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Quality Evaluation of Honey Using Multivariate Analysis

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Abstract: In this research work, a near infrared spectra was analysed with the help of chemometric techniques to determine the adulteration of Indian Honey with either corn syrup or jaggery or both and percentage of adulterants which were presented in the samples. A total of 140 spectra of samples of different brands of honey adulterated with different concentrations of both adulterants, were analysed using a NIR spectrometer in the wavelength range of 1100nm to 2100nm. The collected spectral data is then compressed using Principal Component Analysis and models were developed to classify and quantify the adulterants present in each brand of honey. The classification of honey samples based on adulterant is done using PCA with a cross validation error of 2.93463×10^{-7} for Honey-1 samples and cross validation error of 3.04331×10^{-7} for Honey-2 samples. Amount of the adulterant present in the Honey-1 samples was found using PLS regression with the Root Mean Squared Error of Prediction (RMSEP) of 0.384437 and R^2 value of 0.996593 for corn syrup and RMSEP value of 0.351706 and R^2 of 0.998958 for jaggery and that in Honey-2 samples were found with RMSEP values of 0.492859 and R^2 values of 0.994806 for corn syrup and RMSEP values of 0.510477 and R^2 value of 0.997932 for jaggery. The analysis shows that NIR spectroscopy can also be used for classification of Honey samples into different groups based on adulterants present in the honey. These results also show that, the amount of adulterant can also be predicted with very good accuracy using NIR spectroscopy. By reducing the band in which the spectral analysis is done, it can be used in online processes at a considerably good rate industrially.

Key words: Chemo metrics · Adulteration · Multivariate Analysis

INTRODUCTION

Honey is the natural sweet substance produced by honey bees from the nectar of blossoms or from secretions of plants which honey bees collect, transforms and store in honey combs for ripening [1]. Honey is one of the most important dietary and medicinal materials in India and other parts of the world. Honey on an average is composed of 38.2% of fructose, 31.3% of glucose, 7.3% of maltose, 1.3% of sucrose, 17.2% of water and other elements in small quantities [2]. Honey has high nutritional and medicinal values because of which it is used very frequently and also has a higher price due to which it is prone to adulteration. In addition to this, honey composition and colour are not constant and varies in a range of values depending on the origin, environment and species of Honey which makes the adulteration easier and difficult to trace.

Honey is being adulterated with a variety of substances which include refined cane sugar, beet sugar, jaggery and corn syrup. Common adulterants in honey in India are jaggery and invert sugar [3]. Jaggery is very easy to obtain being a major food ingredient in India and is being used in honey as an adulterant. Jaggery contains 50% of sucrose, 20% of invert sugar, 20% of moisture, with the remainder made up of other insoluble matter such as wood ash, proteins and bagasse fibers [4]. Corn syrup which is similar to Invert Sugar mainly contains fructose and glucose in different ratios. Adulteration of honey with these adulterants though might not lead to medical problems but definitely decreases the medicinal and nutritional properties of Honey. As said earlier the composition of honey is not constant which makes it difficult to measure the quantity of adulteration in honey. For this reason a large number of methods were developed to detect the adulteration like Gas and Liquid

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chromatography analysis, Near Infrared Transflectance spectroscopy, Fourier Transform Infrared spectroscopy with Attenuated Total Reflectance, Protein characterization, High-Performance Anion-Exchange Chromatography with Pulsed Amperometric Detection, Liquid Chromatography Coupled to Isotope Ratio Mass Spectrometry, Calorimetric methods, Stable Carbon Isotope Ratio analysis, Fourier Transform Raman spectroscopy and Microscopic detection [5]. Though there are many methods most of them are time consuming, requires considerable expertise, destructive in nature and cannot be used in online processes and also involve many chemicals. Spectroscopic techniques are one such technique which is non-destructive and can be used in online processes. These are different types of spectroscopic techniques like Fourier Transform Infra–Red (FTIR) spectroscopy, Mid Infra-Red Spectroscopy (MIR) and Near Infra-Red (NIR) spectroscopy. MIR spectroscopy was used to find the adulteration of Honey with sugar solutions [6]. FTIR spectroscopy was used in detection of inverted beet sugar adulteration of honey [7]. NIR spectroscopy can also be used for detection of adulterants but so far no one has described the separation of samples into different groups based on the more than one adulterants present in the honey.

