara, CA, USA) with a measuring adapter and wiring.

Before each series ($n = 6$) of electrical measurements of the 7 honey varieties, the LCR meter was calibrated using the built-in calibration function. Then, a metal tank (2) with a measuring sensor (1) filled with approx. 200 mL of the honey sample at a temperature of 40 ± 0.05 °C was connected to the LCR meter using cables. Conductivity parameters (impedance— Z , conductance— G) and dielectric capacitance parameters (serial— C_s and parallel— C_p) were measured at a frequency (f) in the range of 20 Hz–2 MHz, and voltage of 200 mV. The meter's external memory stored the readings. The equivalent electrical model of food product RCC (resistance + capacitance: equivalent serial and parallel) was used for analyses (Figure 1).

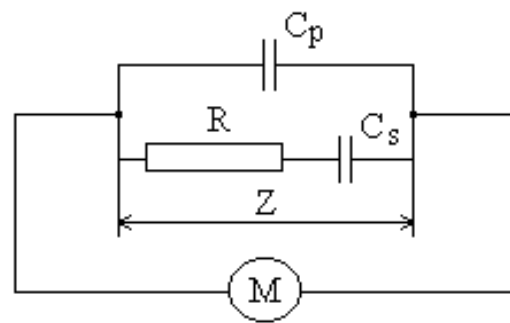


Figure 1. RCC equivalent model for measuring of electrical properties of food products (Z —impedance; R —resistance; C_s —series equivalent capacitance; C_p —parallel equivalent capacitance; M —measuring device) [55].

The RCC model adopted for analyses was considered by the authors to be more versatile than the RRC model [56] used in the analyses of physicochemical properties of food products, in which the equivalent parallel capacitance (C_p) is replaced by the equivalent parallel resistance (R_p). The RCC model used by scientists [57,58] proved to be useful in assessing the quality of various food products; therefore, it was also adopted in research on the development of an alternative electrical method for assessing the quality of honey.

2.3. Statistical Analysis

The measurement results were statistically processed using Statistica 13.3 software (StatSoft Inc., Tulsa, OK, USA). The data were analyzed using procedures that allowed the following: (1) statistical evaluation of the level and variability of physicochemical and electrical parameters; (2) identification of differences between the analyzed features of the 7 varieties (linden, rapeseed, buckwheat, goldenrod, phacelia, multifloral, and acacia) and 16 species ($p < 0.05$) of honey; and (3) determination of correlations between dependent variables (variables: cluster 1 and 2) and independent (electrical) variables and then, on their basis, indication of the usefulness of electrical parameters for controlling selected quality and health-promoting parameters of the honey varieties studied.

The analysis (ANOVA, Tukey HSD test) was aimed at distinguishing homogeneous groups at the $\alpha = 0.05$ significance level. The Tukey HSD test (multiple comparisons

of means) allowed determination of which groups differed significantly from each other. As a result, honeys with similar electrical and physicochemical properties were grouped together, which may indicate similarities in the chemical composition or properties of the samples tested.

The results of Tukey's HSD test for electrical and physicochemical variables indicate that honey groups (marked as: a, b, c, ...) can be classified based on their physicochemical and electrical properties. Homogeneous groups allow drawing of conclusions about similarities or differences between samples, which can be useful for assessing the quality of honey depending on its chemical composition and electrical properties.

The first stage of analysis involved grouping the studied parameters using Ward's agglomerative method. This method was used to ensure a system with minimal differentiation of parameters within clusters [59]. Grouping was performed for standardized data in order to increase data comparability (eliminating distortions of further statistical analyses resulting from differences in scale) and to increase the accuracy of calculations. Two clusters of parameters were distinguished (cluster 1 and 2) within the physicochemical parameters studied (qualitative and health-promoting). These actions were taken to reduce the number of variables in the next stage.

In the second stage of analysis, the obtained average values for clusters were used in the analysis of correlations between selected qualitative and electrical parameters of honeys, measured at the frequencies of 100 Hz, 1 kHz, 10 kHz, 100 kHz, 1 MHz, and 2 MHz.

3. Results and Discussion

3.1. Evaluation of the Value of Standardized Quality Parameters

A detailed summary of the results obtained for individual honey varieties is provided in Tables 2 and 3.

Table 2. The mean values of physicochemical parameters.

Honey Type	Water Content [%]	SD	5-HMF Content [mg/kg]	SD	Acidity [mval/kg]	SD	Reducing Sugar Content [%]	SD	Sucrose [%]	SD	LD	SD
linden	17.84	1.69	3.21	0.58	20.0	0.18	74.46	3.62	1.10	0.20	10.20	1.78
buckwheat	17.90	0.67	13.56	0.54	27.0	0.07	72.10	3.81	1.47	0.19	21.05	0.02
acacia	18.20	1.59	16.57	0.73	10.4	0.10	72.08	2.26	3.99	0.24	9.61	1.40
rapeseed	17.99	0.12	3.01	1.34	14.5	0.54	79.23	0.43	1.27	0.34	9.30	4.86
phacelia	17.90	0.70	4.44	0.69	20.1	0.04	72.35	2.58	2.11	0.27	11.85	1.61
goldenrod	19.30	0.94	6.31	2.63	27.1	0.41	73.00	1.92	2.70	0.56	4.75	2.30
multifloral	16.18	1.25	6.50	0.29	20.2	0.22	74.46	4.75	2.60	0.47	13.87	1.41
Requirements ¹	≤20		≤40		≤50		≥60		≤5		≥8	

¹ According to the Regulation of the Minister of Agriculture and Rural Development, from 29 May 2015, amending the Regulation on detailed requirements for the commercial quality of honey (Journal of Laws 2015, item 850) [15].

Table 3. Average values of color parameters (L*, a*, b*), polyphenol content (TP), and antiradical activity (DPPH).

Honey Type	L*	SD	a*	SD	b*	SD	TP [mg GAE/100 g]	SD	DPPH [%]	SD
linden	28.91	1.72	−0.31	1.28	12.85	4.28	49.70	5.37	62.94	7.83
buckwheat	21.08	5.80	3.25	0.58	4.49	1.23	101.50	3.37	73.60	2.80
acacia	25.24	0.71	−0.54	0.75	5.40	1.82	51.26	2.90	50.17	9.40
rapeseed	34.21	3.23	−0.87	0.77	7.76	5.96	40.91	6.20	40.26	11.65
phacelia	31.06	4.79	0.90	0.47	11.05	2.37	51.40	3.20	66.71	2.71
goldenrod	24.27	2.85	1.90	0.72	10.59	2.74	11.98	11.71	18.55	9.15
multifloral	25.15	1.06	2.59	0.42	9.70	1.08	66.47	0.47	42.28	1.05

The honeys tested were characterized by an appropriate water content. The average water content ranged from 16.18% in multifloral honey to 19.30% in goldenrod honey. The average content of reducing sugars ranged from about 72% to 79%, which is a value range typical for nectar honeys. The average content of sucrose ranged from 1.01 to 4%, and in all

honeys it was within the limits set out in the Regulation of the Minister of Agriculture and Rural Development [15].

