

Detection of coconut (*Cocos nucifera*) sugar adulteration in palm (*Arenga pinnata* Merrill) sugar by Fourier Transform Infrared (FT-IR) Spectroscopy

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Abstract

Palm sugar which is also named brown sugar is powdered sugar produced from palm extract. Due to the high price of palm sugar, its contamination of materials that are cheap or low quality is inevitable. Usually, adulteration detection is done by conventional methods such as HPLC, TLC, or NMR which are time-consuming and require high-priced equipment, thus impractical for routine and large sample analysis. The aim of this research was to detect adulteration in palm sugar using Fourier Transform Infrared (FT-IR) spectroscopy. The samples used in this study were palm sugar as the main ingredient and coconut sugar as the adulterant. Two chemometric methods namely principal component analysis (PCA) and partial least squares regression (PLSR) were used for analysis. The absorbance data were taken at wavenumber 4000-650 cm^{-1} . Several concentrations of coconut sugar as an adulterant ranging from 0 to 100% were added to palm sugar. A total of 110 spectra of both pure and adulterated palm sugar samples were divided into two groups, i.e. 73 samples for developing calibration model and 37 samples for developing prediction model. The spectral obtained were pre-processed and analyzed using The Unscrambler X version 10.4. a total of six pre-processing methods were used, i.e., Normalization, Standard Normal Variate (SNV), Multiplicative Scatter Correction (MSC), and Baseline. Results showed that PCA was able to classify palm sugar based on adulterant concentrations. PLSR calibration model with a coefficient of determination (R_c^2) of 0.94 and root mean square error of calibration (RMSEC) of 8% was obtained by applying the MSC method. The model was able to predict coconut sugar adulteration in palm sugar with R_p^2 of 0.89 and root mean square error of prediction (RMSEP) of 10.68%. The results confirmed the potential of FT-IR spectroscopy for detecting adulteration in palm sugar.

1. Introduction

Palm sugar or brown sugar (gula semut) is a popular name for powdered or crystalline brown sugar made from palmae family, such as aren (*Arenga pinnata* Merrill), coconut (*Cocos nucifera*), or siwalan (*Borassus flabellifer* L.) extract. Indonesia is one of the ten biggest palm sugar exporter countries in the world with a market share of 8.7% (Direktorat Jenderal Pengembangan Ekspor Nasional, 2017). Recently, people have started to use palm sugar products in their diet to alternate conventional refined sugar. Palm sugar contains higher fructose and fructose but lower sucrose than conventional refined cane sugar (Srikaeo *et al.*, 2019). In addition, palm sugar from *Arenga pinnata* has glycemic index (GI) of 40 ± 3 (Merr and Haagen, 2014) while cane sugar has GI of 91 (Srikaeo *et al.*, 2019).

The price of brown sugar in the market made from *Arenga pinnata* (in this paper is called palm sugar) is more expensive than brown sugar made from coconut (*Cocos nucifera*). Due to the high price of palm sugar, it is possible to contaminated with coconut sugar which is cheaper but has similar color and texture thus difficult to differentiate using naked eyes. Usually, adulteration or authentication is detected by conventional methods such as HPLC (Domingues *et al.*, 2014), chromatographic *et al.*, 2016), or NMR (Bergana *et al.*, 2019) which require long time analysis and high-priced equipment, thus not practical for large samples and routine analysis.

Spectroscopy techniques at near-infrared (NIR) and mid-infrared (MIR) regions have been popular for quality and quantitative food analysis. MIR spectroscopy at 4000-400 cm^{-1} provides a sharper and larger intensity

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of chemical information compared to NIR since it describes the fundamental vibrations rather than the overtones and combination bands measured in NIR region (Lohumi *et al.*, 2015). Fourier Transform Infrared (FT-IR) spectroscopy have been used for classification or identification, such as classification of tuber powder having similar color (Masithoh *et al.*, 2020), quantification sugar in honey (Anjos *et al.*, 2015), or identification of anthocyanin (Amanah *et al.*, 2020). Several studies also reported the possibility of FT-IR for detecting the presence of adulterants of corn starch in onion powder (Lohumi *et al.*, 2014), common wheat in durum wheat pasta (De Girolamo *et al.*, 2020), or adulteration in black pepper (Wilde *et al.*, 2019). However, studies that reported the application of FT-IR for detecting adulteration in palm sugar is not available; therefore, it will be reported in this study.

