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Archives of Applied Science Research, 2014, 6 (6):55-60
(http://scholarsresearchlibrary.com/archive.html)

ISSN 0975-508X
CODEN (USA) AASRC9

A feasibility study for the authentication of Palmyrah Jaggery using NIR spectroscopy

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ABSTRACT

Palmyrahjaggery is a popular traditional sweetener in Jaffna. It is a nutrient rich crude sugar which is also used in the traditional medicine. The authenticity of the product in markets is questionable since there is no analytical methods exist to detect adulterations. Adulteration spoils the good recognition for the jaggery, which results in lessprofit for the industry, also, it affects the livelihood of those people who directly involved in the production of jaggery. Other than the economic aspects, since jiggery is used in traditional medicine, adulteration of jaggery has some health related consequences as well. In this study the NIR spectroscopyis used to study the principal component analysis for the authentication of jaggery and identification of the adulterant. A reasonable amount ofjaggery samples were used as data set for calibration-validation procedure. Jaggery was produced in a laboratory scale as pure, adulterated with sugar and rice bran at different concentrations. Aqueous solutions of these samples were prepared and NIR spectra of the samples were recorded via using the UV/VIS/NIR spectrophotometer (Jasco V570) with scanning range of 750-1300 nm wavelength. Principal component analysis of the spectra is useful for the identification of the adulterations and for the authentication of jaggery.

Keywords: Jaggery, Palmyrah, Adulterations, NIR spectroscopy

INTRODUCTION

Palmyrah palm *Borassusflabellifer* is a celestial tree which is abundant in the northern Sri Lanka. Other than northern Sri Lanka, it is widespread in the arid tropics of South America, East Africa, India and South-East Asia. Palmyrah palms are economically useful: leaves are used for thatching, mats, hats, etc.., stalks are used to make fence, black timber used in constructions, young plants, fruits, jelly like seeds are consumed as foods. A sugary liquid oozed from the inflorescence of palmyrah pam, called sap, can be obtained from the young inflorescence either male or female ones. The sap is a sweet clear watery liquid and contains sugars, vitamins and minerals. Also fresh sap is a good source of vitamin B complex[1]. The sap can be consumed directly. Further, there are several products can be made by processing the sap: jaggery, treacle, sugar candy, toddy, vinegar, arrack and wine.

Jaggery is a main product made out of sap in Sri Lanka. jaggery is much more nutritious than crude cane sugar, containing 1.04 % of protein, 0.19 % of fat, 76.86 % of sucrose, 1.66 % of glucose, 3.15 % of total minerals, 0.861 % of calcium, 0.052 % of phosphorus; Also 11.01 mg of iron per 100 g and 0.767 mg of copper per 100 g. Furthermore, the previous analysis on jaggery has shown the presence of vitamins such as 402 mg/100g of riboflavin, , 15 mg/100g of vitamin B_{12}, , vitamin C, Thiamine and nicotinic acid[1]. Jaggery is used as a popular traditional sweetener in northern Sri Lanka and south India. Furthermore, jaggeryposses medicinal properties therefore it is used in indigenous medicine [2]and also it posses antitoxic and anti-carcinogenic properties as well[3] Traditionally palmyrahjaggery has high demand among the occupants of northern Sri Lanka. This can be attributed to the use of jaggery as traditional sweetener and it use in indigenous medicine. Palmyrahjaggery is expensive

relative to commercial white crystalline sugar. Due to its relative high price and popularity, Palmyrahjaggery is often adulterated with cheap adulterants such as cane or beet sugar, rice bran, corn flour, etc. A previous studyreveals that the ratio between reducing sugar is to non-reducing sugars can be used as a measure to identify the adulterations in the kithuljiggery [4]. However there is no research works carried out to determine the authentication of palmyrahjaggery.

Adulteration is the practice of adding low-value substances to a relatively high value food in order to increase the financial return. It is often unlikely for consumers and food processors to detect the adulterations without special chemical or physical analysis. But it is a fraudulent practice. There are several cases of adulterations: sugars in honey[5], proteins in yogurt[6]. Adulteration has several consequences such as decrease in the demand, unwanted health effects, unfair competition and so on.

