Fast and robust quality assessment of honeys using near infrared spectroscopy

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Abstract. In this present study, near infrared spectroscopy (NIRS) is employed to detect adulteration and predict soluble solids content (SSC) of raw honey samples based on reflectance spectral data. Diffuse reflectance near infrared data were acquired in wavelength range from 1000 to 2500 nm. Adulterated honey, made by mixing pure honey with commercial sugars, was detected and classified using principal component analysis (PCA). On the other hand, SSC content as predicted from pure honey samples using partial least square regression (PLSR). Standard normal variate (SNV) was applied as spectra correction method. The results showed that PCA based on spectra data, can accurately detect adulteration and classify honey samples with total explained variance from 2 principal components is 97%. Moreover, SSC of pure honey samples can be predicted with achieved correlation coefficient (r) of 0.96 and residual predictive deviation (RPD) index of 2.88 for raw un-corrected spectra, while r = 0.98 and RPD = 3.67 for corrected SNV spectra data. It may conclude that near infrared spectroscopy, can be used as fast and robust method to evaluate quality of raw honey samples.

1. Introduction

Honey is one of the most important commodity in worldwide market and acknowledged as a healthy sweetener substance. It can be used also as a medicine and become popular among people. Honey is defined as a naturally sweet mixture produced by bees (Apis mellifera) from the nectar of flowers, from secretion of parts of the living plants or excretions of plant-sucking insects on the living part of plants. Physically, honey is a viscous material, where all the sugars (33.3–43.0% fructose, 25.2–35.3% glucose, 0–2% sucrose, maltose as well as more complex sugars and trace polysaccharides) are present in an amorphous, devitrified state. Sugars are the main constituents of honey [1]–[3].

To ensure good chain supply of honey, it is very important to evaluate honey samples quality prior to export. Consumers intended to pay and purchase pure and good honey quality even it is expensive. Nowadays, since there is a great demand of high quality honey worldwide, many fraudulences are happening. Although the adulteration of honey is not injurious to health, problems of honey fraud negatively influence market growth by damaging consumer confidence [4], [5].

Because of its high nutritional value and unique flavour, the price of natural bee honey is relatively much higher than that of other sweeteners. Honey is susceptible to adulteration with cheaper sweeteners; those that have been detected in adulterated honeys include sugar syrups and molasses inverted by acids or enzymes from corn, sugar cane, sugar beet and syrups of natural origin such as maple [6]. Recently, guaranteeing honey quality, including its purity, are becoming increasingly important and critical issues for consumers, producers and regulatory authorities [7], [8].
To determine honey quality and other food products, several methods were widely implemented and used. However, most of them are based on solvent extraction, followed by laboratory analysis and procedures in which destructive in nature, time consuming, expensive, and involve chemical materials. Thus, it is not suitable for industries and environment [4], [9]. To overcome these issues, numerous studies has been performed to find a rapid and non-destructive alternative method [10], [11].

Near infrared reflectance spectroscopy has become one of the most promising and non-destructive methods of analysis in many field areas including in agriculture due to its advantage: simple sample preparation, fast, and environmental friendly since no chemicals are used [12], [13]. More importantly, it has the potential ability to determine multiple quality parameters simultaneously [14], [15]. Numerous studies have been carried out to investigate and apply NIRS in quality assessment of foods and agricultural products [12], [16]–[20]. Therefore, the main aim of this present study is to study and apply NIRS as a fast and robust method to evaluate raw honey samples, including adulterant detection and soluble solids content (SSC) prediction simultaneously.

2. Materials and Methods

2.1. Instrument and sample preparations

Fresh Pure honey samples were obtained from 4 different floral origins in Aceh and North Sumatra Province. They were stored in room temperature (25 °C) for approximately 3 days prior to near infrared (NIR) spectra acquisition. Samples were placed in 50 ml bottle. One day before NIR scanning, five honey samples were added with white sugar and commercial syrup for adulteration purpose. To ensure their purities, all honey samples were tested according SNI for pure honey standard in authority bureau. Near infrared spectroscopy instrument was used to acquire transmittance spectra data. The instrument was set to record spectra data in wavelength range from 1000 to 2500 nm with 0.2 nm resolution and co-added 32 scans.