MATERIALS AND METHODS

NIR Spectral Data Collection: The NIR spectra of these samples were taken using the NIR Spectrometer FOSS XDS Optiprobe Analyser which has an immersion probe that analyses aqueous products, clear liquids and solvents and transmits the NIR light via a fiber-optic waveguide. It generates spectral data ranging from 400nm to 2500nm. This Optiprobe interfaces with a Personal Computer on which the collected spectral readings are stored as absorption vs wavelength data matrices. But the data from 1100nm to 2100 nm was only used for the analysis.

Sample Preparation: Honey samples used in the research are that of two different brands of Indian honey bought from local market (Let's say Honey-1 and Honey-2). The jaggery syrup solution was prepared using 2 parts by volume of water and 1 part by weight of jaggery [9]. Corn syrup solution was diluted using 1 part by volume of water and 1 part by volume of corn syrup. The amount of jaggery and corn syrup in each of the honey samples is shown in the Table 1. Similarly the samples were prepared for both the brands of honey.

Table 1: Honey samples used in analysis and their composition

Honey	Jaggery	Corn Syrup	Water	No of spectra taken
150 ml	—	—	—	10
150 ml	10 gm	—	20 ml	10
150 ml	15 gm	—	30 ml	10
150 ml	—	10 ml	10 ml	10
150 ml	—	15 ml	15 ml	10
150 ml	15 gm	10 ml	40 ml	10
150 ml	15 gm	15 ml	45 ml	10

Multivariate Analysis: The data collected was analysed using a chemometric software PLS Toolbox (Eigen vector Research, Toolbox version 7.8) based on MATLAB. PCA analysis was performed using this software to find the direction in which data variance is maximum and then the data is re plotted with that axis as the reference axis. This way PCA was used to represent the data in terms of very few variables (like 2 to 4 variables) which are the linear combination of wavelengths in the spectral data. After plotting in the new variables the clustering of various samples was analysed and thus the classification was done. A model was also developed to find the amount of adulterant present in the samples. The data was divided into calibration and validation sets and after the model was built using the calibration set, validation set was used to test the accuracy of the model.

RESULTS AND DISCUSSION

The spectra of honey and honey adulterated with jaggery, corn syrup and both of the adulterants in both the Honey brands, in the wavelength range of 1100nm to 2100nm is analysed. The spectra for the pure honeys were shown in fig.1.

Analysis

Principal Component Analysis for Honey Samples: Classification of Honey samples based on the adulterant present was done using PCA by pre-processing the data with normalize (1-Norm) and mean centre. The classification of both Honey-1 and Honey-2 samples was attempted by building a PCA model on this pre-processed data and the following scores plot was found showing that the both Honey samples are clearly classified as shown in fig.2 & fig.3.

From these scores plots, it can be observed that increase in PC1 score is corresponding to the increase in concentration of water and either of the adulterants. Loadings plots of PC1for the tested honey samples are shown in Fig.4 & Fig.5.