This research aimed to study the potential of the FT-IR spectroscopy method to detect adulteration of brown sugar made of coconut sap in palm sugar made from *Arenga pinnata* sap. Chemometric methods namely principal component analysis (PCA) and partial least squares regression (PLSR) were used for analysis. In this study, PCA was used to classify various concentration of adulterant in palm sugar and PLSR was used to predict the adulterant concentration in palm sugar using FT-IR absorbance.

2. Materials and methods

2.1 Sample preparation

Palm sugar and coconut sugar were obtained from several local markets in Indonesia. Coconut sugar which had a cheaper price but similar color to palm sugar was used as the adulterant, while palm sugar was used as the adulterated samples. Several concentrations of coconut sugars ranging from 0 to 100% were added to palm sugar making the final concentrations of 50 g scaled using an analytical balance (Ohaus Scout Pro SPS202F). The sample arrangement was set as shown in Table 1.

Table 1. Percentage and weight combination of coconut sugar and palm sugar used as samples

Class	Coconut sugar		Palm sugar	
	%	Weight (g)	%	Weight (g)
0%	0	0	100	50
10%	10	5	90	45
20%	20	10	80	40
30%	30	15	70	35
40%	40	20	60	30
50%	50	25	50	25
60%	60	30	40	20
70%	70	35	30	15
80%	80	40	20	10
90%	90	45	10	5
100%	100	50	0	0

Although coconut and palm sugar were purchased dry, the mixed sugar samples were dried at 65-70°C for 12 hrs in a dehydrator to remove excess water as infrared spectroscopy are significantly affected by moisture content. In this study, the water content of coconut sugar and palm sugars were 1.2% and 0.7%, respectively. After drying, the samples were sieved manually with an 80-mesh sieve (0.18 mm; ASTM Standard) in order to obtain uniform size samples. Samples that did not pass 80-mesh were ground and sieved to pass 80-mesh. Each combination was placed in a closed bottle and mixed for 2 mins. A total of ten samples of each concentration combination were used making the total of 110 samples. The samples were put into the desiccator (Normax ISO 13130) and stored at room temperature before spectra acquisition.

2.2 Spectra acquisition

FT-IR spectra scanning were performed with a Thermo Nicolet iS10 (Thermo Nicolet Corp., Madison, WI), equipped with a ZnSe crystal plate. The spectra were measured in the mid-infrared area in absorbance mode at a wavelength of 4000-650 cm^{-1} . The sampling method used was attenuated total reflectance (ATR) using a deuterated triglycine sulfate (DTGS) detector, controlled by OMNIC software. A background scan was performed on each sample scan with an empty sample plate. The ATR crystal plate and pointed tip were cleaned to remove interference from the previous sample using ethanol. Spectra were acquired by placing a 30 mg sample on a diamond crystal plate and clamped with a pointed tip (Figure 1). Reflectance spectra of 110 samples were collected using 4 cm^{-1} intervals resulted in total of 6950 variables.



Figure 1. Spectra acquisition using Thermo Nicolet Is10

2.3 Spectral data analysis

Spectra collection was obtained using the OMNIC Software which was then converted into an Excel® file for further analysis. The raw data obtained from the IR instrument were in reflectance values which were then converted into absorbance values. The absorbance data was then imported to the Unscrambler X version 10.4

(CAMO Software AS, Oslo, Norway) for spectra pre-treatment and multivariate analysis, i.e. PCA and PLSR analysis. Spectroscopy contains large data variables but only several variables are important to describe chemical substances. PCA can be used to reduce dimensions to explain the most important features of the data set. Prediction of concentrations of adulteration in the palm sugar samples is developed based on spectra data using PLSR.

The whole data set (110 samples) was divided into two sets, i.e. a calibration set consisting of 73 samples and a prediction set consisting of 37 samples. Due to possible noise in the spectra resulting from light scattering, particle size, and instrument, raw spectra must be corrected by applying several spectra preprocessing methods (Lohumi *et al.*, 2014). In this study, FT-IR spectral data were processed using Normalization, Standard Normal Variate (SNV), Multiplicative Scatter Correction (MSC), and Baseline.

