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Impedance spectroscopy for rapid determination of honey floral origin

Graziella Scandurra [a,*], Gianluca Tripodi [b], Antonella Verzera [b]

[a] Department of Electronic Engineering, Industrial Chemistry and Engineering, University of Messina, 98166 Messina, Italy
[b] Department of Chemical Sciences, University of Messina, 98166 Messina, Italy

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ABSTRACT

In this work electrical impedance spectroscopy was applied as an alternative method for floral origin determination of unifloral honeys, which may supplement the labeling according to the European Legislation. Impedance measurements, in agreement with data from routine analyses, allowed to distinguish the unifloral honey samples and to acquire information on chemical and physical properties, such as conductivity, ash content and acidity. Equivalent electrical circuits have been extracted for each unifloral honey sample, which have been validated by means of electrical simulation, and every electrical component has been associated to a specific honey characteristic. It can be concluded that the method developed here permits rapid and easy determination of honey floral origin, no sample preparation procedure is required and it could be used in the official control laboratories.

1. Introduction

Impedance measurements are largely employed in many fields of electronic engineering, such as devices, circuits and sensors characterization and reliability. Nevertheless, these kinds of measurements, known as Impedance Spectroscopy (IS) technique, have been applied also in medicine and biology (Cole, 1932; Laufer et al., 2012; McGivney et al., 2012) and recently as an alternative, fast and low cost method for food quality control, such as fish (Chevalier et al., 2006; Fernandez-Segovia et al., 2012), meat (Damez et al., 2008), fruit and vegetables (Kuson and Terdwongworakul, 2013; Wu et al., 2008).

The standardization and accreditation of quality evaluation methods is a pressing need for the certification of food products, particularly for those frequently subject to adulteration such as honey. The European Union legislation (2001/110/EC) defines honey as "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". It is a supersaturated solution of sugars, mainly composed of fructose (38%) and glucose (31%), containing also minerals, proteins, free amino acids, enzymes and vitamins (Pérez, 2002; Terrab et al., 2003). A wide range of minor constituents are also present, such as phenolic acids and flavonoids (Martos et al., 2000; Tomas-Barberán et al., 2001; Dimitrova et al., 2007), certain enzymes (glucose oxidase, catalase) (Molan and Betts, 2004) and amino acids (Patzold and Bruckner, 2006; Pérez et al., 2007). The chemical composition of honey is highly dependent on the floral origin of the nectar foraged by bees (Cuevas-Glory et al., 2007); honey of unifloral origin usually commands higher commercial value, thus the floral determination and certification play an important role in quality control. European legislation specifies that the term "honey" may be completed by a reference to the origin, whether blossom or plant, provided the product comes predominantly from the indicated source and has the appropriate organoleptic, physicochemical, and microscopic properties corresponding to that origin (Codex Alimentarius Commission, 1970; Council Directive 74/409/EEC, 1974). In order to determine the legitimacy of the floral origin of honey, analysis of pollen (melissopalynology) and organoleptic or physico-chemical properties are traditionally employed. However, melissopalynology requires a very experienced analyst, is very time consuming, and depends on the expert's ability and judgment (Radovic et al., 2001); particular difficulties in this method are associated with the need of good experience and knowledge of pollen morphology and the availability of a comprehensive collection of pollen grains. Minerals and trace elements (Fernandez-Torres et al., 2005; Hernandez et al., 2005; Latorre et al., 1999), volatile compounds (Verzera et al., 2001; Guyot et al., 1999; Radovic et al., 2001; Soria et al., 2004), flavonoids (Fallico et al., 2004; Acquarone et al., 2007; Corbella and Cozzolino, 2006; Devillers et al., 2004; Marini et al., 2004), etc. have been considered too, but until now not any of the proposed methods furnish undoubtful information for investigators wishing to determine the botanical origin of honey.

Here, we report on the development of a novel alternative method for the assessment of floral origin in honey samples based

* Corresponding author. Tel.: +39 090 3977533; fax: +39 090 3977464.
E-mail address: gscandurra@unime.it (G. Scandurra).

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on impedance measurements. The proposed method appears to be quite promising since it allows a fast and reliable classification of unifloral honeys. Impedance measurements were applied to different unifloral Sicilian honeys and the data correlated with physicochemical parameters.

2. Materials and methods

2.1. Sampling

Unifloral honey samples were provided by local beekeepers with a guarantee of genuineness in respect of geographical and botanical origin. The honeys were produced in the east part of Sicily (South Italy) and are representative of the most common unifloral honeys. Five samples of honey for each of the different types listed below: chestnut (*Castanea sativa* L.), eucalyptus (*Eucalytus camaldulensis* L.), thyme (*Thymus capitatus* H.), orange (*Citrus sinensis* L.), sulla (*Hedysarium coronarium* L.) and acacia (*Robinia pseudoacacia* L.) were analyzed. The samples were transferred to the Author's laboratory for the analyses, stored at room temperature (27 °C) and protected from light. Physicochemical analyses and impedance measurements were carried out on each honey sample and the data statistical elaborated. Exactly all the measurements were repeated randomly ten times on each honey during the shelf-life up to and after the indicated expiration date (usually 24–36 months); each measurement was performed in triplicate.