The content of free acids in the honeys was also within the norm and ranged from slightly over 10 to 27 mval/kg, which is typical of nectar honeys. Most of the honey samples tested (60%) were characterized by a high diastase number (LD)—over 10. Only the LD of the goldenrod honey was too low compared to the legal requirements. In terms of 5-HMF content, all honeys met the criterion, as in most honeys the 5-HMF content was over ten times lower than the permissible value, which indicates that the honey samples tested were fresh, unheated, and unadulterated with sucrose (Table 2).

Visual assessment of color is subjective and may be burdened with a number of errors. Therefore, the trichromatic colorimetry method was used to determine the color of the tested honey samples. Color was expressed in the CIE $L^*a^*b^*$ system, where L^* denotes lightness, while the a^* and b^* coordinates indicate the contribution of green (negative a^* values), red (positive a^* values), blue (negative b^* values), and yellow (positive b^* values) in the color profile. The L^* parameter value ranged from about 21 (buckwheat honey) to slightly over 34 (rapeseed honey), which means that most of the tested honeys can be classified as light-colored types. The a^* parameter value ranged from about -0.31 to 2.59 , while the b^* parameter value ranged from almost 5 to about 13. The b^* parameter determined for all honeys tested had positive values, which indicates the contribution of yellow color and the lack of blue color in the honey color profile. This is mainly due to the presence of yellow carotenoid pigments in nectars (Table 3).

The total phenolic content (TP) ranged from slightly over 41 to 101 mg GAE/100 g of honey. The value of this parameter is not standardized. Polyphenolic compounds contained in honeys exhibit, among others, antiradical, bactericidal, anti-inflammatory, antiallergic, antithrombotic, and anticancer effects. The content of individual polyphenols depends on the plant source. The values obtained in this study are typical of honeys classified as light-colored varieties.

Another analyzed parameter, indicating the antioxidant activity of honeys, is the DPPH radical scavenging activity (DPPH), which in the tested honeys ranged from 18 to 74%. The buckwheat honey was characterized by the highest phenolic content and antiradical activity and at the same time had the highest diastase number. It was also the darkest among all analyzed honeys.

Summarizing the results of physicochemical tests, it can be concluded that all quality parameters of the tested honeys, except LD in goldenrod honey, meet the requirements specified in the Regulation of the Minister of Agriculture and Rural Development, from 29 May 2015, amending the Regulation on detailed requirements for the commercial quality of honey [15], which means that the tested honeys were of good quality. The values of the color parameters indicate that the honeys tested are predominantly light honeys, except buckwheat honey. Similar research results were provided in other works regarding the assessment of honey color [60].

The biological activity of most examined samples, expressed as the total phenolic content (TP) and the ability to scavenge DPPH radicals (DPPH), was also characteristic for light honeys. Among the honeys tested, buckwheat honeys showed the highest value of TP and DPPH, which is consistent with findings reported by other researchers [61–65]. Similar results, indicating that dark honeys exhibited higher antioxidant activity, were also obtained in our previous study [66].

However, it was not possible to prove that the values of individual parameters were characteristic for individual honey varieties; the botanical origin of these honeys cannot be clearly determined, although Pauliuc et al. [64] claim it is indeed possible. Therefore, the next stage of our research involved the measurement of electrical parameters, which is realized in a short time and does not require any chemicals.

3.2. Electrical Parameters

Electrical properties of biological materials (honeys) are typically determined using parameters such as complex resistance (Z —impedance), consisting of active resistance (R —resistance), and passive resistance (X_c —reactance, associated with electrical capacitance) or admittance (Y —complex conductance) consisting of conductance G (active conductance) and susceptance— B (passive conductance) [67]. To verify the suitability of the proposed electrical method, only selected parameters were used, i.e., impedance, conductance, and electrical capacitance, resulting from the adopted equivalent electrical model RCC (resistor–capacitor–capacitor).

With the aim to conduct a more detailed analysis of the results and indicate differences in ionic conductivity and dielectric properties, the authors plotted graphs describing impedance changes in a wide range of frequencies (from 20 Hz to 2 MHz)—see Figure 2. These analyses allowed for more precise determination of the electrical characteristics of honeys, taking into account both low and high frequencies. Then, the results of the analysis were presented together with their interpretation, thereby expanding existing knowledge and providing grounds for future research.