The adulterants are often having same chemical composition. Since the chemical composition is similar, the detection of adulteration is difficult. Nevertheless, there are several methods exists to detect and characterize the adulterations. These detection processes have different approaches for the authentication process. Highly-sophisticated analytical techniques such as GC-MS, HPLC, GC, IR-MS, NMR and DNA based techniques are used in the authentication process[7]. Although these methods provide desirable solution to the problem, they are usually time consuming, require dedicated laboratories equipped with costly instruments and require highly-skilled personnel to do the analysis. However, in contrast to those methods, infrared spectroscopy, specifically mid-infrared (MIR) and near-infrared (NIR) spectroscopic methods used to address this problem because of its desirable characteristics such as minimal or no sample preparation, short analysis time, does not require chemical reagent purchase or disposal, relatively cost effective and easy deployment once initial method is developed.

NIR Spectroscopy operates in 750-2500 nm (12500 – 4000 cm^{-1}) region of electromagnetic spectrum. The NIR spectrum give rise to overtones and combinations of fundamental vibrations, also the NIR absorption bands overlap with each other. This renders the NIR spectrum more complex than the IR spectrum and hence the chemical information from NIR spectra is poorly resolved. In NIR asymmetric vibrations takes place such as C-H, N-H and O-H this makes NIR spectroscopy useful in the studies of products of biological origin.

The use of multivariate statistical techniques in the analytical chemistry is named as *chemometrics and it* can be used for qualitative and quantitative studies. Chemometrics techniques are necessary to utilize multivariate statistical analysisto resolve useful information from NIR spectra. These techniques analyze the correlations between variables, since absorptions in NIR wavelengths are correlated with each other chemometrics is exploited in NIR analysis.Principle Component Analysis (PCA) is a kind of chemometric technique which can be used to reduce the number of variables when the systems (samples) are characterized by several variables. This is a variable reduction technique and analyzes correlation between the variables, reduce the noise and combine the variables into artificial variables called Principle Components (PCs) which explains the most variation among the samples. PCA can be used to study the characteristics of different samples and different groups of samples by analyzing the absorptions at certain wavelength regions which accounts for the similarity/dissimilarity among the samples.Chemometric analysis of NIR spectra is used for classification of samples and discrimination analysis[8-11].

The practice of adulteration is to make more money by the addition of cheap substances. But there are several consequences. Adulterations spoil the good recognition for the jaggery, which results in lessprofit for the industry and it affects the livelihood of those people who directly involved in the production of jaggery. Other than the economic aspects, adulteration of jaggery has some health related consequences as well. Further, due to its lower sugar content relative to commercial white sugar and for its nutritional value, jaggery is used as substitute to the commercial sugar by those affected by diabetes. Therefore, a suitable analytical method is essential to detect the adulteration in order to ensure the quality of the product in the market.

MATERIALS AND METHODS

Sap was collected at morning time from a sap based production facility in Chavakacheri, Jaffna.The Chavakacheri collection centre was situated nearby the research centre, so that the transportation time can be minimized. The de-liming and the subsequent jaggery production should be done on same day as the de-limed sap will denature if it allowed to stand. The sap was collected using sterile polyethylene containers and brought to the laboratory immediately and it wasimmediately de-limed using saturated super phosphate[12]. Pure jaggery is prepared in the laboratory by heating the de-limed sap to about 1/6th of its original volume forms thick dark syrup called treacle. Thetreaclewas further concentrated by heating to 116 °C to yield Jaggery[12]. Adulterated jaggery was prepared

similar to pure, with the addition of specific amount of adulterant to the sap.The composition of jaggery samples which is used for this research work is listed in Table 1.

Table 1 Composition of jaggery samples prepared for the analysis

No	Adulterant	Amount of adulterant per 500 ml of sap (g)	Percentage (w/v)	No of Samples
1	None	00.0	0.0	5
2	Sugar	02.5	0.5	4
3	Sugar	05.0	1.0	4
4	Sugar	07.5	1.5	4
5	Sugar	10.0	2.0	3
6	Sugar	12.5	2.5	3
7	Rice Bran	02.5	0.5	3
8	Rice Bran	05.0	1.0	4

Sample Preparation for NIR spectra

Jaggery was dried in an oven in order to remove moisture until constant weight is obtained. Then 5.00 g of Jaggerywas added into 20.0 mL of distilled water and the mixture was stirred at 1000 rpm for five minutes using magnetic stirrer. The resulted solution was filtered (by Whatman no. 10) to remove the solid residue. Then the above solutions were used to obtain the NIR spectra.

NIR Spectrum

The NIR transmittance spectra were obtained at room temperature in Jasco V-570 UV/VIS/NIR spectrometer in the range of 750 to 1300 nm.The spectra were reproduced in five times and finally record the average of individual NIR transmittance spectrum. The average NIR transmittance spectra were exported as ASCII files using the Spectra Manager v 1.53 (Jasco Inc.), then the ASCII files were imported into the Unscrambler X package (version 10.1, Camo ASA, Oslo, Norway) for PCA analysis. All the NIR spectra were baseline corrected prior to analysis.

