

Study of Quality Factor (Q) and Phase Angle (θ) obtained per electrical impedance to characterization and detection adulteration in honey

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Abstract

The quality control of honey is very important for the food industry and for the final consumer. Honey has constantly been the target of adulteration, usually with the aim of illegally increasing profit. However, the analytical methods used in the fraud investigation sometimes are very complex and beyond time-consuming. Electrical measurements appear as a good alternative to the traditional methods of analysis due to its practicality and low costs. In order to show the applicability of some electrical parameters derived from the impedance technique for honey quality control analysis, in the present study, samples were purposefully adulterated with syrup to simulate adulteration conditions. Then, they were submitted to electrical impedance analysis with frequency scanned from 10 Hz to 2 MHz. The impedance module (Z), the phase angle (θ) and the quality factor (Q) data were collected and studied. The results showed that there is a linear correlation between the frequencies relative to the peaks of the Q for samples and adulterant concentration with coefficient of determination of ~ 0.992 . The proposal to use the Q as a property to be used in methodologies of analysis is the main contribution from this study, since it is traditionally little mentioned in the literature.

Keywords: Electrical measurements, Frauds detection, Honey analysis, Quality control.

1. Introduction

Honey is the natural sweet substance produced by honey bees from the nectar of plants or excretions of plant sucking insects, which honey bees collect, transform by combining with specific substances of their own, deposit, dehydrate, store, and leave in the honeycomb to ripen and mature [1].

The chemical composition of honey can vary according to the plant and honey bee species, geographical factors, pollen source and climatic conditions of production [2, 3].

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Qualitatively, it consists of saccharides (glucose, fructose, maltose, and sucrose), water, amino acids, phenolic acids, lipids, vitamins, and inorganic compounds.

Worldwide, honey production has a strong socioeconomic value, encouraging family farming, reducing rural exodus and generating profits. Moreover, honey production has an ecological role in which the honey bees naturally pollinate and cultivate vegetal species, conserving the vegetation [4]. Beekeeping offers the producer other profitable products from honey such as wax, propolis, and royal jelly, which are used in the cosmetics industry and in the production of medicines [5].

Unfortunately, the adulteration of honey is a common practice in the whole world. Sucrose, inverted beet syrup, corn syrup, and brown sugar syrup are examples of cheaper products that are used to increase the mass of honey. However, these substances decrease the nutritional properties and the final quality of the product [6, 7]. Another fraud is overheating, which can lead to the inactivity of enzymes caused by heat and result in a variation in the composition of the product [8, 9].

The techniques currently applied to check the physicochemical parameters of honey quality are very complex, time-consuming and require qualified personnel [2]. Thus, it is necessary to develop methods to ensure the quality of honey, guaranteeing that the consumer obtains a genuine product. The determination of electrical measurements appears as an alternative, due to practicality, as they are non-destructive and generally low-cost methods [10]. This technique has been applied as a method for quality control and detection of adulterations in other foods, such as milk [11, 12].

The present work aims studied the impedance module (Z), phase angle (θ) and quality factor (Q) as potential parameters to be used in characterization, quality control and adulteration detection in honey. For this purpose, solutions of the syrup (sucrose solution diluted in water at 20% w/v) were prepared and purposefully added in the honey samples, in order to adulterate the samples and evaluate the changes in their electrical parameters. From the results of Q a model adjustment was traced.

2. Theoretical Referential

The Electrical Impedance Spectroscopy (EIS) is a very useful technique to characterize the electrical behavior of solid and liquid materials (ionic, semiconducting and even dielectric) [14]. It consists of analyzing the material sample by applying an external electrical stimulus, measuring the response of the electrical properties that are relevant to the system. Electrical quantities derive from the mobility of the ionic species in solution that depend on several factors related to the material. The most common stimulus is through the use of an alternating voltage of the sinusoidal type, followed by the measurement of the real ($\text{Re}[Z^*]$) and imaginary ($\text{Im}[Z^*]$) parts of the complex impedance as function of frequency [14]. However, this work aims to explore another physical quantity (Q), as a new proposal for the detection of adulteration in honeys.