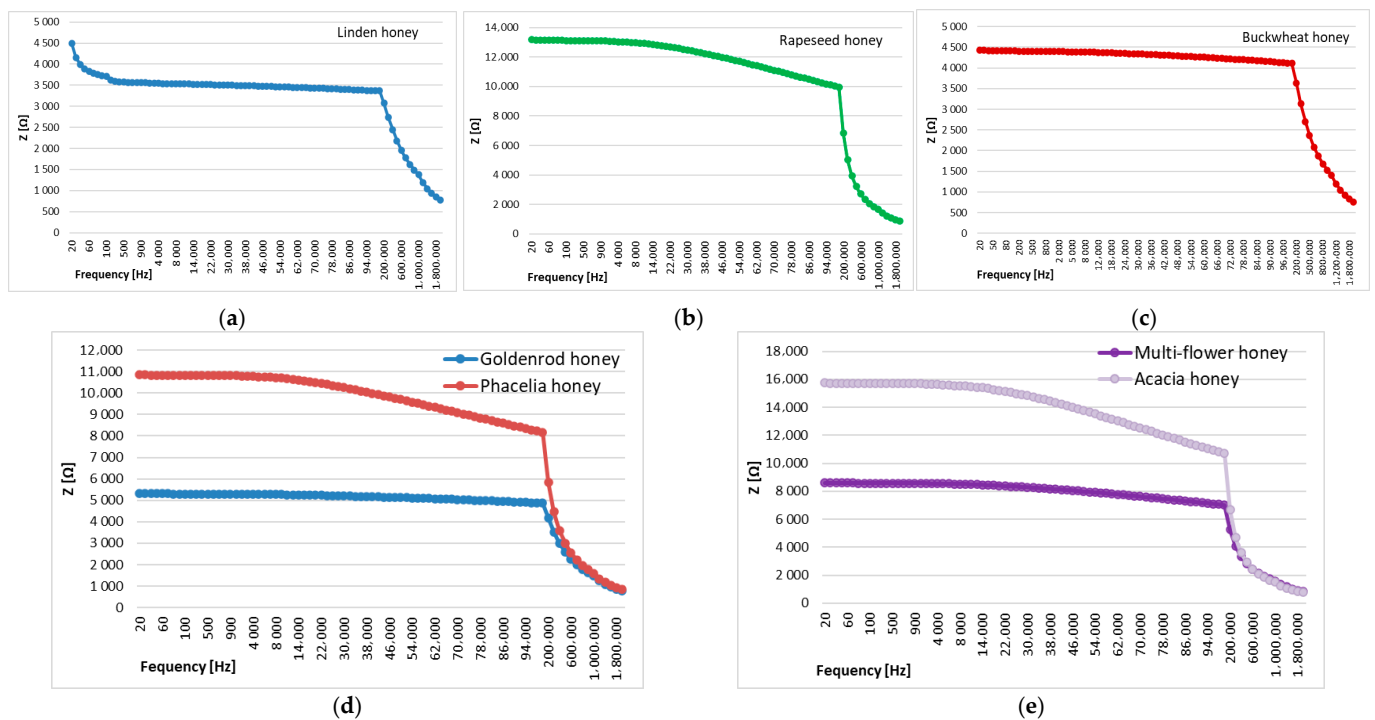


Figure 2. Impedance changes as a function of the measurement current frequency (from 20 Hz to 2 MHz) for honey: (a) linden; (b) rapeseed; (c) buckwheat; (d) goldenrod and phacelia; (e) acacia and multi-flower.

Lime honey (Figure 2a) was characterized by moderate impedance in the low-frequency range (~4.5 kΩ at 20 Hz), stable up to 10 kHz, and then decreasing at higher frequencies. Thus, these changes suggest the preponderance of solution resistance at low frequencies.

Rapeseed honey (Figure 2b) was characterized by the highest impedance at low frequencies (~13 kΩ at 20 Hz), indicating a unique ionic structure. This indicates high impedance stability in a wide frequency range, with abrupt changes at high frequencies.

Buckwheat honey (Figure 2c) showed a relatively low impedance (~4.4 kΩ at 20 Hz) compared to rapeseed honey, which may be due to higher ionic conductivity. Impedance stability up to 100 kHz and a sharp drop in higher frequencies were also observed.

The goldenrod and phacelia honeys (Figure 2d) showed similar characteristics, with moderate impedance and stable behavior up to approx. 100 kHz. Phacelia was characterized by a slightly higher impedance in the mid-frequency range, which may result from differences in the content of minerals.

Acacia honey (Figure 2e) showed the highest impedance at high frequencies, which may be due to its specific chemical structure, while multi-flower honey (Figure 2e), with a more complex composition, had intermediate impedance values between linden and goldenrod.

The obtained results confirm that impedance analysis in a wide frequency range is an effective tool for differentiating honey types and their chemical and physical characteristics.

In the low-frequency range (20 Hz–1 kHz), the impedance of honeys was high, which results from limited ionic conductivity and dielectric properties, and also suggests the preponderance of diffusion effects. These phenomena may be due to mass transport processes, which are important for the ionic characteristics of honeys. The observed differences in this range may be related to differences in the chemical composition and water content of the tested samples [42,68–71].

The rapid changes observed in impedance values with increasing frequency indicate a decreasing effect of ion diffusion and an increasing preponderance of electrical conductivity processes. Such a variability emphasizes the specificity of the electrical properties of honeys, which can be used to differentiate them and analyze their quality.

In the high-frequency range (10 kHz–2 MHz), a stabilization of impedance values was observed, which reflects the preponderance of electrical resistance. This is consistent with the assumptions of the RCC model, where resistance dominates over capacitance at higher frequencies. The stability of these values may be crucial for distinguishing samples with respect to their botanical origin.

High frequencies in electrical measurements allow for determination of parameters such as resistance or diffusion time constants, while diffusion phenomena related to the movement of ions in the honey structure may appear in the low-frequency range [42].

Although the current data are presented as impedance vs. frequency dependence, in future studies we plan to extend the analysis with Nyquist plots and data fitting to the modified Randles model [42,45,47–49,69]. This approach will allow for the detailed determination of electrical circuit parameters, such as diffusion resistance (R) and double layer capacitance (CC), and assessment of their statistical significance. Verification of the model using χ^2 values will allow for a more comprehensive assessment of the validity of the applied approach [70].

The results of the measurement of the conductivity parameters (Z and G) showed that the impedance values (Z) decreased and the conductivity values (G) increased with frequency increase (100 Hz–2 MHz). Despite the wide frequency range used in the work, many authors [55,56,68] have indicated that electrical measurements performed at low frequencies can be particularly useful in the study of low-conductivity foods, e.g., honey. With this in mind and in order to more easily illustrate the phenomena occurring between honeys of different botanical origin (7 varieties), Tables 1 and 2 contain the results of measurements of electrical parameters for six selected frequencies (100 Hz, 1 kHz, 10 kHz, 100 kHz, 1 MHz, and 2 MHz), and they are discussed based on the values measured at $f = 100$ Hz.

Among the tested single-flower honeys, the highest values of complex resistivity (Z) and thus the lowest values of electrical conductivity were characteristic of the rapeseed, phacelia, and acacia honeys (group I). The values of $Z_{100\text{Hz}}$ were at $1.41 \times 10^4 \Omega$, $1.08 \times 10^4 \Omega$, and $1.57 \times 10^4 \Omega$, respectively, while the values of $G_{100\text{Hz}}$ were at $7.13 \times 10^{-5} \text{ S}$, $1.23 \times 10^{-5} \text{ S}$, and $6.36 \times 10^{-5} \text{ S}$, respectively (Table 3). According to Felsner and Schwab [72] as well as Sajwan and O'Connor [73], the low conductivity of acacia and rapeseed honeys results from their minimal content of minerals, which imparts a delicate taste and light color to them.