3. Results and discussion

3.1 Interpretation of Spectra

Figure 2 illustrates the original and SNV processed-spectra of pure and palm sugar adulterated coconut sugar at infrared region ($4000\text{--}650\text{ cm}^{-1}$) at which spectra are divided into two major regions, i.e. below and above 1500 cm^{-1} showing fingerprint and functional group region, respectively. Molecular vibrations located in the infrared region but at the region below 1500 cm^{-1} , sharp and narrow spectra can be observed, while region above 1500 cm^{-1} reveals wide and fewer spectra.

It can be seen in Figure 2a the original spectra show similar trends for all spectra which is difficult to determine which spectra it belongs to which concentration. After applying the SNV method to original spectra, spectra can be differentiated according to adulterant concentration at wavebands as shown in

Figure 2b Those spectra revealed at $1500\text{--}700\text{ cm}^{-1}$ are functional groups which corresponded to C=C (Amanah *et al.*, 2020), C-H, O-H, C-O (Musingarabwi *et al.*, 2016) and C-N (Masithoh *et al.*, 2020), $2300\text{--}1700\text{ cm}^{-1}$ corresponding to the vibration of C=C, C=O, C=C, and C≡N, and $3000\text{--}2800\text{ cm}^{-1}$ corresponding to the vibration of -C-H. Broad and high absorption at $3300\text{--}3200\text{ cm}^{-1}$ which are vibrations of O-H might be associated with water content of samples (Anjos *et al.*, 2015).

3.2 Principle Component Analysis (PCA)

PCA is an exploratory method used to study the relations among data variables, to cluster the samples, and to visualize data in a low dimension (Szymańska *et al.*, 2015). As shown in Figure 3a, PCA using PC-6 and PC-7 cannot differentiate clearly palm sugar based on adulteration concentration, but pure and low concentrations of adulteration palm sugar are in the negative axis of PC-6. By using SNV pre-processing spectra and clustering level of adulteration concentration into 3 groups instead of 11 groups, more distinct classifications are observed by using PC-2 and PC-6. In Figure 3b, although some samples are still grouped together, pure (0%) and low-level adulteration (10-20%) palm sugar were observed at the positive axis of PC-2, medium-level adulteration (30-60%) were located at the negative axis of PC-6, and high-level of adulteration (70-100%) were at the positive axis of PC-6.

Figure 4 shows the high loadings at 1050 and 1150 cm^{-1} assigned to the combination of C-C-H and O-C-H as well as C-O-C associated with sugar molecules (Zhou *et al.*, 2020). Sugar content in palm sugar mainly sucrose as well as glucose and fructose but in lower concentrations (Srikaeo *et al.*, 2019). Although spectra of individual sugars are unable to specifically determine, samples on the PC-2 positive axis belong to pure and low-level adulterated palm sugar which have higher sucrose compared to coconut sugar. The interpretation is similar