When we move from a direct current (DC) circuit to an alternating current (AC) circuit, the notion of resistance, associated only with dissipated energy, needs to be extended and includes reactance concepts, which describes the energy stored in the system. The joint action of resistances (R) and reactances (X) is defined as Z^* , named impedance [14]. The spectra can be described and fitted using an equivalent circuit built up of a parallel resistance-capacitance ($R//C$) network, according to the original Debye model, where the impedance represented by Z^* is a complex variable, therefore having a real and an imaginary component (which is multiplied by $j = \sqrt{-1}$). Z^* is a function of the angular frequency ω ($\omega = 2\pi f$) [15, 16] whose impedance dispersion obeys:

$$Z^*(\omega) = Z'(\omega) - jZ''(\omega) = \frac{R}{1+j\omega\tau} = \frac{R}{1+\omega^2\tau^2} - j\frac{\omega R\tau}{1+\omega^2\tau^2} \quad (\text{Equation 1})$$

In this equation, $\tau = RC$ refers to the relaxation time, directly linked to the relaxation frequency through the simple $f_0 \equiv \frac{1}{2\pi\tau}$ relationship. Resistance (R) depends on the composition of the sample and it is related to the resistivity. These models are discussed in more detail by M'Peko et al. (2013) [17].

There are several electrical quantities that derive from the impedance equations and each one has a physical interpretation that could be used to study specific characteristics of each material of interest. The impedance module (Z), θ and Q , discussed in this paper, are examples of these quantities.

Z is an analogue of resistance in a DC circuit, but in an AC circuit. θ is observed according to equation 2 and represents the measure of the delay between the measured signal of the sample and the alternating electric field applied (external excitation).

$$\theta = \arctan \frac{X}{R} \text{ (Equation 2)}$$

As shown, electrical impedance can be described in terms of an approach involving complex numbers and equated by a real part and an imaginary part. Q measures the ratio between these two quantities. It measures the ratio of the imaginary part by the real part, of the impedance. Phenomenologically, $Re[Z^*]$ refers to the energy dissipated by the system and at low frequencies is equivalent to the resistance of the sample, while the $Im[Z^*]$ measures the energy stored in the solution in the form of an electric field [14].

From a practical point of view, all these quantities can be measured directly by the equipment (impedance analyzer) and organized as several spectra in function of the frequency. The spectral profile of each of them allows the electrical characterization of the samples.

Pure honey contains very low percentages of ionic compounds mainly in the form of mineral salts and ashes. The current work deals with different diluted honey samples, in which the syrup (from the mixture of water and sucrose) was added in a controlled manner, simulating adulteration. Honey, water and sucrose are polar in nature, thus making the net solution purely polar and consequently, increasing the impedance of samples. As discussed by Das et al. (2017) [2] and according to Gauss's theorem for dielectrics, a certain amount of polarization charge exists in the system along with its net free charge. The expression of polarization (\vec{P}) is linked to the applied electric field (\vec{E}) expression as,

$$\vec{P} = (\varepsilon - \varepsilon_0)\vec{E} \text{ (Equation 3)}$$

where ε is the permittivity of samples and ε_0 is the permittivity of free space.

Thereby, the inclusion of polar sucrose-water molecules in the pure polar honey solution alters the net dielectric constant of the system due to the relative changes of pure polar dipoles over the ionic dipoles [2].

As shown by M'Peko et al. (2013) [17], there is a strong correlation between the resistivity (ρ) and viscosity of the solution (η). This can be seen in equation 4. This relationship will be important to support discussions in the result section of this work.

$$\rho = \left(6 \frac{\pi r}{Nq}\right) \eta \text{ (Equation 4)}$$

where N represents the density of charge carriers contributing to conductivity, q is the charge value of these carriers, r is the radius of the diffusing charge in the viscous medium. This expression shows that the viscosity and the resistivity are directly proportional properties.

3. Material and Methods

The sample of honey from the *Eucalyptus* flower was purchased at a local store in the city of Governador Valadares – MG, Brazil. The sample was kept under the same temperature in which it was acquired and was transported to the laboratory in its original packaging. The suppliers are major producers in their regions and had a Federal Inspection Service (SIF) seal from the Brazilian Ministry of Agriculture, which attests to the quality of products of animal origin.