The second group of single-flowered honeys identified was as follows: the linden, buckwheat, and goldenrod honeys, which were characterized by the lowest resistance values (Z) and the highest conductivity values (G). Their average $Z_{100\text{Hz}}$ values were $3.71 \times 10^3 \Omega$, $4.41 \times 10^3 \Omega$, and $5.30 \times 10^3 \Omega$, respectively. Good electrical conductivity of these honeys is indicated by the high $G_{100\text{Hz}}$ values, which were $3.23 \times 10^{-4} \text{ S}$, $2.64 \times 10^{-4} \text{ S}$, and $2.01 \times 10^{-4} \text{ S}$, respectively (Table 4). According to Chudzińska and Baralkiewicz [74], the high electrical conductivity of buckwheat and goldenrod honeys may result from their high content of minerals, such as iron and magnesium, and organic acids (which also affects their dielectric properties). According to the research of Łuczycka and Tomaszewska [75], linden and phacelia honeys, due to the presence of essential oils and medium mineral content, are characterized by moderate conductivity.

The results of our own research showed that the next group of honeys was multi-flower honeys, which showed moderate conductivity properties: $Z_{100\text{Hz}} = 8.53 \times 10^3 \Omega$, $G_{100\text{Hz}} = 1.95 \times 10^{-4} \text{ S}$. The content of minerals and moderate conductivity level in multi-flower honeys may vary depending on the mixture of nectar from different flowers [72,76]. The basis for distinguishing these three groups of honeys, with different conductivity properties, was the significant differences ($p < 0.05$) between individual honey varieties (Table 4).

According to data in the literature [77] single-flower honeys usually have lower electrical conductivity than multi-flower honeys, although this depends on the plant from which the honey derives. This is evidenced by the fact that acacia honey has a lower conductivity, while buckwheat honey, despite being single-flower, has a higher conductivity, similar to that of multi-flower honeys. In addition, the impedance in multi-flower honeys changes dynamically depending on the frequency, due to the ionic diversity and mineral content. María, Madueño-Luna, and Ruiz-Canales [42] analyzed the usefulness of electrical conductivity and impedance in assessing the quality of single-flower and multi-flower honeys, and found that conductivity was more viable in the botanical identification of honeys. The usefulness of impedance spectroscopy and conductivity for the identification of honeys from different botanical sources was also demonstrated by Elamine et al. [44].

The measurements of dielectric parameters (Table 5) also enabled the division of honeys into three groups, but these tendencies were not as clear as in the case of conductivity measurements (Z , G). The values of the equivalent parallel electrical capacitance (C_p) parameter indicated the possibility of grouping honeys, but the statistical analysis of the differences between the three groups of honeys distinguished earlier did not confirm these differences and similarities (especially at lower frequencies, i.e., 100 Hz and 1 kHz). Group I consisted of the linden, buckwheat, goldenrod, and multifloral honeys with $C_{p100\text{Hz}}$ values 1.99 pF, 3.12 pF, 1.92 pF, and 1.65 pF, whereas group II consisted of the rapeseed, phacelia, and acacia honeys ($4.48 \times 10^{-10} \text{ F}$, $7.60 \times 10^{-10} \text{ F}$, $3.11 \times 10^{-10} \text{ F}$). With an increase in the measurement frequency (10 kHz–2 MHz), significant differences between honeys were more noticeable, but still not as clear as with parameters Z and G . C_p values at $f = 10 \text{ kHz}$ allowed indication of honeys similar in terms of dielectric properties: group I honeys—linden, buckwheat, goldenrod, and group II—acacia, phacelia, and rapeseed.

Taking into account the dielectric profile of the botanically different honeys, it can be stated that homogeneous honeys are characterized by a simpler dielectric dispersion profile, because their chemical composition is more uniform. The response to frequency changes is less diverse, which facilitates their analysis and classification. Multifloral honeys, on the other hand, show a more complex profile, which results from their botanical diversity. The diversity in chemical composition causes them to respond differently to various electric field frequencies.

Table 4. Values of Z (impedance) and G (conductance) of honeys of different varieties and types, measured at a frequency of 100 Hz–2 MHz.

Varieties and Types of Honey		Z [Ω]						G [S]					
		100 Hz	1 kHz	10 kHz	100 kHz	1 MHz	2 MHz	100 Hz	1 kHz	10 kHz	100 kHz	1 MHz	2 MHz
Linden	X	3.71×10^3 a	3.55×10^3 a	3.53×10^3 a	3.36×10^3 a	1.37×10^3 a	7.73×10^2 a	3.23×10^{-4} c	3.29×10^{-4} c	3.30×10^{-4} c	3.34×10^{-4} c	3.58×10^{-4} c	3.95×10^{-4} c
	SD	1.64×10^3	1.45×10^3	1.42×10^3	1.29×10^3	1.63×10^3	5.30×10^1	1.48×10^{-4}	1.43×10^{-4}	1.42×10^{-4}	1.43×10^{-4}	1.39×10^{-4}	1.30×10^{-4}
Rapeseed	X	1.41×10^4 d	1.41×10^4 d	1.39×10^4 d	1.08×10^4 d	1.81×10^3 b	9.31×10^2 b	7.13×10^{-5} ab	7.15×10^{-5} a	7.20×10^{-5} a	7.38×10^{-5} a	8.56×10^{-5} a	1.08×10^{-4} a
	SD	2.12×10^3	2.10×10^3	2.04×10^3	1.06×10^3	5.73×10^1	2.75×10^1	9.71×10^{-6}	9.66×10^{-6}	9.64×10^{-6}	9.42×10^{-6}	1.03×10^{-5}	1.19×10^{-5}
Buckwheat	X	4.41×10^3 ab	4.40×10^3 ab	4.38×10^3 ab	4.11×10^3 ab	1.40×10^3 a	7.62×10^2 a	2.64×10^{-4} bc	2.65×10^{-4} bc	2.65×10^{-4} bc	2.68×10^{-4} bc	2.88×10^{-4} bc	3.23×10^{-4} bc
	SD	1.77×10^3	1.77×10^3	1.76×10^3	1.56×10^3	1.42×10^2	5.03×10^1	1.06×10^{-4}	1.07×10^{-4}	1.07×10^{-4}	1.08×10^{-4}	1.10×10^{-4}	1.11×10^{-4}
Goldenrod	X	5.30×10^3 abc	5.29×10^3 abc	5.27×10^3 abc	4.87×10^3 abc	1.48×10^3 a	7.90×10^2 a	2.01×10^{-4} abc	2.02×10^{-4} abc	2.02×10^{-4} abc	2.05×10^{-4} abc	2.24×10^{-4} abc	2.58×10^{-4} abc
	SD	1.47×10^3	1.46×10^3	1.45×10^3	1.21×10^3	6.92×10^{-1}	1.89×10^1	5.62×10^{-5}	5.62×10^{-5}	5.62×10^{-5}	5.72×10^{-5}	5.85×10^{-5}	5.71×10^{-5}
Phacelia	X	1.08×10^4 cd	1.08×10^4 cd	1.07×10^4 cd	8.18×10^3 cd	1.60×10^3 ab	8.40×10^2 ab	1.23×10^{-5} ab	1.23×10^{-4} ab	1.24×10^{-4} ab	1.26×10^{-4} ab	1.46×10^{-4} ab	1.84×10^{-4} ab
	SD	5.98×10^3	5.98×10^3	5.86×10^3	3.51×10^3	1.23×10^2	5.36×10^1	6.77×10^{-5}	6.78×10^{-5}	6.79×10^{-5}	6.82×10^{-5}	6.60×10^{-5}	6.10×10^{-5}
Multifloral	X	8.58×10^3 bc	8.57×10^3 bc	8.50×10^3 bc	7.03×10^3 bc	1.57×10^3 ab	8.43×10^2 ab	1.95×10^{-4} abc	1.95×10^{-4} abc	1.96×10^{-4} abc	1.98×10^{-4} abc	2.18×10^{-4} abc	2.03×10^{-4} ab
	SD	4.72×10^3	4.72×10^3	4.66×10^3	3.49×10^3	2.41×10^2	9.35×10^1	1.62×10^{-4}	1.62×10^{-4}	1.62×10^{-4}	1.64×10^{-4}	1.62×10^{-4}	1.55×10^{-4}
Acacia	X	1.57×10^4 d	1.57×10^4 d	1.55×10^4 d	1.07×10^4 d	1.50×10^3 a	7.75×10^2 a	6.36×10^{-5} a	6.37×10^{-5} a	6.41×10^{-5} a	6.44×10^{-5} a	8.85×10^{-5} a	1.38×10^{-4} a
	SD	9.71×10^1	9.69×10^1	9.30×10^1	1.85×10^1	2.38×10^1	1.58×10^1	6.34×10^{-7}	6.36×10^{-7}	6.39×10^{-7}	7.97×10^{-7}	5.31×10^{-6}	1.24×10^{-5}