RESULTS AND DISCUSSION

The NIR absorption spectraof pure jaggery sample, jaggery samples adulterated with sugar and rice bran have shown almost similar absorption spectra more or less and the absorption peaks are weak (Figure 1).

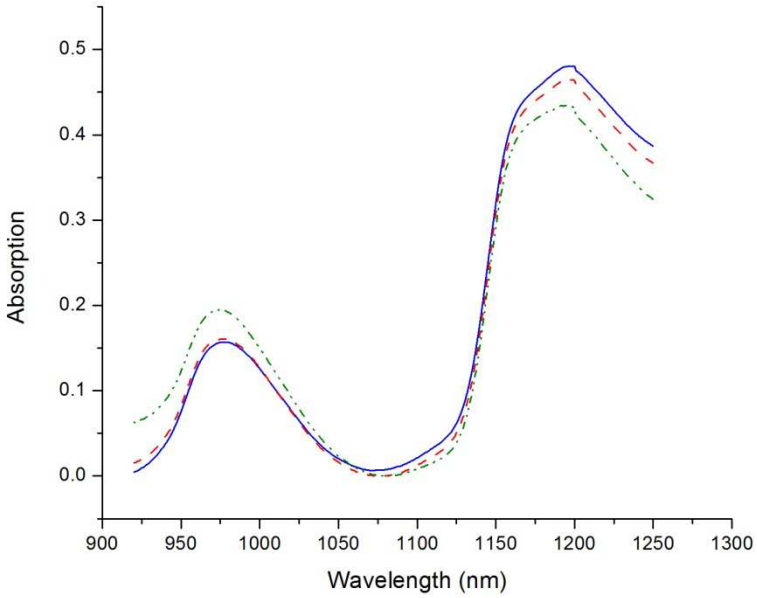

Figure 1: NIR absorption spectra of pure (solid blue lines), jaggery sample adulterated with sugar (dotted red) and jaggery sample adulterated with rice bran (dash black)

This NIR spectra shows two broad absorption peaks one centring around 974 nm and other one centring around 1197 nm. The samples which were adulterated with sugar and rice bran shows significantly higher absorption in the first region compared to the pure jaggery due to the presence of sucrose and starch respectively. Theanjumpol, P., et al also reported that the NIR absorption of sucrose and starch occurs at 900 – 1000 nm[13]. Further, it can be observed in Figure 2, that the absorption at this region increases with increased addition of sugar.

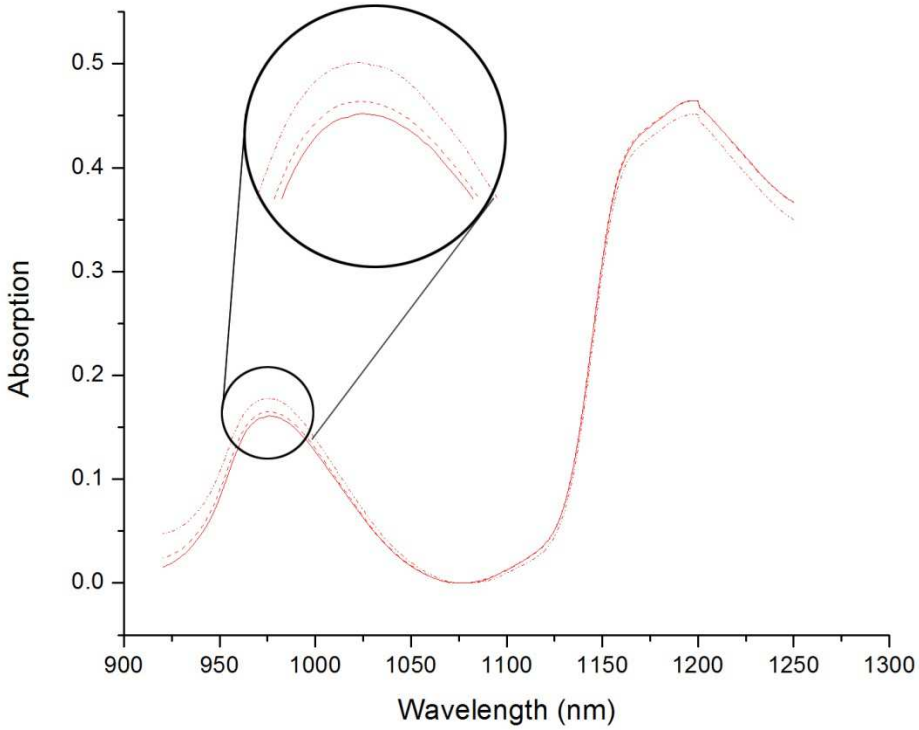

Figure 2: NIR absorption spectra of jaggery samples adulterated with different amount of sugar