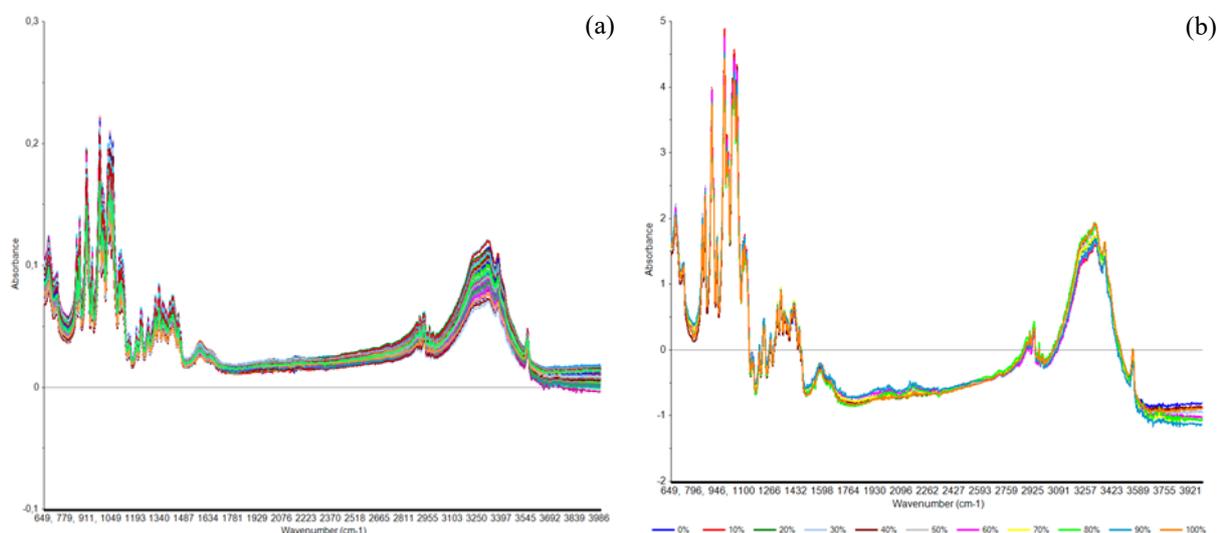


Figure 2. (a) Original and (b) SNV Spectra of different concentration of pure and adulterated palm sugar

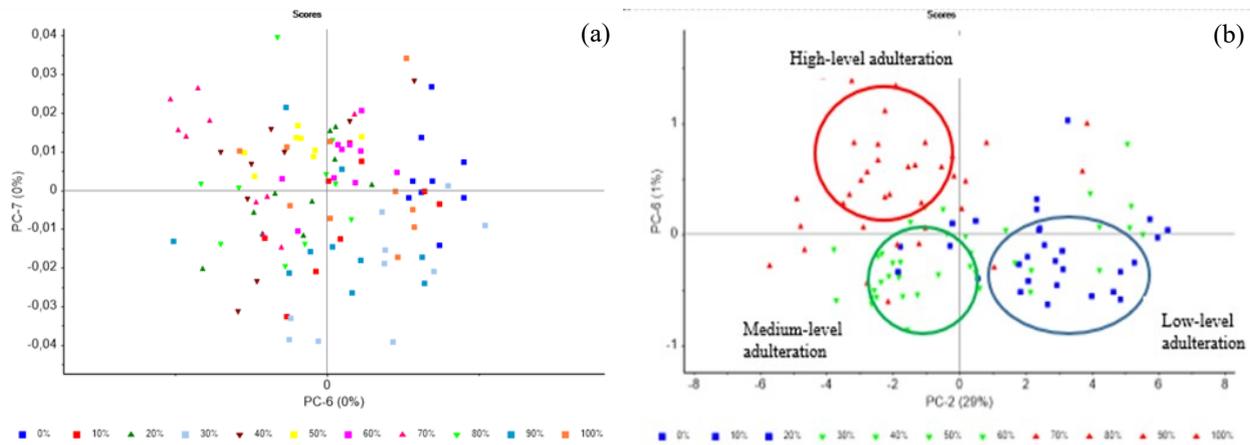


Figure 3. PCA of (a) Original and (b) SNV Pre-processed of FT-IR spectra showing clustering based on adulteration level to findings reported by (Asghar *et al.*, 2020) in which compared to palm juice, coconut sap has lower sucrose but higher fructose and glucose.

Peaks at 1614 and 3280 cm^{-1} assigned to OH deformation and stretch of water (Anjos *et al.*, 2015) which affects sugar OH absorption (Bahrami *et al.*, 2020). In this study, coconut sugar has higher water than palm sugar which is reflected from Figure 4 in which samples with medium and high-level adulteration including pure coconut sugar located at the negative axis of PC-2 showed by absorbance at 3280 cm^{-1} .