X—average; SD—standard deviation, ^{a–d}—mean values marked with different letters are statistically significantly different ($p < 0.05$) between honey species, ^{a–a, b–b}—average values marked with the same letters do not have statistically significant differences between honey species.

Table 5. Values of dielectric parameters (Cp, Cs) of honeys of different varieties and types, measured at a frequency of 100 Hz–2 MHz.

Varieties and Types of Honey		Cs [F]						Cp [F]					
		100 Hz	1 kHz	10 kHz	100 kHz	1 MHz	2 MHz	100 Hz	1 kHz	10 kHz	100 kHz	1 MHz	2 MHz
Linden	X	6.45×10^{-5} b	1.17×10^{-5} a	2.50×10^{-7} a	3.09×10^{-9} a	1.37×10^{-10} a	1.09×10^{-10} a	1.99×10^{-9} b	5.22×10^{-10} b	1.28×10^{-10} b	1.07×10^{-10} a	1.01×10^{-10} ab	9.80×10^{-11} ab
	SD	4.73×10^{-5}	9.42×10^{-6}	1.95×10^{-7}	2.28×10^{-9}	2.93×10^{-11}	1.08×10^{-11}	2.29×10^{-9}	4.20×10^{-10}	5.44×10^{-11}	5.17×10^{-12}	3.94×10^{-12}	4.19×10^{-12}
Rapeseed	X	3.35×10^{-5} a	1.12×10^{-6} b	1.38×10^{-8} b	2.48×10^{-10} b	8.91×10^{-11} b	8.59×10^{-11} b	4.48×10^{-10} a	1.23×10^{-10} a	9.97×10^{-11} c	8.99×10^{-11} b	8.71×10^{-11} c	8.52×10^{-11} c
	SD	1.56×10^{-5}	3.35×10^{-7}	3.59×10^{-9}	4.11×10^{-11}	3.19×10^{-12}	2.76×10^{-12}	1.19×10^{-10}	2.28×10^{-12}	2.30×10^{-12}	2.69×10^{-12}	2.80×10^{-12}	2.66×10^{-12}
Buckwheat	X	6.52×10^{-5} b	8.96×10^{-6} c	1.57×10^{-7} a	1.96×10^{-9}	1.26×10^{-10} a	1.08×10^{-10} a	3.12×10^{-9} a	2.06×10^{-10} a	1.24×10^{-10} ab	1.08×10^{-10} a	1.04×10^{-10} ab	1.01×10^{-10} a
	SD	6.26×10^{-6}	4.73×10^{-6}	1.05×10^{-7}	1.26×10^{-9}	1.95×10^{-11}	9.10×10^{-12}	1.96×10^{-9}	5.54×10^{-11}	9.73×10^{-12}	6.50×10^{-12}	5.20×10^{-12}	4.97×10^{-12}
Goldenrod	X	6.01×10^{-5} b	6.42×10^{-6} c	9.33×10^{-8} c	1.19×10^{-9}	1.15×10^{-10} a	1.03×10^{-10} a	1.92×10^{-9} a	1.73×10^{-10} a	1.19×10^{-10} ab	1.05×10^{-10} a	1.01×10^{-10} ab	9.85×10^{-11} ab
	SD	2.10×10^{-5}	3.10×10^{-6}	4.85×10^{-8}	5.80×10^{-10}	3.65×10^{-12}	1.37×10^{-12}	3.04×10^{-10}	7.08×10^{-12}	1.32×10^{-13}	1.83×10^{-12}	3.36×10^{-12}	3.45×10^{-12}
Phacelia	X	5.58×10^{-5} b	3.20×10^{-6} c	4.15×10^{-8} b	5.86×10^{-10}	1.03×10^{-10} a	9.63×10^{-11} b	7.60×10^{-10} a	1.41×10^{-10} a	1.14×10^{-10} a	1.01×10^{-10} a	9.67×10^{-11} ab	9.39×10^{-11} abc
	SD	2.21×10^{-5}	2.66×10^{-6}	3.54×10^{-8}	4.18×10^{-10}	1.01×10^{-11}	6.77×10^{-12}	5.41×10^{-10}	1.93×10^{-11}	7.52×10^{-12}	5.55×10^{-12}	5.41×10^{-12}	5.47×10^{-12}
Multifloral	X	6.91×10^{-5} b	7.27×10^{-6} c	1.22×10^{-7} a	1.52×10^{-9} a	1.13×10^{-10} a	9.82×10^{-11} b	1.65×10^{-9} a	1.59×10^{-10} a	1.12×10^{-10} a	9.99×10^{-11} a	9.57×10^{-11} b	9.29×10^{-11} bc
	SD	3.08×10^{-5}	8.49×10^{-6}	1.53×10^{-7}	1.81×10^{-9}	2.76×10^{-11}	1.34×10^{-11}	1.87×10^{-9}	5.35×10^{-11}	1.26×10^{-11}	9.54×10^{-12}	8.43×10^{-12}	8.19×10^{-12}
Acacia	X	3.52×10^{-5} a	7.93×10^{-7} c	9.46×10^{-9} d	2.05×10^{-10} b	1.07×10^{-10} a	1.03×10^{-10} a	3.11×10^{-10} a	1.30×10^{-10} a	1.12×10^{-10} ac	1.08×10^{-10} a	1.05×10^{-10} a	1.02×10^{-10} a
	SD	1.42×10^{-6}	1.94×10^{-8}	2.32×10^{-10}	1.91×10^{-12}	1.56×10^{-12}	1.98×10^{-12}	3.22×10^{-11}	7.07×10^{-13}	9.82×10^{-13}	1.20×10^{-12}	1.83×10^{-12}	2.22×10^{-12}