2.2. Physicochemical analyses

The following chemical determinations were carried out on the honey samples:moisture was determined measuring the refractive indices at 20 °C by a Carl Zeiss 16531 refractometer and the corresponding moisture content (%) was calculated according to AOAC (1980); electrical conductivity was measured at 20 °C in a 20% (w/v) solution (dry matter basis) in deionised water (Louveaux et al., 1973) by a Delta Ohm HD 8706 conductivity meter; ash was indirectly determined using the measured electrical conductivity and applying the following equation: $X_1 = (X_2 - 0.143)/1.743$ were: X_1 = ash value; X_2 = electrical conductivity in µS cm^{-1} at 20 °C (Piazza et al., 1991); free acids, lactones, total acidity and pH were measured using a Mettler Toledo MP 220 pH meter according to Official Method (Repubblica Italiana: GU. No. 185, 11/08/2003).

2.3. Impedance measurements

The measurements can be executed directly on the honey samples as provided by the suppliers; they were performed by means

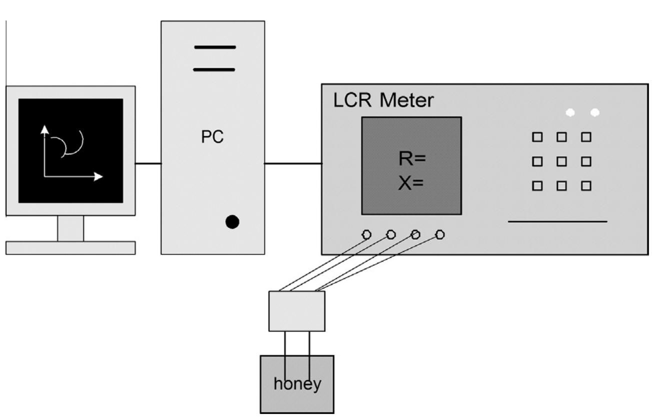

Fig. 1. Schematic diagram of electrical impedance measurements set-up.

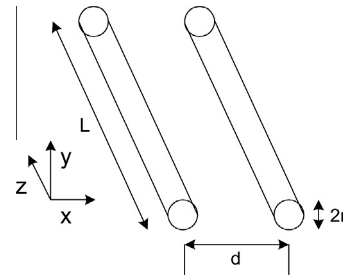

Fig. 2. Gold electrodes geometry and dimensions.

of a Precision LCR Meter (Agilent 4284A), in the frequency range 100 Hz–1 MHz, with a voltage amplitude of 100 mV. As it is shown in Fig. 1, the LCR Meter was interfaced with a personal computer by a dedicated software developed in Lab Windows CVI in order to allow an easier visualization of the measured impedance and data storage for postprocessing, performed by OriginPro 8 (Origin Lab Inc.). Open-circuit and short-circuit corrections were performed before measurements in order to eliminate errors due to cables impedance. The impedance is obtained as the ratio between the imposed voltage phasor and the measured current phasor and is, in general, a complex quantity:

$$Z = R + jX \tag{1}$$

where R is called "resistance" and X "reactance".

In some cases the study of the admittance could result in an easier interpretation of results. The admittance is defined as the inverse of the impedance, that is:

$$Y = \frac{1}{Z} = \frac{1}{R + jX} = \frac{R - jX}{R^2 + X^2} = G + jB \tag{2}$$

where G is called "conductance" and B "susceptance".

As the results of this kind of measurements depend on the geometry of the sample and of electrodes, all the honey samples were put in a 5 ml cylindrical containers and a mechanical structure, consisting in a metallic arm hinged in such a way to be positioned at fixed desired angles and ended with two cylindrical parallel gold electrodes, was developed in order to insure the same distance between the electrodes and the same electrodes immersion depth for each measurement. In Fig. 2 a schematic of the electrodes geometry is reported. The distance d between the electrodes is 7 mm, their length L is 15 mm and the diameter $2r$ 1 mm.

2.4. Statistical analysis

XLSTAT and OriginPri 8 were used to perform statistical analysis of the data. Principal Component Analysis (PCA), One – Way ANOVA and Fisher's Least Significant Difference (LSD) test were performed with experimental data.

3. Results and discussion

3.1. Physico-chemical characterization

Table 1 shows the physical–chemical characteristics of the analyzed honeys. The results obtained for the Sicilian honeys of the different floral origin were in agreement with the data reported in literature (Fiumara et al.,1999); some of the considered parameters appear to be similar in the different types of honey, such as ex. moisture and pH, while others such as electrical conductivity had distinctive values. Chestnut honeys showed the highest values for ash and electrical conductivity, while the lowest are related to sulla, acacia and orange samples in agreement with Persano Oddo