3.1 Preparation of sucrose syrup

The sucrose syrup, a mixture of sugar dissolved in water, was used to simulate possible adulteration, so that fraud by adding syrup is commonly described in the literature [3]. In this

work, a stock solution of this syrup was prepared in a concentration of 20% w/v and added purposefully to the pure honey. For weighing sucrose, a digital scale from the Shimadzu brand, model AUX 220, was used.

3.2 Addition of the sucrose syrup to the honey

The adulterated honey samples were prepared by adding of the sucrose syrup to the honey at levels 5, 10, 15, 20 and 25% v/v using a graduated pipette to measure the syrup volume, transferring into a volumetric flask of 100 mL and completing with honey. The choice of the addition range was based on reports in the literature on levels of frequent adulteration, as demonstrated by Sivakesava and Irudayaraj [13].

3.3 Pre-treatment of samples

All honey samples (non-adulterated and adulterated) were subjected to a standard pre-treatment based on dilution in distilled water, at 40% v/v, before electrical impedance measurements. This procedure was necessary due to the high original viscosity of the samples, which would make electrical analysis difficult and slow, since the analytical signals are unstable in these conditions. The dilution was performed by using a graduated pipette to measure the water volume, transferring into a volumetric flask of 100 mL and completing it with the sample to be analyzed.

3.4 Experimental Procedure

The electrical impedance measurements were performed using a HIOKI analyzer, model 3170, stimulated with an external electrical field alternating with 1 V peak to peak, in a sinusoidal wave type, in a frequency range from 10 Hz to 2 MHz. An electrode of platinum plate parallel (geometric constant $K = 1 \text{ cm}^{-1}$), commonly used for measurements of electrical conductivity of liquids, was adapted to the instrument. All the electrical properties studied (Z , θ and Q) were directly measured by the impedance analyzer, however, the quantities Q was calculated internally by the equipment through interrelation from the data of impedance (Z) and θ . Figure 1 shows the apparatus used *in the* experiments. The software platform used to obtain the spectra and correlation models was OriginPro 9.0.0 (64-bit) SR2 b87.



Figure 1: Picture of the equipment and simplified geometry of the adapted cell for measurements in liquids

4. Results and Discussion

The behavior observed for the Z spectrum for the non-adulterated and adulterated honey samples is presented at Figure 2. The pure honey solution has a capacitive character and can be described as a parallel RC circuit, according to equation 1. Therefore, it has the frequency value in its denominator, indicating that, as the frequency increases, there is a decrease in the real part of the impedance tending to zero.

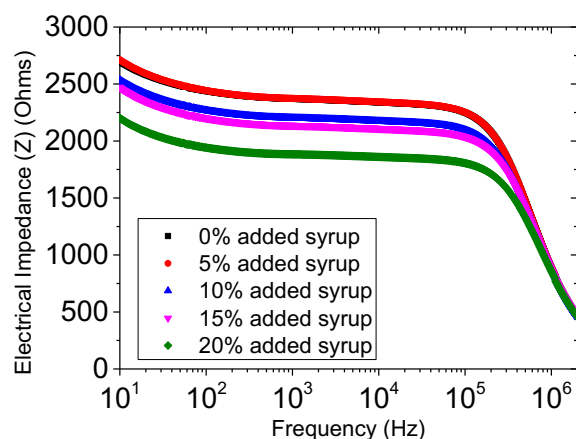


Figure 2: Impedance module (Z) spectrum in unadulterated and adulterated honey samples

For low frequencies, it is possible to demonstrate that $Re[Z^*]$ tends to be constant. This value refers to the resistance of the sample and is directly related to the resistivity explained in the equation 4. There is a geometric factor between these quantities (resistance and resistivity) that depends on the geometry of the electrode used. At the figure, in frequencies near of zero a small variation is view it is due the adsorption effects per interactions with electrode [18]. In this study, as cited, the same electrode was standardized and used for all measurements performed. It is seen in Figure 2 that when the syrup solutions are added to the honey samples, there is a reduction in the measured impedance, in regular variations for the added levels. This is due to the solubilization of ionic components of honey and reduction in the viscosity of the samples when the syrup is added, since it is water based. The viscosity of water is much lower than that of genuine honey. This reduction of viscosity causes a proportional decrease in the resistivity and consequently in the resistance and impedance. The results showed that these variations in the spectra profiles were evident.