X—average; SD—standard deviation, ^{a–d}—mean values marked with different letters are statistically significantly different ($p < 0.05$) between honey species, ^{a–a}, ^{b–b}—average values marked with the same letters do not have statistically significant differences between honey species.

In the case of measurements of the Cs parameter (Table 5), its usefulness for identifying the type of botanical variety of honey (no trend in the significance of differences) was even lower than for the Cp parameter. Nevertheless, the variability of the Cp and Cs parameters as a function of frequency changes (f) is much greater than for the Z and G parameters.

The observed lack of clear similarities or differences between single-flower honeys may result from the fact that the honeys tested were fresh, unheated, and unadulterated with sucrose, as indicated by the values of physicochemical parameters, and therefore they adopted characteristic values of similar dielectric parameters. As honeys are subject to changes during storage, with water evaporation and changes in chemical composition, these differences may become more visible. Monitoring electrical capacity enables assessment of whether the honey is fresh or already showing signs of degradation [44].

3.3. Suitability of the Electrical Method for Controlling Quality Parameters

The last stage of our research involved a two-stage statistical analysis aiming to determine which of the standard physicochemical tests can be replaced by measurements of electrical properties.

Stage 1. Analysis of the degree of similarity of changes in the tested physicochemical parameters (qualitative and health-promoting) among the seven honey varieties showed that the first cluster of honey quality parameters most similar to each other was cluster no. 1, including the following: water content, acidity, and color parameters L* and b*. The second cluster characterized by a very high degree of similarity and a large number of parameters was cluster no. 2, including the following: sucrose, 5-HMF, TP, diastase number, DPPH, reducing sugars, and color parameter a* (Figure 3).

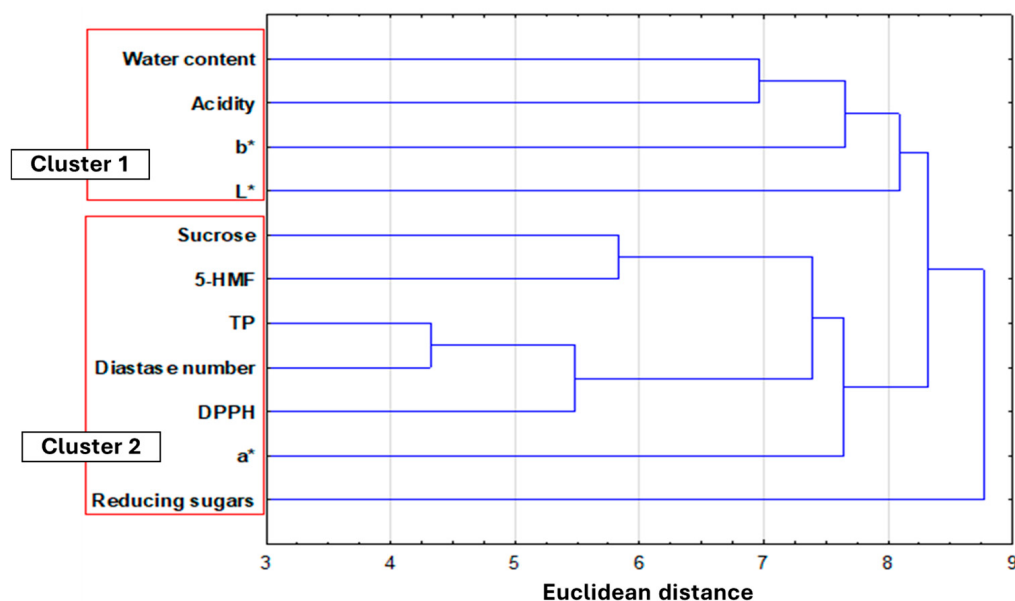


Figure 3. Hierarchical structure of the set (clusters 1 and 2) of variables due to the similarity between changes in the average values of physicochemical, health-promoting, and color parameters.

The second stage of the analysis aimed to demonstrate the correlation between dependent variables (variables grouped into clusters 1 and 2) and independent (electrical) variables. Profit analysis was conducted to this end, which enabled understanding of how different levels of dependent variables affect the physicochemical, health-promoting, and color parameters of the honeys, as well as which features of individual honey species are the most important (Figure 3).

The obtained perception map (multidimensional scaling—MDS) (Figure 4) of electrical conductivity parameters (Z and G) of honeys in relation to their four quality parameters, characterized as cluster 1 (Figure 4a), indicates the existence of strong correlations between

water content and G (in the entire frequency range) of the buckwheat and lime honeys, and between the color parameter L^* and Z of rapeseed honey ($f = 100\text{ Hz}$, $1\text{--}100\text{ kHz}$) and phacelia honey ($f = 1\text{--}2\text{ MHz}$). In the variant of the analysis of dielectric parameters (C_s and C_p) in relation to the parameters of cluster 1 (Figure 4b), correlations were found between them in the lime, phacelia, and goldenrod honeys. Significant correlations were also found between acidity and water content and the C_s parameter ($f = 100\text{ Hz}$, $f = 1\text{--}100\text{ kHz}$) of goldenrod honey, and between the color parameters (L^* , b^*) and $C_{p100\text{Hz}}$ and $C_{p1\text{kHz}}$ of the linden and phacelia honeys.