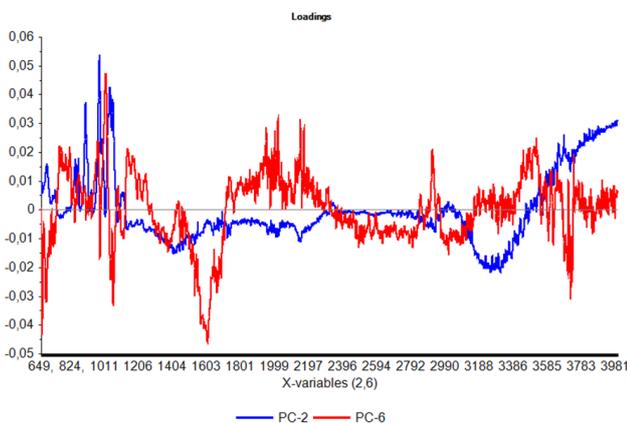


Figure 4. Loadings of SNV Spectra of FT-IR

3.3 Partial Least Squares Regression for prediction of adulteration concentration

Samples with all adulteration concentration as in Table 1 are used in building calibration and prediction models using the PLSR method. By using original spectra and several spectra pre-processing methods, the accuracy of the calibration model is evaluated based on a high coefficient determination of calibration (R_c^2) and low root mean standard error of calibration (RMSEC) as shown in Table 2. It can be seen in Table 2, applying pre-processing methods improve the performance of the models in which R_c^2 increases and RMSEC decreases. The best PLSR calibration model with R_c^2 of 0.94 and RMSEC of 8% is obtained by applying the MSC method. The model is able to predict coconut sugar

adulteration in palm sugar with R_p^2 of 0.89 and root mean square error of prediction (RMSEP) of 10.68%.

Table 2. Calibration and prediction results by using original and pre-processing spectra at the wavelength of 4000-650 cm^{-1}

Method	Calibration			Prediction		
	N	R_c^2	RMSEC (%)	N	R_p^2	RMSEP (%)
Original	73	0.87	11.41	37	0.84	12.34
Normalize	73	0.94	8.25	37	0.84	12.38
SNV	73	0.94	8.01	37	0.89	10.70
MSC	73	0.94	8.00	37	0.89	10.68
Baseline	73	0.89	10.31	37	0.79	14.04

N: number of samples, SNV: Standard Normal Variate, MSC: Multiplicative Scatter Correction

The PLSR loadings or regression coefficients are used to determine which bands highly significant in developing a calibration model for predicting coconut sugar adulteration in palm sugar as illustrated in Figure 5. Several distinct peaks which might be related to calibration model observed at 850, 994, 1024, 1125, 1430, 1613, 1684, 1734, 2026, 2941, 3565, and 3628 cm^{-1} . Some of those wavelengths agree with wavelengths assigned to sucrose at 850 and 1124 cm^{-1} , fructose at 978 cm^{-1} , glucose at 1121 cm^{-1} , saccharine at 1595 and 1698 cm^{-1} found by (Güven *et al.*, 2019). (Anjos *et al.*, 2015) reported wavelengths at 1500-900 cm^{-1} were contributed by sucrose, glucose, and fructose in honey.

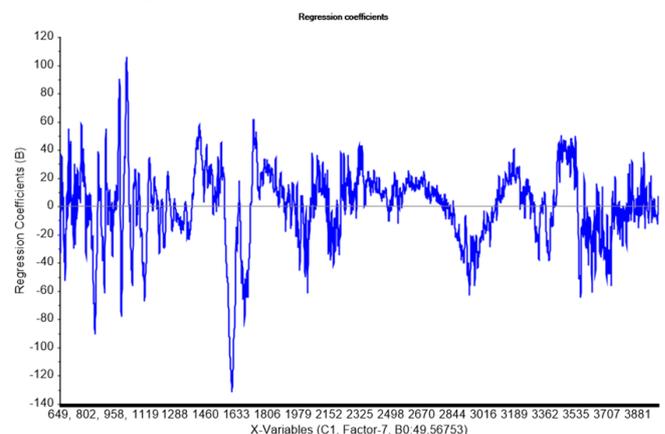


Figure 5. Regression coefficients of PLSR model using MSC Pre-processing Spectra for predicting level of coconut sugar adulteration in palm sugar

4. Conclusion

This research studied the potential of FT-IR spectroscopy to detect adulteration of coconut sugar in palm sugar at various concentrations. By using MSC pre-processing spectra to develop the PLSR model, the calibration model results in R_c^2 and RMSEC of 0.94 and 8%. When applied to prediction data sets, the model resulted in R_p^2 of 0.89 and RMSEP of 10.68%. Those results indicated that the PLSR model can be used in food authentication.

Conflict of interest

The authors declare no conflict of interest.

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