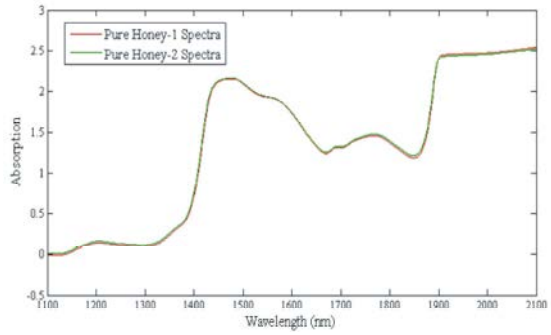

Fig. 1: Pure Honey-1 and Honey-2 Spectra

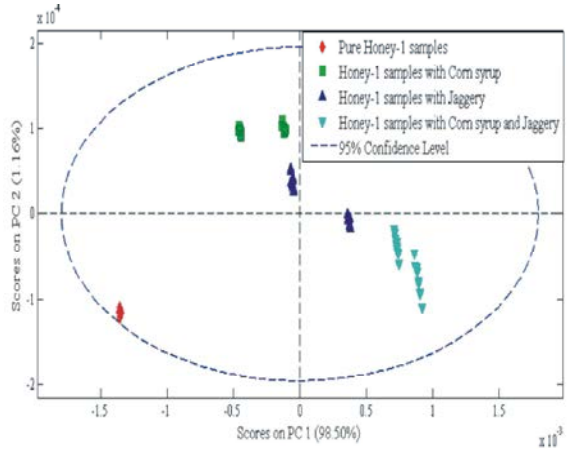

Fig. 2: Scores plot of Honey-1 samples

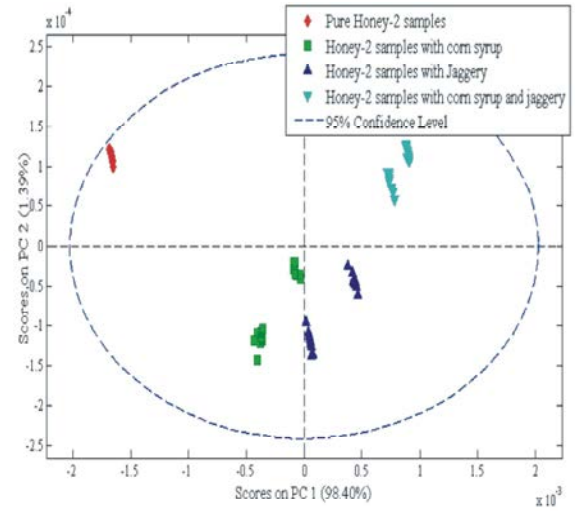

Fig. 3: Scores plot of Honey-2 samples

The spectral peaks in both loading plot shows the molecular interaction between the C-H and O-H bonds C-H and C=O bonds [8], which contributed by the O-H bond as in water molecule and C-H,C=O bonds presented in the adulterants components.

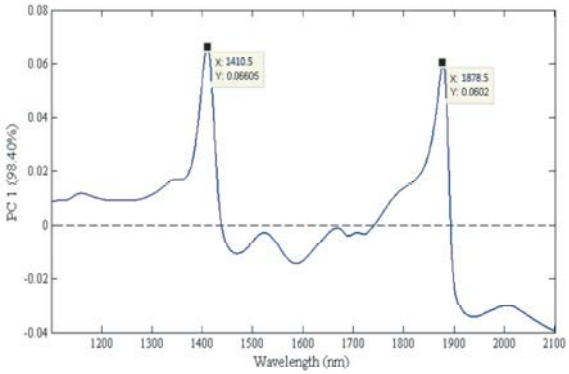

Fig. 4: Loadings plot of PC1 of Honey-1 samples

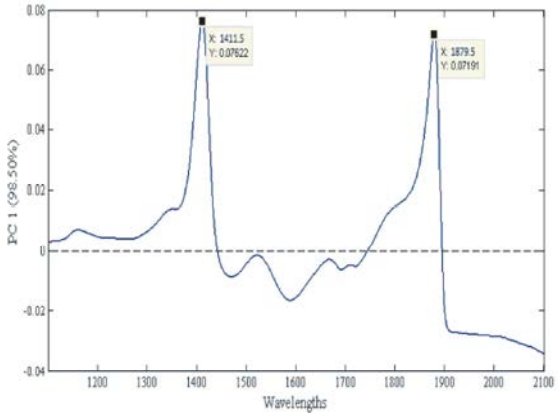

Fig. 5: Loadings plot of PC1 of Honey-2 samples

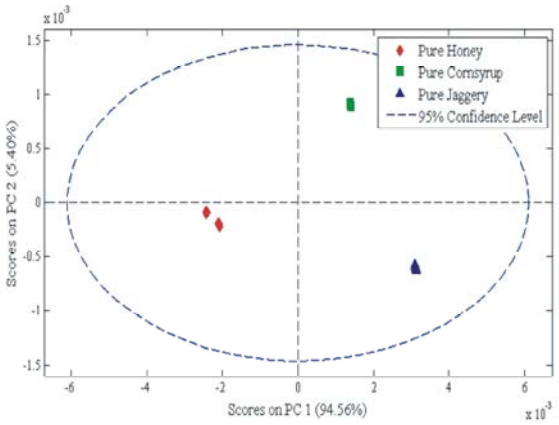

Fig. 6: Scores plot to find whose spectra among jaggery and corn syrup.

Principal Component Analysis For Pure Honey Samples And Adulterants: PCA analysis is performed using the Pure Honey, Pure Jaggery and Pure Corn Syrup spectra. Then scores plot is as shown in Fig.6 in which PC1 is 94.56% and PC2 is 5.40% constituting almost a 100% for the first 2 PC's so we can consider the data is almost a 2 dimensional one in plane passing through PC1 and PC2.