The second peak in Figure 1 may be arises from the absorption of C-H 2nd overtone and O-H combinations, which is normally occurs in the region of 1100-1200 nm[14].The absorption at1197 nm decreases for both adulterated jaggery samples compared to the pure jaggery sample, and adulterated with rice bransamples shows very low absorption compare to other two categories. These observations clearly noticed that the second peak is notcorrelated with the amount of sucrose or a constituent of rice bran but it may be correlated to the presence of specific metabolite in the jaggery.

Although some visible differences observed between the three sample groups, this cannot be applied for the purpose of authentication of jaggery due to the small differences in the absorptionand there are no new peaks or specific shifts can be observed in order to indicate the presence of adulterants. Moreover, the slight differences in the absorption regionscan be caused by several factors such as harvest time, geographical origin, climate, etc. Since the composition of the sap may change due to the aforementioned factors it can be result in slight different biochemical composition, so that the NIR spectra also show some slight differences.

The NIR spectra composed combinations of peaks and overtones. By comparing and correlating the absorptions between several variables in different wavelengths a fingerprint can be developed. The characteristic fingerprint of jaggery can be deduced from the NIR spectra and this fingerprint can be used to analyse for the adulterations from the pure samples.

The amount of sucrose increases with addition of sugar into the jaggery but the amounts of other metabolites have still remained. Similarly, the adulteration with rice bran yield more different composition due to the presence of various metabolites in rice bran. The multivariate analysis is a best method to analyse the above problem rather than the uni- or bi-variate approach. The PCA method is a one kind of multivariate analysis and it is used for this research analysis.

PCA Analysis

The PCA analysis was performed on the full set of spectra to examine possible clustering or grouping samples in the principal component space. The grouping samples were selected according to their similarities and dissimilarities; it was analysed by the biplots. The detected outliers were removed from the original set and the model was rebuilt.

The PCA analysis of baseline corrected spectrum has shown in Figure 3.However, only one component (i.e., PC-1) is reported as the optimum component in this analysis. Therefore, other data pre-treatments were used to process the data prior to PCA analysis.

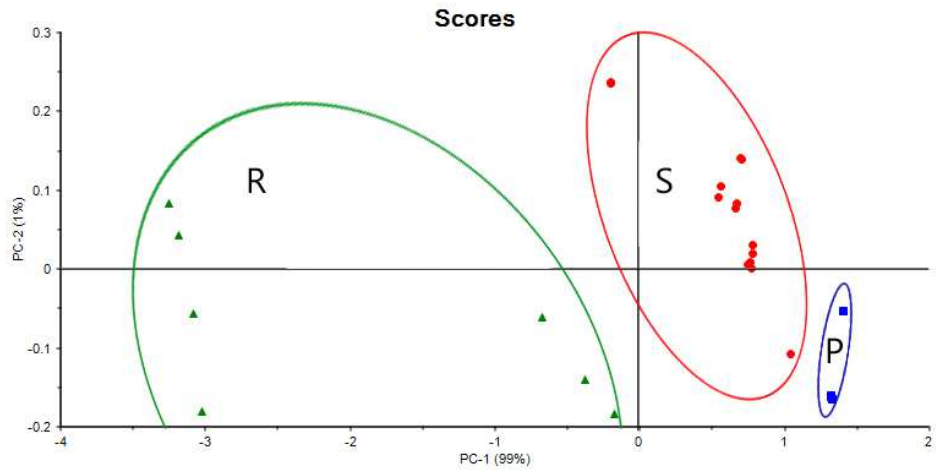

Figure 3: PC1 versus PC2 biplot for the baseline corrected spectra showing three clusters of samples: P – pure, S and R are samples adulterated with sugar and rice bran, respectively

The Savitzky-Golay 1st derivative spectrais one kind of pre-treatment method and it was applied to the baseline corrected spectra using the software.The firstthree PCs extracted: PC-1, PC-2 and PC-3 accountsfor 84 %, 6 % and 3 % of variations respectively. The PC-1 and PC-2 variants are more important and it covers around 90 % of variation present in the original data. The biplot of PC-1 versus PC-2 (Figure 4) and PC-1 versus PC-3 (Figure4) discriminates the samples in to three groups, shown in figure 4.