Figure 3 shows the phase spectra measured for the non-adulterated and adulterated honey samples. As shown, the phase is a measure of the delay between the measured signal at the sample and the alternating electric field applied (external excitation).

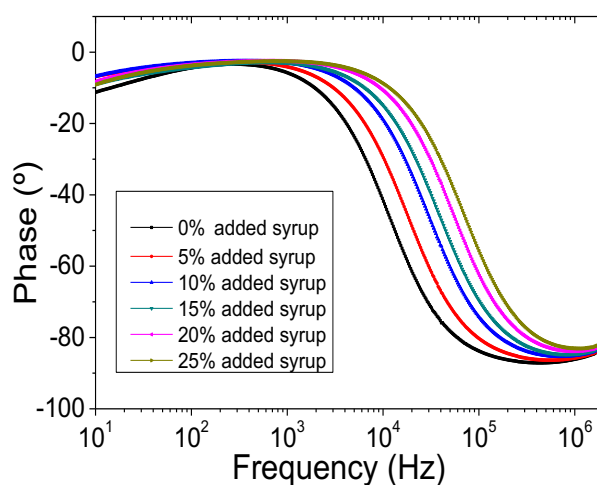


Figure 3: Phase impedance spectrum in unadulterated and adulterated honey samples

It is observed that for low frequencies ($f < 10$ kHz), all spectra of the phase approach zero, indicating that there is a resonance profile to these frequencies. This is due to the fact that most charge carriers are aligned with the external excitation field. Therefore, although the

conditions of the samples are different, mainly in relation to viscosities, the interactions of the charges with the medium are not sufficient to generate delays in the measured electrical response, that is, they all present a delay close to zero. At the figure, in frequencies near of zero again a small variation is view it is due the adsorption effects per interactions with electrode [18]. Both the solutions of pure honey and added syrup show a capacitive behavior. This is indicated by the negative sign of the phase in all of the spectrum, which is in accordance with the RC electric models as used in this study.

For high frequencies ($f \sim 1$ MHz) there is a marked increase, in module, of the phase, in which all samples tend to have a maximum delay of 90° . At these frequencies, we have the maximum delay between the applied excitation field and the electrical response of the material, to express a disorientation of the ions present. Therefore, both for low and high frequencies, the spectra show that we would have low sensitivity for analysis of adulterations.

However, for intermediate frequencies ($10 \text{ kHz} < f < 100 \text{ kHz}$), it is noticed that there is a specific spectrum profile for each sample, depending on the present level of dilution with syrup. As the dilutions occur, by adding the syrup, there is a decrease in the measured delay. This is justified by the decrease in viscosity. The reduction in viscosity leads to an decrease of electrophoretic effects of interaction with the middle and consequently the increase of ionic mobility, increasing the tendency for the ions to be more aligned with the external electric field. Therefore, in pure honey, the resistance is greater in relation to the one adulterated with syrup, resulting in a greater delay. For this range of frequency there was a linear variation of the phase as a function of the dilutions.

The spectra of Q for the non-adulterated and adulterated honey samples are shown in Figure 4(A). Q was obtained from the electrical impedance measures as the ratio between stored and dissipated energy in the system. A part of the energy is stored in the excited sample in the form of electric and magnetic fields, while a part is dissipated in the joule effect. These energies are represented in the theoretical models by the imaginary ($Im[Z^*]$) and real ($Re[Z^*]$) part of the impedance, respectively, and the ratio between them is measured by the Q .