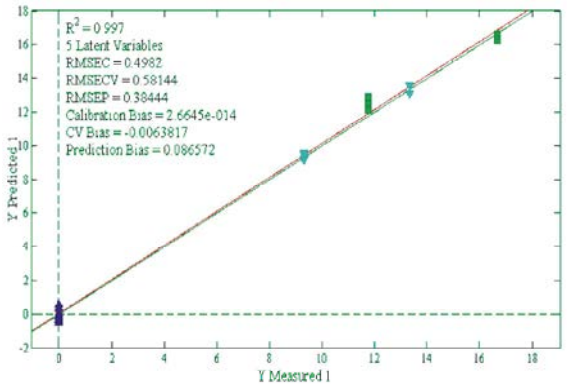

Fig. 7: Plot of Predicted vs actual concentration of corn syrup in Honey-1 samples

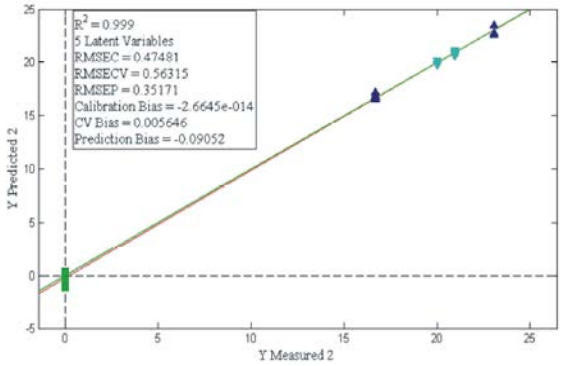

Fig. 8: Plot of Predicted vs actual concentration of Jaggery in Honey-1 samples

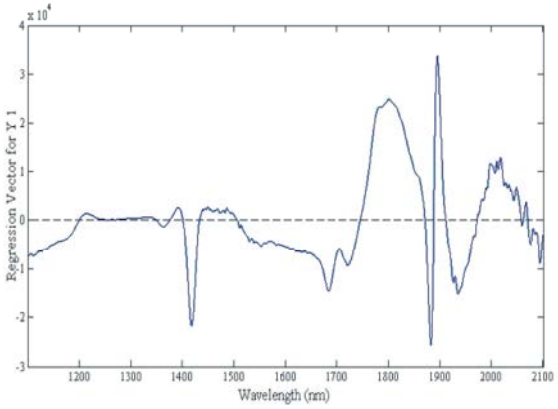

Fig. 9: Regression vector for corn syrup for Honey-1 samples

So to find which adulterant has spectral data more different in between Jaggery and Corn Syrup compared to Pure Honey, we can find the distance between the clusters in the plot as the data is 2 dimensional. From the scores plot it is quite evident that the scores of jaggery is more different from that of Corn syrup which is

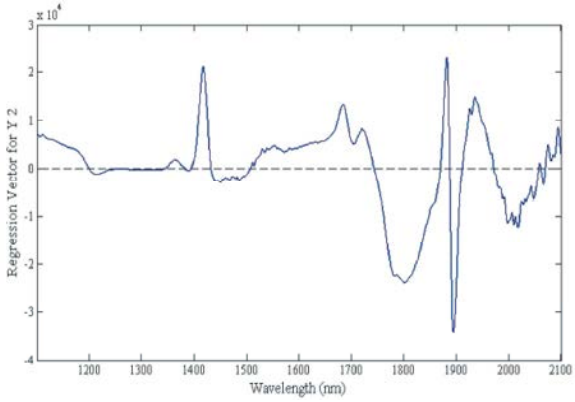

Fig. 10: Regression vector for jaggery for Honey-1 samples

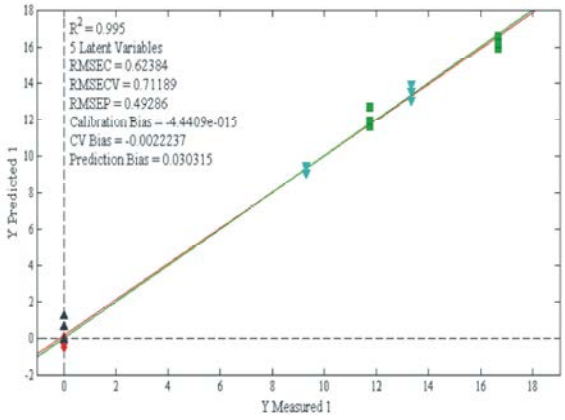

Fig. 11: Plot of Predicted vs actual concentration of corn syrup in Honey-2 samples

expected as the jaggery contains fructose and glucose same as that of honey and jaggery which mainly contains sucrose. This shows that adulteration with jaggery is comparatively easily detectable with NIR spectroscopy when compared to Corn syrup as shown in fig.6.