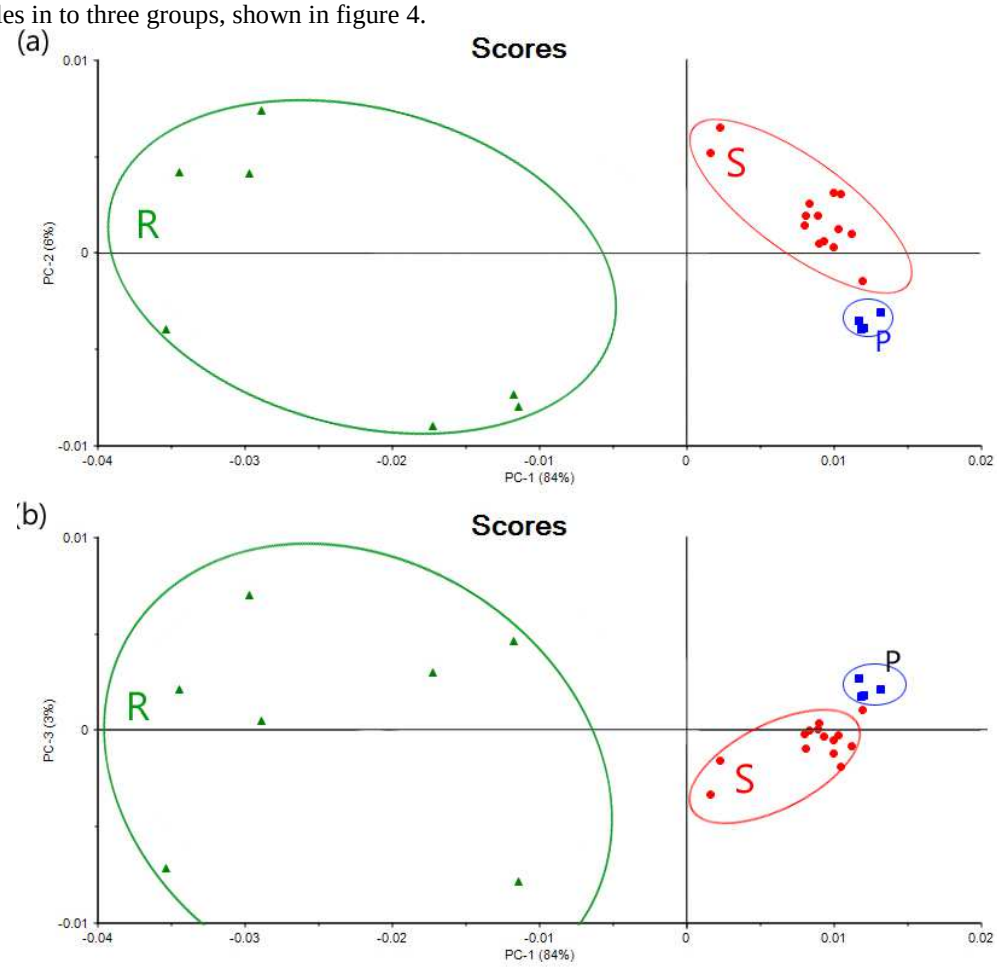

Figure 4: Biplots for the PCA of spectra pretreated with Savitzky-Golay 1st Derivative (a). PC1 versus PC2 and (b). PC1 versus PC3

The samples in each subset (P, S and R) are distributed well in all three biplots of PCA (Figure 3 and 4). This may explained by the influence of several factors which can potentially reflect the chemical composition.For instance, in group P (pure samples) the variation might occur due to the origin of sap, processing time, temperature etc.

CONCLUSION

This feasibility study has been shown that PCA analysis of NIR spectral data is useful in the authentication of palmyrah jaggery and this method also useful to identify the adulterant. Furthermore, this research study clearly shows that the addition of the foreign substance (i.e., rice bran) can be easily identified. However, the model lacks natural variations expected in the chemical composition between samples from various harvest and geographic locations, due to the lack of sample collection. Hence extended work is needed to build a robust model that can include the aforementioned variations.

Acknowledgements
We like to thank the Head/Department of Chemistry, University of Jaffna, Sri Lanka and General Manger, Palmyrah Research Institute, Jaffna, Sri Lanka for allowing permission to conduct this research successfully.

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