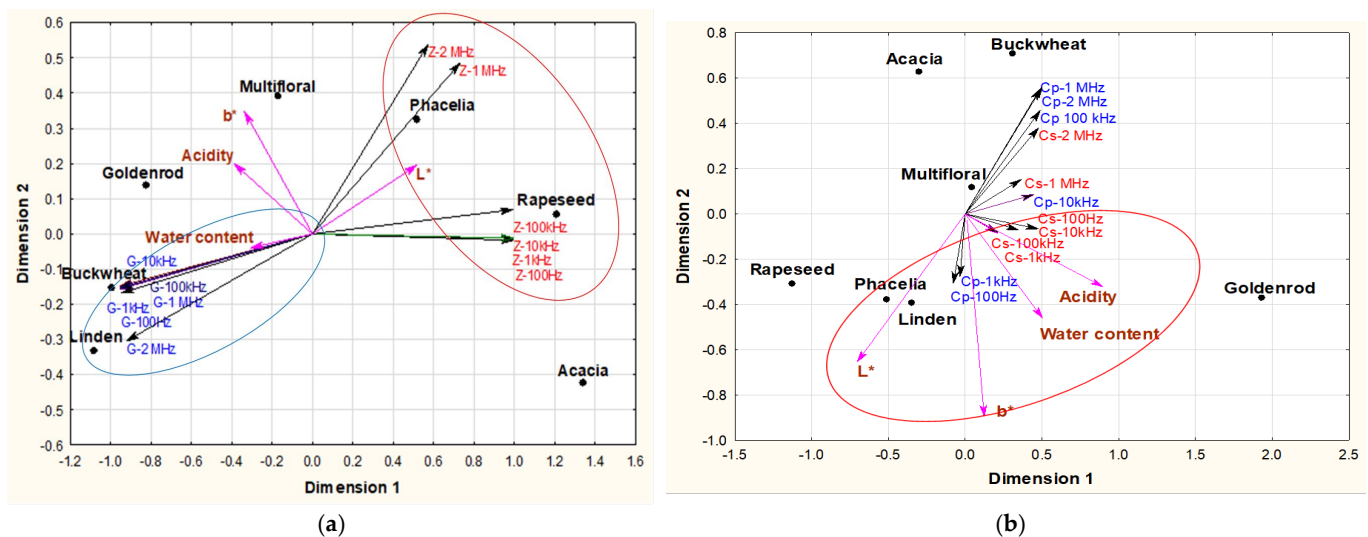


Figure 4. Location of water content, acidity, and color parameters (cluster 1) vs. (a) conductivity parameters (Z , G) and (b) dielectric parameters (C_p , C_s) of the 7 honey varieties in a multidimensional space.

The distribution of points and vectors for physicochemical and color parameters (cluster 1) and electrical parameters (Z , G , C_p , C_s) indicates that preference assessments are mainly determined by two dimensions. The most expected from the point of view of assessing water content in the buckwheat and linden honeys is the use of the G parameter (irrespective of the measurement frequency), and the 0 parameter for goldenrod honey ($f = 100\text{ Hz}$, $f = 1\text{--}100\text{ kHz}$). The color lightness (L^*) of phacelia honey can be assessed using the Z parameter (at high frequencies $1\text{--}2\text{ MHz}$), whereas the $C_{p100\text{Hz}}$ and $C_{p1\text{kHz}}$ parameters are found suitable in assessing the lightness and yellow color (L^* , b^*) of the linden and phacelia honeys.

The significant correlations obtained indicate the feasibility of replacing water content determination in honeys with measurements of conductivity parameters, in order to assess their quality non-invasively and quickly. The water content of honey is a key quality parameter, as it affects its stability, ability to crystallize, and susceptibility to fermentation [36]. Another advantage of the observed possibilities of quick quality control of honeys, especially in the case of lime honey (alleviating cold symptoms and supporting the health of the respiratory tract) and buckwheat honey (supporting the circulatory system and the ability to neutralize free radicals), is that they are often chosen by consumers in many countries [78], including Poland, due to their health benefits. Studies conducted by Chua et al. [79] and Bogdanov, Ruoff, and Oddo [80] also indicated the possibility of using electrical conductivity for consumer assessment of visual quality elements (color)—especially in dark honeys (e.g., buckwheat) with a higher mineral content.

The results of the Profit analysis regarding the quality and health-promoting parameters (cluster 2) and electrical parameters allowed for the interpretation of similarities and differences between the studied parameters, i.e., sucrose content, reducing sugar content, 5-HMF content, diastase number, DPPH, TP content, and the color parameter a^* .

When interpreting the honey perception map presented in Figure 5a (correlations between parameters: conductivity vs. cluster 2), it was observed that the strongest correlation was obtained between impedance— Z (100 Hz, and 1, 10, and 100 kHz) and contents of reducing sugars and sucrose for the rapeseed honey variety, while a slightly weaker correlation was observed for the phacelia and acacia honeys. This is probably due to the fact that an increase in sugar content hampers the mobility of ions and thus increases impedance and reduces conductivity. In turn, the diastase number, TP, DPPH, and 5-HMF correlated most strongly with conductivity G (in the entire frequency range) in the buckwheat and linden honeys.