For the samples, Q shows a spectral profile containing a peak positioned at high frequencies ($f \sim 1$ MHz) and there is a decrease of the intensities of this peak and shift to higher frequencies with increase adulterant concentration. This shift is due to the fact that with the dilution of the syrup and the significant change in the viscosity of the samples, there is a change in the relaxation times of the system [17]. The lower the viscosity, the lower the interaction effects with the medium and, consequently, the lower the τ and more the f_0 . The Q spectrum had a regular variation in the position of the maximum peaks measured in relation to the x-axis (frequencies) when the syrup was added to the honey samples. This variation of the position of the maximum frequencies for Q in function of adulterant concentration was plotted in the Figure 4(B) and demonstrated a linear trend of variation.

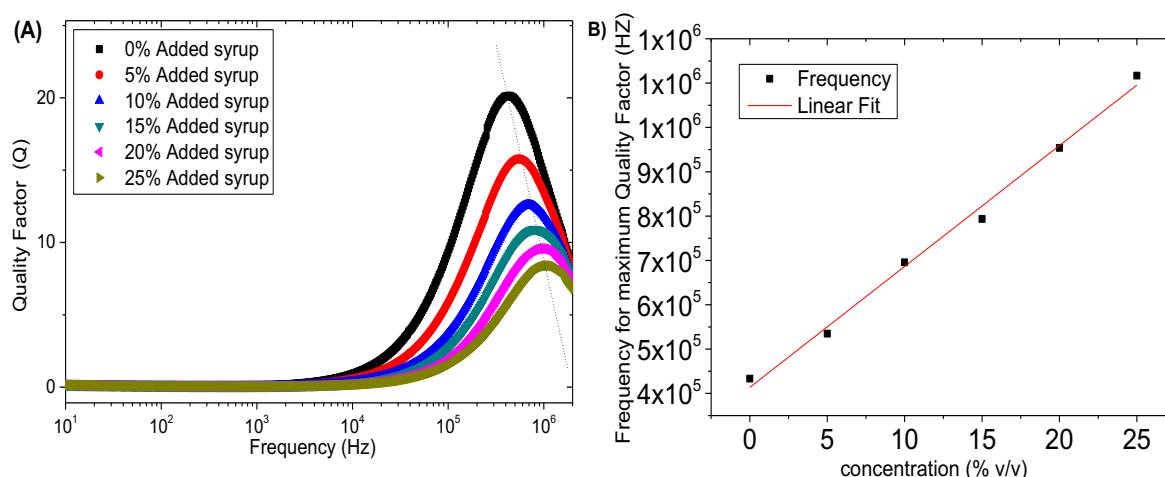


Figure 4(A): Quality Factor spectra in unadulterated and adulterated honey samples. Figure

4(B): Frequency for maximum quality factor (Q) as a function of concentration for non-adulterated and adulterated honey samples

The mathematical models of the adjustments obtained from the linear regressions for Q was $F_{MPQ} = (27269 \pm 1082)C + (413790 \pm 16374)$, where F_{MPQ} is the position of the frequencies of the maximum peaks while C is concentration of syrup added. The determination coefficient (R^2) calculated was ~ 0.992 . Through the linear adjustments, it can be seen that Q has a regular correlation model.

5. Conclusions

The presented results indicated that it is possible to use the technique of electrical impedance spectroscopy to evaluate the quality of honeys produced, mainly in the detection of adulterations by syrups. Changes in the spectral profiles of Z, θ and Q were observed as a result of additions of sucrose syrup as an adulterant, showing to be promising as a basis for new analytical methodologies. A model of adjustment was realized for Q. The positions of the Q peaks in relation to the frequency indicated good potential for this purpose, as it presented a variation with a linear trend with a high linear determination coefficient (R^2). The Q parameter appears as a good alternative of electrical property to be used in methodologies. In future work will be carried out with a focus on statistical validation of the models proposed, with a larger number of samples and tests such as assumptions of normality, homoscedasticity and independence of the data, along with the calculation of the model's lack of fit test, detection limits (LOD) and quantification (LOQ), similar to what has been done in other works with other foods [10]. Other possibilities of methodologies based on these electrical measures will also be studied, such as exploring specific frequency ranges, in addition to evaluating other quantities related to EIS with potential to be used.

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