Scientific paper

Water Content of Acacia Honey Determined by Two Established Methods and by Optothermal Window

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Abstract

The major objective of the research study described here was to explore the potential of the optothermal window (OW) technique as a new approach towards a simple, rapid determination of water content in honey. Water, major component of foods, influences their physical and chemical properties. Single mode RLT-1480-40G laser diode and the standard addition method were used to calibrate the response of the OW detector at analytical wavelength of 1478 nm and to determine water content of Acacia honey. The performance of the OW method was compared to that of well established gravimetry and refractometry; the values obtained by the three different methods are practically the same.

Keywords: Gravimetry, refractive index, optothermal window, honey, water content

1. Introduction

Water is one of the major components of foods and raw food materials and influences their physico-chemical properties (i.e. colour, rheological and microbiological status, shelf-life etc.) and hence also the quality. Due to its abundance, water is the least expensive and most frequently added substance to various foods in an attempt of economic fraud.

The objective of research described here was to explore the potential of the optothermal window (OW) method as a new approach towards a simple, rapid and user friendly determination of moisture content in honey. Moisture content not only plays a paramount role in preserving the quality of honey but it is also of importance for the characterization of unifloral honeys.[1]

Measurement of refractive index (RI),[2] Karl-Fischer titration method[2–3] and oven drying[4] are among the techniques commonly used to characterize unifloral honeys. Although these methods yield reproducible results when used to characterize unifloral honeys,[5] significant differences have been observed when determining the total water content.[7] Likewise, determination of water content is independent of honey's botanical origin. Routinely, the moisture content of unifloral or multifloral honeys is determined by Abbé refractometer.[4] In determining the moisture content the absolute error achievable by most methods (0.9-and 5.1 %) is inferior to that of a more accurate Karl-Fischer method. The latter is however time consuming and also requires considerable skill and advanced laboratory equipment. On the other hand RI is widely used due to its simplicity.

Depending on sort flowers used to produce honey, RI values obtained by refractometer are either too low or too high. The true moisture content can be determined by Karl-Fisher (K-F) titration method[6] that yields reproducible results for total moisture content.[6] Drying by infrared radiation is another method used to determine the moisture content. Resulting weight loss depends on selected parameters (drying period and drying temperatures) and includes all volatile products.[7] Since it is not possible to remove all water from the samples by drying, the assessed moisture content is usually lower than the true moisture content.

Determination of water by means of spectrophotometric methods relies on the availability of broad NIR absorption features associated with the overtones and combination bands. The spectrum features four peaks found at 970 nm, 1190 nm, 1450 nm and 1940 nm. These peaks are associated with the second overtone of OH stretching band ($3\nu_1$,3), the combination of the first overtone of the O–H stretching and the OH-bending band ($2\nu_1$,3+ ν_2), first overtone of the OH-stretching band ($2\nu_1$,3) and the combination of OH-stretching and O–H bending bands ($2\nu_1$,3+ν_2), respectively.[8]

The OW method proposed here as a new approach towards determination of moisture content of honey makes use of the 40 mW NIR laser diode emitting at 1478 nm wavelength that coincides with a strong absorption line of water molecule. The suitability of the proposed method was evaluated by comparing its overall performance to that achieved by two traditional techniques.

2. Basic Concepts of the OW Method

The OW technique is a variant of photoacoustic (PA) spectroscopy.[9,10] The heat generated in honey by selective absorption (at a given wavelength optical absorption coefficient of sample per unit length is β (m^{-1})) of radiation that is periodically modulated at a frequency f (s^{-1}), diffuses into a disk (it has large thermal expansion coefficient) loaded with the test sample. Good thermal contact between honey and the disc is an impetus. The periodic expansion and contraction of disk produces an acoustic wave which is detected (OW signal) by means of the piezoelectric transducer. In general, the magnitude of the OW signal decreases for higher frequencies; the sensitivity of the sensor follows the same trend. Next to β, another physical parameter that plays a decisive role in generation of OW signal is sample's thermal diffusion length μ (m) defined as:

$$\mu = \sqrt{\alpha / \pi f} \tag{1}$$

with α (m^2s^{-1}) being the thermal diffusivity of the test sample.

Physically, μ is a distance in honey across which the amplitude of the generated thermal wave reduces to e^{-1} of its initial value. Only the heat that originates from a honey layer one thermal diffusion length thick is detected by the piezoelectric transducer. If the physical thickness L of honey is larger than its thermal diffusion length μ, the sample is referred to as „thermally thick".