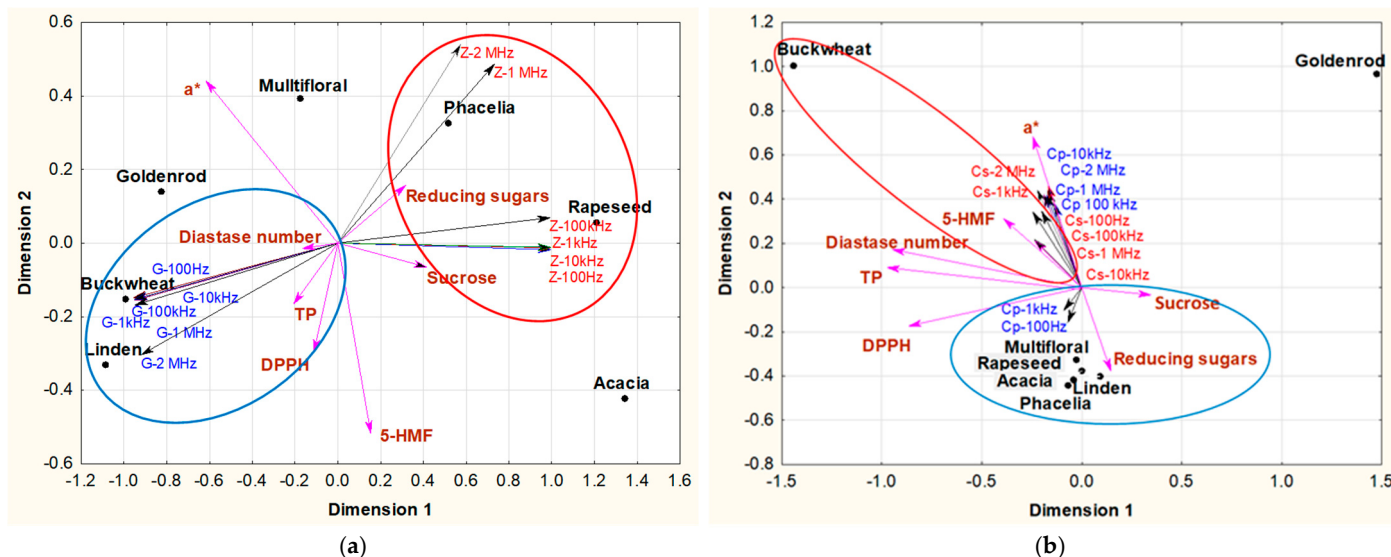


Figure 5. Location of quality and health-promoting (cluster 2) vs. (a) conductivity parameters (Z , G) and (b) dielectric parameters (C_p , C_s) of the 7 honey varieties in a multidimensional space.

The diastase number is a measure of enzymatic activity in honey and is usually the highest in fresh, unheated honeys, while the 5-HMF content is an indicator of overheating honeys [81]. Conductance may, therefore, reflect changes in enzymatic activity and an increase in 5-HMF content. The total content of polyphenols (TP) in honey and its ability to scavenge free radicals (DPPH) correlate with its conductivity, because compounds with antioxidant activity (mainly phenolic acids) can probably increase ion mobility [82].

The analysis of correlations between quality parameters (clusters 2) and dielectric parameters (C_s , C_p) of honeys showed that the C_p parameters, measured at $f = 1$ kHz and $f = 100$ kHz (Figure 5b), were most useful for controlling the content of sucrose and reducing sugars (all types of honey except buckwheat and goldenrod honey). The correlations found between dielectric parameters are related to the structure of sugars and the presence of large sugar molecules that affect polarization in the electric field. Capacitance (in the RCC model) can, therefore, be used to assess their concentration in honey. Compared to water, sugars are less polar, but their presence increases viscosity, which affects ion mobility and polarization. In addition, multi-flower honeys have a higher mineral content, which is why their quality parameters correlate more with dielectric parameters [83].

The possibility of assessing the sugar content using the electrical method will allow for indirect assessment of the organoleptic properties (taste, consistency), stability, and crystallization rate of honey. The parameters C_s (at lower frequencies) and C_{p2MHz} were shown suitable for the assessment of 5-HMF content and the a^* value of buckwheat honey. A high content of 5-HMF is an indicator of thermal processing or aging of honey, which may reduce its quality. Dielectric analysis is helpful in detecting heat treatment and adulteration. The use of dielectric parameters in relation to the diastase number, TP, and DPPH is unjustified.

Taking into account the results presented in Figures 4b and 5b, it was found that the C_p parameter (100 Hz, 1 kHz) proved the most useful in assessing the quality (acidity and contents of water, sucrose, and reducing sugars) of a larger number of honey varieties.

The obtained results of measurements of electrical parameters of honeys and the analysis of their correlations with quality parameters confirm the results of the research by Yang et al. [40], who found that conductivity parameters, compared to dielectric parameters, are of greater utility value in everyday quality analyses of honeys. The RCC model may be valuable in more detailed studies on the quality and authenticity of honeys, especially where the analysis of complex dielectric properties and differences in composition is crucial.

The analysis of measurement results shows that the electrical method applied to assess the quality of honeys has both significant advantages and certain limitations.

It is characterized by high sensitivity, allowing distinction of differences between honey species based on electrical parameters of conductivity (Z , G) and capacitance (C_p , C_s). The results also suggest that this method is particularly useful for botanically homogeneous honeys. Low values of standard deviations of the analyzed parameters confirm the stability and repeatability of measurements. Compared to physicochemical methods, the proposed approach is less time-consuming and does not require complicated and destructive sample preparation, which makes it a viable practical tool in honey diagnostics on a large scale. The method should be considered more user-friendly and allows maintenance of sample integrity. Its efficiency is, however, limited by external factors, such as temperature variability, which affects the results of impedance measurements. In a narrow measurement frequency range, it is also necessary to take into account diffusion effects, which may be significant in the case of honeys with a higher water content. Therefore, further research will be aimed at fitting the results to more advanced electrical circuit models, such as the modified Randles model, and at assessing the accuracy of the fit.

4. Conclusions

In the studied population of honeys, the following were observed and statistically confirmed:

1. Results of physicochemical analysis showed that the tested honeys were fresh, not overheated, not adulterated, and collected at the appropriate stage of maturity. The darkest honey, buckwheat, was characterized by the highest antioxidant activity and diastase number, while other honey varieties did not show any significant differences in the values of these parameters.
2. The results of the statistical analysis of the values of conductivity parameters (Z , G) allowed classifying the seven tested honey varieties into three groups. Among the single-flower honeys, two groups were distinguished: I—with high electrical conductivity (linden, buckwheat, goldenrod) and II—with low conductivity (acacia, phacelia, rapeseed). Group III consisted of multi-flower honeys characterized by moderate conductivity. The separation of these three groups of honeys indicates the possibility of identifying their botanical origin using electrical methods, which are characterized by non-invasiveness, measurement speed, and high sensitivity.
3. Analysis of the correlation between quality parameters (separated in clusters—1 and 2) and electrical parameters measured using an innovative method (own-design measurement system) showed that the conductivity parameters (Z , and G , in the entire frequency range), and to a slightly limited extent the dielectric parameters (C_p , C_s), were most useful for assessing the quality of selected honey varieties.
4. The usefulness of the Z and G parameters in replacing the quality parameters defined in cluster 1 (acidity, water content, L^*) and quality and health-promoting parameters in cluster 2 (reducing sugars, sucrose, diastase number, TP, DPPH, and 5-HMF) was observed mainly for the single-flower honeys: buckwheat, linden, rapeseed, and phacelia. In the case of the multi-flower honeys, the Z , G , and C parameters were useless in their quality assessment.

The proposed electrical method shows potential for assessing the quality and for differentiating honeys, but its implementation requires further development, including the assessment of the influence of diffusion effects and critical analysis of the fit of measurement results to electrical models.

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