2.2. Infrared spectrum

Infrared data spectrum, in form of transmittance, were obtained by placing raw honey samples upon sample holder. Sample measurement with integrating sphere was chosen as a basic measurement in this study. Background spectra correction was performed every hour and data were saved in SPA and CSV extension formats.

2.3. Spectra data correction

Spectra data, Infrared data spectrum needs to be corrected in order to achieve robust and accurate prediction result. In this study, infrared spectra data were corrected using standard normal variate (SNV) algorithm.

2.4. Data analysis

Infrared adulteration, mixed in taw honey samples were detected by projecting spectra data onto principal component analysis (PCA). Maximum number of principal components (PCs) involved were set to 7 PCs. The first two PCs were then plotted to inspect and detect honey adulteration.

2.5. Prediction model

Raw uncorrected and SNV corrected spectra data were then used to establish SSC prediction models. These models were developed using partial least square regression (PLSR) method and validated using full cross validation. Prediction models performance were evaluated and quantified by looking statistical indicators: correlation coefficient (r), root mean square error (RMSE), latent variables (LVs) and residual predictive deviation (RPD) index.
3. Result and discussion

3.1. Spectra features and adulterant detection
Absorbance Infrared spectra data indicates the presence of organic materials as derived from the bands that result from the interaction of molecular bonds of O-H, C-H, C-O and N-H with the incident radiation. These bonds are subject to vibrational energy changes in which two vibration patterns exist in these bonds including stretch vibration and bend vibration.

The PCA result as shown in Figure 1, provide an obvious differentiation between pure and adulterated honey based on electro-optics properties derived from near infrared spectra data. Also, the NIRS seems to be able to classify pure honey based on floral origins.

![Figure 1. Honey adulteration detection using PCA based on transmittance spectra data.](image)

The first principal component (PC1) contributed 92% explained variance, while remaining 8% explained variance was obtained by second principal component (PC2). Total cumulative explained variance from two principal components (PCs) was 100% with also classification accuracy.

3.2. SSC prediction model
Further spectra data analysis was performed to predict soluble solids content (SSC) which is highly correlated with sugar content of honey. SSC was formed by C-H-O; thus, it is feasible to predict SSC using NIRS method as shown in Figure 2.

![Figure 2. SSC prediction of pure honey samples based on raw-uncorrected spectra data](image)
Partial least square regression (PLSR) was used as a calibration method and validated using full fold cross validation method. Figure 2 shows prediction result generated from raw uncorrected spectra data. Judging from its validation result, the correlation coefficient (r) is 0.91 with the number of latent variables (LVs) is 5 and residual predictive deviation (RPD) index is 2.02 and root mean square error (RMSE) is 1.97 °Brix.

Moreover, SSC prediction was also developed using SNV corrected spectra using PLSR method. Figure 3 shows prediction result achieved from SNV corrected spectra data. Judging from its validation result, the correlation coefficient (r) was increased to 0.98 with the number of latent variables (LVs) is 5 and residual predictive deviation (RPD) index is also increased to 2.23 and root mean square error (RMSE) clearly decreased to 1.79 °Brix.

![Figure 3. SSC prediction of pure honey samples based on SNV corrected spectra data](image)

Both prediction models (Raw and SNV spectra) are categorized as a good prediction model performance. This result is also in agreement in some literatures from which stated that the RPD between 1.5 – 1.9 means that coarse quantitative prediction is possible, but still need some improvement in calibration. A value between 2 and 2.5 indicates that prediction model is sufficient. Meanwhile, an RPD value between 2.5 and 3 or above corresponds to good and excellent prediction accuracy respectively.

The presence of sugar content was observed at around 1210 – 1372 nm because of C=O–H tone combination and its second overtone. Moreover, the absorption bands in the range of 2200 - 2300 nm are also suggested to be related to C-H-O structures such as glucose, fructose, whilst absorption bands at around 1480, 1780 and 2200 nm are associated with minerals on honey.

4. Conclusion
The present study investigates and apply NIRS method as a fast, robust and non-destructive method in detecting honey adulteration and predicting SSC in raw honey samples. Achieved result shows that NIRS combined with PCA was able to detect adulteration with complete cluster and classification. Moreover, NIRS combined with PLSR was able to predict SSC in raw honey samples with excellent accuracy and robustness.

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