Recording, at a given modulation frequency f, the magnitude H (μV) of the OW signal from honey while varying the wavelength of the incident radiation enables one to obtain the OW spectrum. For OW spectrum to correspond with the true absorption spectrum, the optical penetration depth 1/β must exceed the thermal diffusion length ($\beta^{-1} > \mu$). As the generated heat is directly proportional to the intensity of radiation source, it is necessary to normalize H. To do so one first records, under identical experimental conditions, the OW signal C (μV) from the empty disc; the difference H–C represents the net OW signal (μV) from honey. As a next step, one measures, again under the same circumstances, the OW signal (μV) B from a strongly absorbing reference (such as a black drawing ink) and corrects it (B–C) to obtain the net OW (μV) signal from the ink. The normalization step implies the division of the net OW signals obtained from the experimentally measured signals H, B and C:

$$S_n = \frac{H-C}{B-C} \tag{2}$$

where S_n is the normalized (dimensionless) OW signal for honey at a given wavelength and a given incident power.

As the magnitude of the OW signal in general depends in a complex manner on optical and thermal properties of the test sample, parameters μ and β are expected to appear in the theoretical relationship for the normalized OW signal S_n. When the relationship $\mu < \beta^{-1} < L$ is being satisfied for honey, one can obtain the normalized OW signal using the relationship:[9, 11]

$$S_n = \frac{\sqrt{2}\mu\beta}{\sqrt{(\mu\beta)^2 + (\mu\beta + 2)^2}} \tag{3}$$

The Eq. 3 can be solved for μβ and one obtains:

$$\mu\beta = \frac{2}{\sqrt{2S_n^{-2} - 1} - 1} \tag{4}$$

The product μβ is related to the more familiar absorbance A since:

$$A = 0.4347\,\mu\beta \tag{5}$$

or

$$A = \varepsilon\,(c/M)\,\mu \tag{6}$$

where ε, c and M are extinction coefficient (lit mol^{-1} cm^{-1}) at a given wavelength, the concentration (g lit^{-1}) and the molecular weight (g mol^{-1}) respectively.

3. Experimental

Figure 1 shows the experimental arrangement used in this study. The 1478 nm radiation from a single mode RLT-1480-40G laser diode emitting 40 mW cw output power at 170 mA was modulated at 30 Hz by a mechanical chopper (HMS Light Beam Chopper 220). About 0.25

cm^3 of the honey under investigation is deposited directly onto a surface of a sapphire disc (0.3 mm thin and 13 mm in diameter) the rear face of which is means of a thermally conducting glue fixed to a ring made of $PbZr_x Ti_{1-x} O_3$ (lead zirconium titanate, abbreviated PZT), an inexpensive piezoelectric material. Besides its large thermal expansion coefficient, sapphire disc is highly transparent at 1478 nm.

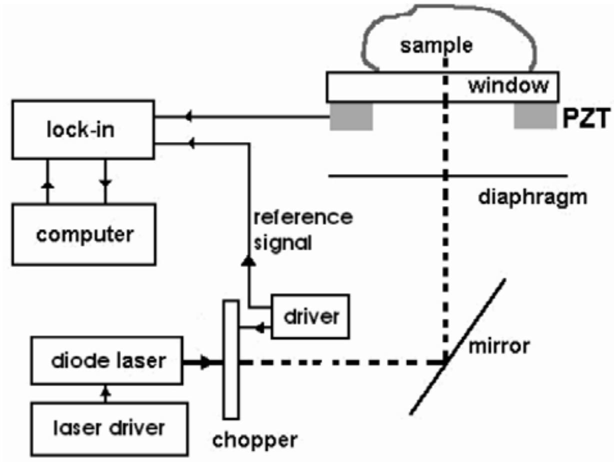

Figure 1: Schematic diagram of the experimental set-up.

Results obtained by the OW method were compared to data collected by gravimetry and refractometry. As to the gravimetric measurements, honey sample was kept in oven maintained at 100 ±2 °C (according to Hungarian norm[4]) until its weight reached a constant value. Refractive index of honey[4] at 20 °C was measured by Abbé refractometer from Zeiss.

4. Materials

Acacia honey was selected as the test sample to test the feasibility of OW method for determining moisture content. A series of calibrating standard solutions (0, 5.11, 10.07, 15.17, 19.89, 25.18 and 30.05% (g/g)) was prepared by adding water to honey- the mixer was used to homogenize all honey/water mixtures.

5. Results

5. 1. Gravimetry

Two samples of Acacia honey were taken; the corresponding weights were 9.78 g and 9.85 g. After a two days long drying period, the loss of weight measured for these two samples was 1.603 g and 1.636 g respectively. The corresponding moisture contents are 1.603/9.78 = 0.1639 and 1.636/9.85 = 0.1661 from which the average moisture content of 16.50 ± 0.16% is obtained.

5. 2. Refractometry

Using refractive index (RI) values measured (at 20 °C) by Abbé refractometer it is possible to assess the moisture content either by an empirical formula or by using the ‘‘conversion’’ tables. For above quoted Acacia honey, RI = 1.4961 which is an average of three independent measurements and corresponds to 16.24 ±0.10%.moisture content.

5. 3. Optothermal Window

The outcome of the OW study is shown in Fig 2. The relationship between the percentage of added water (x) and the net OW signal (y) obtained from the experiment is linear: the equation of the fitted line reads: $y = 0.1949x + 3.1498$ with $R^2 = 0.999$.