Estimation of Jaggery and Corn Adulterants: In this analysis two separate models were built to find the concentration of adulterants in Honey-1 and Honey-2 samples. In each model 90 samples were considered, out of which 60 were used for calibration and 30 were used for validation. Partial Least Squares (PLS) analysis was used to find the percentage of adulterant present and the results of the validation i.e. predicted value vs measured value is shown in the Fig.7 and found that the model predicting the concentration of adulterants in honey-1 samples has RMSEP of 0.384437 and R^2 value of 0.996593 for corn syrup with the regression coefficients for the estimation of corn syrup from the honey-1 mixture are shown in the Fig.9. Similar PLS model for finding the

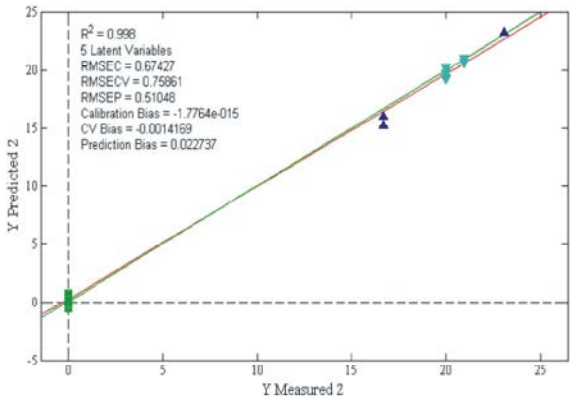

Fig. 12: Plot of Predicted vs actual concentration of Jaggery in Honey-2 samples

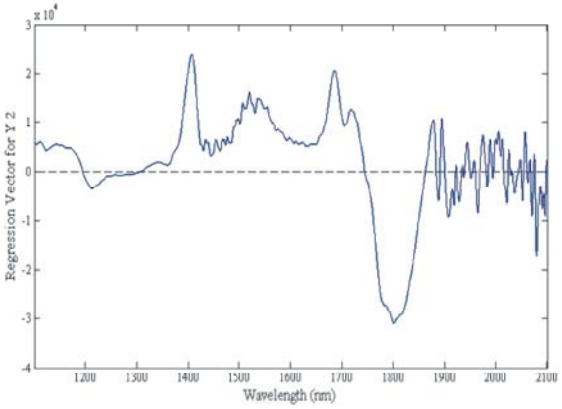

Fig. 13: Regression vector for finding corn syrup adulterant in Honey-2 samples

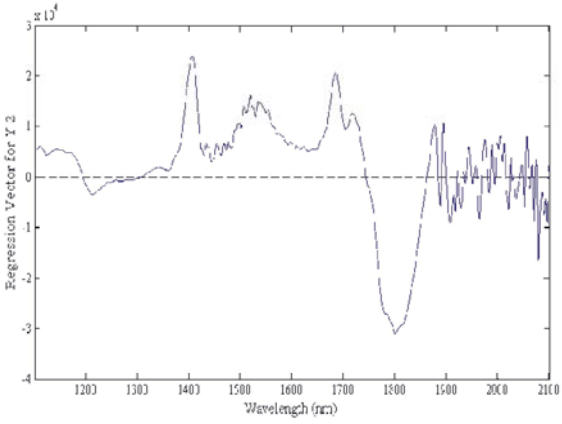

Fig. 14: Regression vector for finding jaggery adulterant in Honey-2 samples

percentage of jaggery adulterant in honey-1 mixture is shown in Fig.8 with the RMSEP value of 0.351706 and R^2 of 0.998958 for jaggery and its regression coefficient for the estimation of jaggery adulterant from honey-1 mixture is shown in the fig.10.

Similar adulterants estimation from the model shown in fig.11 and fig.12 for honey-2 with RMSEP values of 0.492859 and R^2 values of 0.994806 for corn syrup and RMSEP values of 0.510477 and R^2 value of 0.997932 for jaggery. The corresponding regression coefficients with wavelength plots also shown in the fig.13 and fig.14.

CONCLUSION

Two different models were developed to predict the quantity of adulterant for each brand of honey with Standard Error of Prediction (SEP) values of 0.384437 and R^2 value of 0.996593 for corn syrup and RMSEP value of 0.351706 and R^2 of 0.998958 for jaggery in Honey-1 samples and that in Honey-2 samples were found with RMSEP values of 0.492859 and R^2 values of 0.994806 for corn syrup and RMSEP values of 0.510477 and R^2 value of 0.997932 for jaggery. These results show the use of NIR spectroscopy in validation of quality of Honey. The robustness of the models can be improved by using more number of samples for training the model. If more samples with various adulterants are used to build the model then it can actually be used industrially to detect the presence of any adulterant. These results show that the honey samples can be classified based on the adulterant present in the sample and the amount of adulterant can also be predicted with the accuracy obtained from the multivariate model using NIR spectroscopy technique.

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