Journal of Molecular Structure 1076 (2014) 42–48

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Tracking the dehydration process of raw honey by synchronous two-dimensional near infrared correlation spectroscopy

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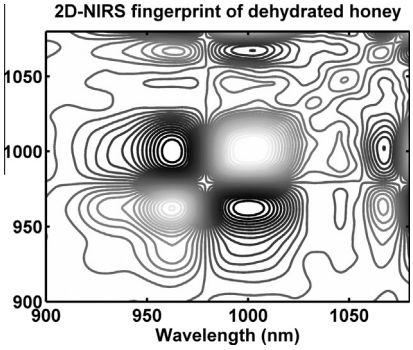
HIGHLIGHTS

- 2D-NIR fingerprint characteristic of manually dehydrated honey was reported.
- Dehydrated honey samples were obtained using drum wind drying method at 40 °C.
- 2D correlation analysis based on temperature perturbation enlarged spectral differences.
- The investigation furthered data mining in NIR short wave region.
- Autopeaks and cross peaks vary with honey floral origin and drying time.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 19 June 2014
Received in revised form 16 July 2014
Accepted 17 July 2014
Available online 23 July 2014

Keywords:
Two-dimensional (2D) correlation spectroscopy
Honey
Dehydration
Near infrared spectroscopy (NIRS)

ABSTRACT

Though much attention is paid to honey quality assessment, few reports on characteristic of manually dehydrated honey have been found. The aim of this investigation is to track the dehydration process of raw honey using synchronous two-dimensional (2D) near infrared correlation spectroscopy. To minimize the impact of dehydration to honey quality, seventy-two honey samples from six different dehydration stages were obtained using drum wind drying method with temperature controlled at 40 °C. Their dynamic short-wave NIR spectra from 600 to 1100 nm were collected in the transmission mode from 10 to 50 °C with an increment of 5 °C and were analyzed using synchronous two-dimensional correlation method. Short-wave NIR spectral data has been exploited less than other NIR region for its weaker signal especially for water absorption's interference with useful information. The investigation enlarged the signal at this band using synchronous 2D correlation analysis, revealing the fingerprinting feature of rape honey and chaste honey during the artificial dehydration process. The results have shown that, with the help of 2D correlation analysis, this band can detect the variation of the second overtone of O–H and N–H groups vibration upon their H-bonds forming or collapsing resulted from the interactions between water and solute. The results have also shown that 2D-NIRS method is able to convert the tiny changes in honey constituents into the detectable fingerprinting difference, which provides a new method for assessing honey quality.

Introduction

Honey is natural sweet substance produced by bees from nectar or secretions of plants, which the bees collect, transform by combining with specific substances of their own, deposit, dehydrate,

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http://dx.doi.org/10.1016/j.molstruc.2014.07.045
0022-2860/

store and leave in the honey comb to ripen and mature. Its moisture content should be not more than 20% or 23% depending on different floral origins [1]. But in China, especially in south China, honey usually has much moisture content due to the humid climate or short stay in honey comb. It need undergo additional dehydration process to meet the requirement of water content. This kind of honey, with fewer biologically active compounds from bees, of course inferior to natural mature honey, is sold very normally in Chinese market, which has damaged consumers' benefits seriously.

Nevertheless, few researches on characteristic of manually dehydrated honey have been reported due to the fact that natural mature honey dominates the international market except China. Another reason is that manufacturing manually dehydrated honey is practically done in China by many honey manufacturers for economic motivation, since it is not prohibited definitely by China national quality standard.

So far, researches on honey quality control by and large focus on determination of constituents and properties [2–5], floral or geographical origin [6–8], adulteration [9] and drug residues [10,11] of honey. Various fingerprinting techniques of spectrum (infrared, Raman, fluorescence, mass spectrometry) and of chromatography (gas and liquid) have been utilized to assess honey quality [4,7–12], among which near infrared spectroscopy (NIRS) has shown certain potential for its characteristic of being rapid, nondestructive and low-cost. But, this technique needs more advanced chemometrics to promote its performance due to serious water absorption interference.

NIRS combined with two-dimensional (2D) correlation spectroscopy may be a good option, especially for the investigation of hydrogen bonding and the characterization of samples. 2D correlation spectroscopy is based on the detection of variations of spectral intensity induced by an external perturbation such as temperature, pressure, concentration. It was first proposed by Noda in 1986 and has been greatly furthered in the following decades in theory, technology and application in combination with other techniques including spectroscopy and chromatography [13,14].