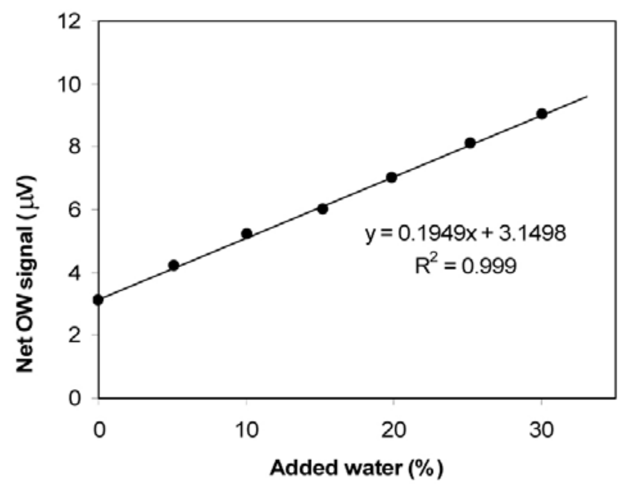

Figure 2: Net OW signal plotted versus the amount of water added to Acacia honey. This ‘‘calibration’’ line allows for determination of the honey’s moisture content.

The uncertainties in values of the slope and the intercept are 0.0027 and 0.0501 respectively. The equation of the fitted line intersects positive Y-axis at y = 3.1498 μV; obviously this value is associated with the moisture content of honey with no water added. If the moisture is removed from honey, fitted line must intersect the vertical axis at y = 0. Taking in account the uncertainties and the propagation of errors, the original moisture content of Acacia honey determined by OW method is 16.16 ± 0.35 %.

From the experimentally obtained net OW signals, one has calculated βμ for all samples studied. As it can be seen in Fig. 3, calculated βμ values depend linearly on the moisture content of the samples.

Substituting y = 0 into the equation of the calibration line (Fig. 3) allows for the calculation of honey’s moisture content. The value obtained 16.42 ± 1.12% is very close to data found by other two methods as well as

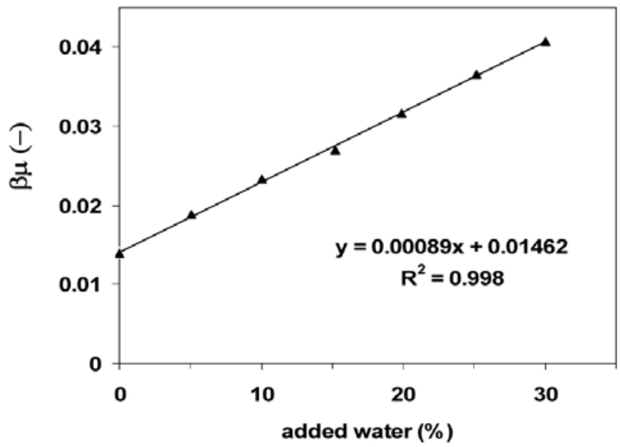

Figure 3: Calculated βμ values plotted versus the amount of water added to honey.

to the outcome provided by OW method when the net OW signals were used in calculations. Based on the obtained results one can state that various methods for determination of water content in Acacia honey produce practically the same results.

6. Summary and Conclusions

The OW method with a single mode RLT-1480-40G laser diode used as the radiation source was applied here for quantitative, direct determination of moisture content in unifloral, realistic and liquid (sugar has not yet crystallized) honeys. In a case of creamy honey (product that has crystallized before it is being measured), the measurement can be carried out by heating which may result in a loss of water. The comparison to liquid honey is therefore difficult to make. Standard addition method must be used whenever the sample's matrix influences the analytical sensitivity of the method. The most common approach is that of Standard Addition (also known as a "Known Addition") that involves adding a small volume of concentrated standard to a much larger volume of sample. The combination of the standard addition method and OW technique yields the same results as the established techniques such as gravimetry and refractometry. The OW method might emerge as a more suitable technique for applications in practice. The intrinsic precision (better than that of RI approach), reasonably high speed (considerably faster than drying oven) and the fact that it is a total amount of water in honey that is being measured, are the most important pros of the newly proposed method.

7. References

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Povzetek

Glavni cilj opisanih raziskav je bil proučiti možnosti za uporabo tehnike optotermičnega okna (OW) pri razvoju nove enostavne in hitre metode za določevanje koncentracije vode v medu. Za umeritev instrumenta OW, ki je bil opremljen z diodnim laserjem RTL-1480-40G, smo uporabili metodo standardnega dodatka. Koncentracijo vode v akacijevem medu smo določevali z meritvami odziva OW pri valovni dolžini 1478 nm. Metodo OW smo primerjali z že uveljavljenimi metodami za določevanje vode, kot sta gravimetrija in refraktometrija, dobljeni rezultati pa so pokazali dobro ujemanje.