As far as 2D-NIRS is concerned, this technology was ever performed to characterize the spectral intensity variations of chicken muscles with various chilled and frozen storages or thermal treatments [15,16]. And it was even developed into a kind of hetero-spectral 2D correlation technology coupled with mid-infrared to determine characteristic NIR wavelengths for each sugar in sugar solutions [17].

Besides, owing to its ability of providing more detailed information regarding the variations of molecular structures, 2D-NIRS has also been found in such applications as detection of graphic origins of Chinese herbal medicine [18] and phoxim in water [19], study of pressure-induced variation of cellulose tablet [20], low-density polyethylene [21] and epoxy curing reaction [22]. In particular, Xu and Wu studied dehydration mechanisms of the polyamide 6 soaked with water at different temperature by 2D-NIRS, indicating the existence of three species of water molecules in different states of hydrogen bonding [23]. Nicoletta et al. utilized 2D-NIR technique to monitor blueberry osmo-air dehydration process. Their results showed that 2D-NIRS was a suitable tool to implement control systems for osmo and air dehydration processes of various products [24]. 2D-NIRS was also successfully used by Kyeol et al. to study variation in NIR water absorption bands in the presence of inorganic acids [25].

To our knowledge, 2D-NIRS technique has not been applied to honey quality control. The aim of this study is to utilize this technique to characterize the manually dehydrated honey by tracking the dehydration process of raw honey.

Materials and methods

Honey samples

Two different floral origins of honey were selected for this investigation, namely rape honey and chaste honey. They were obtained directly from beekeepers during their harvests in 2013 from different geographic origins in China. Rape honey was produced from Jiangsu apiculture division and chaste honey from Shandong. Moisture content of six rape honey samples varies in the range of 29.5–31.1% w/w and that of six chaste honey samples in the rage of 27.0–28.8%. All of them are natural unripe raw honey without any artificial processing.

Dehydration process

Prior to dehydration, moisture content of all rape honey samples was adjusted to the standard level of 31.1% and that of chaste honey was adjusted to 28.8%. Six bottles of uniform honey samples with 200 g net weight were then prepared for each honey sample. One bottle of samples corresponding to the initial stage of dehydration need not be dehydrated and the remaining five bottles were dehydrated at 40 °C using drum wind drying method (DHG – 101, electric drum wind drying oven, Medical instrument Co., Ltd., Shanghai). The five bottles samples were taken out successively after different drying time and they corresponded to five different dehydration stages. By this way, seventy-two samples corresponding to six dehydration stages were obtained with six rape samples and six chaste samples in each dehydration stage. All these samples were stirred manually for homogeneity before measuring moisture using Abbe refractometer. They were finally sealed in their bottles and stored in laboratory refrigerator at 4 °C for further analysis.

Samples preprocessing

Prior to NIR spectrometry, all samples were put in a water bath (HH-60 Fast Digital Thermostat Tank) of 55 °C for an hour and stirred to dissolve the crystals and then in water bath of 30 °C for 48 h to remove bubbles.

Dynamic spectra collection

Each sample of about 5 g was poured into a cubical quartz cuvette (45 × 10 × 10 mm), including an identical sample used for controlling sample temperature. They were covered a layer of food preservation film and placed into a constant temperature incubator (LRHS-250B, Shanghai BT laboratory equipment, China) with the controlling sample inserted a thermometer (WT-1). Temperature of samples was controlled from 10 to 50 °C at an interval of 5 °C.

After the temperature of a sample was stabilized for half an hour, its spectral data was collected using a NIR spectrometer (SupNIR-1100, Focused Photonics, Hangzhou, China) equipped with optical cables connected to a standard transmission baseplate with a cuvette inserted in it. Spectra were recorded in triplicate with 10 mm optical length in the transmission mode from 600 to 1100 nm. Spectrum average number is 3 and both of reference integral time and measurement integral time are 30 ms. Between samples, the cuvette was cleaned with hot water, rinsed with distilled water and then dried in a drying oven. Thus nine dynamic NIR spectra depending on temperature from 10 to 50 °C were obtained for each sample.