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Research Article

Rapid Classification of Rice Varieties using (ATIR-FTIR) Spectroscopy and Multivariate Chemometrics

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ABSTRACT

Rice is one of the most commonly consumed cereal crops in the world. Rice varieties are difficult to identify, especially when different varieties of rice are mixed (cheap varieties mixed with expensive ones) and packaged for consumers to purchase. Quality control is of great concern in the food industry in that food products are sorted and graded distinctly depending on the quality parameters after harvest. Fourier Transformed Infrared-Attenuated Total Reflectance (FTIR-ATR) Spectroscopy and multivariate chemometrics were applied to classify four rice varieties bought from local shops in the UK for this study. A total of 80 samples were analyzed using principal component analysis and hierarchical cluster analysis. This method was developed with the aim of classifying rice varieties as fast as possible without sample alteration. The spectral profile of the rice varieties was obtained at a wave number range of 4000-450 cm^{-1}. Result shows that FTIR-ATR spectroscopy could be used successfully to discriminate rice varieties. When PCA and HCA were used to analyze the spectra data, cluster were identified with few samples of the rice varieties mixed up in the four different clusters identified. Based on this analysis, a suggestion was therefore made that parameters used for this study were not sensitive enough to produce the required outcome and since rice varieties have the same component, this makes it difficult to discriminate them. Although FTIR-ATR has not been widely applied in the discrimination of rice varieties. Multivariate statistical analysis has been successful. The findings of this study therefore pave the way for further research.

Keywords: *Cereals, Rice, Oryza sativa, Crops.*

INTRODUCTION

Cereals are grain or edible seeds belonging to the grass family known as Gramineae/ Poaceae (Bender & Bender, 1999), one of which is *Oryza sativa* L. (Rice). It is a staple food and is presently one of the most consumed crops in the world (Wen-Shin Lin et al., 2012, Xinwei, 2013 & Abdhulraman et al., 2014 & Srivastava, 2018). There are two cultivated species: *Oryza glaberrima* (in West Africa) and *O. sativa* in the rest of the world (Lanares, 2002).

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There are also two subspecies of *Oryza sativa*, indica and japonica (Lui et al., 2013). The cultivation of rice can be traced back to about 10,000 years ago, but the origin of its first development remains a subject of debate (Maclean et al., 2002). As a result of natural and artificial selection, rice has developed into a crop with a high level of diversity in terms of morphology, physiology and genetics, with more than 120000 different known varieties across the globe (Vaughan et al., 2008). Rice varieties are difficult to identify, especially in a situation where different varieties of rice are mixed (cheap varieties mixed with expensive ones) and packaged for consumers to purchase. The main issues generally associated with the topic of food authenticity are economic adulteration and secondly misbranding of products. Economic adulteration of food refers to the blending of a cheaper product with commodities of higher economic value, while the misbranding of products involves the deviation from production system, denomination of geographical origin, genetically modified food/food ingredients (Rodriguez-Saona & Allendorf, 2011). Quality control is of great concern in the food industry in that food products are sorted and graded distinctly depending on the quality parameters after harvest. The addition of substances that should not be found within other materials for authorized or other reasons is known as adulteration. It is of paramount importance that unrefined materials used in food production meet the right standards, which can be attained through the institution of law-making agency to whom manufacturers, food ingredient suppliers and retailers owes obligation (Loannis et al. (2011).

The objective of this work was to develop a fast technique using FTIR-ATR and Chemometric data analysis to classify different rice varieties. Fourier Transform Infrared (FTIR)-Attenuated total reflectance (ATR) Spectroscopy is a promising tool for the fast identification of samples (Andrew et al., 2001). In the last 10-15 years this technique has shown significant application in both quantitative and qualitative analyses of various samples. Using this method, the surface of samples can be characterized without alteration.

MATERIALS AND METHODS

Rice Sample

Four Rice varieties were used in this study; samples were purchased from the local shops in Gillingham, UK. These include: Basmati Rice, Long Grain Rice, Pudding Rice and Arborio Rice. For this research, these varieties were labelled with brand name as follows; Aycan long grain, Bodrum Long grain, Bodrum short Grain, Cucina short grain, respectively.

Spectra measurements

The FTIR spectra were obtained with a Perkin-Elmer Spectrum 500 FT-IR spectrometer (Perkin Elmer Inc, Wellesley, MA). The instrument consists of a parallel ATR sampling appliance (ZnSne crystal 45 C). The ATR crystal (ZnSe crystal) was cleansed with few drops of isopropanal placed in a soft wipe, the spectral was set at Wavelength =4000-450 cm^{-1} with 8 scans and pressure was set at 10. And finally, it was set at 4 (Four) wave number. A background scan was done in other to measure the cleanliness of the ART crystal. A grain of each of the varieties was placed directly in the ATR crystal using a spatula and a pressure was applied, the scan was then taken. For all spectra scan, a new reference air background spectrum was taken. This was done for 20 grains of each of the samples. Data were then collected and transferred to excel.

Data Analysis

The data generated were analyzed using Excel 2010 and Matlab 7.0

RESULTS AND DISCUSSION

Table 1a: Sample of the varieties studied

S/n	Brand name	Variety	Grain type
1.	Bodrum	Pudding Rice	Short
2.	Bodrum	Long grain	Long
3.	Aycan	Basmati	Long
4.	Cucina	Arborio	Short

Table 1b: Four sets of rice varieties

S/N	Rice varieties	Abbreviation	Shops
1	Aycan long grain	Aycan LG	Lahore meat and grocers, Gillingham, UK
2	Bodrum long grain	Bodrum LG	Lahore meat and grocers, Gillingham, UK
3	Bodrum short grain	Bodrum SG	Lahore meat and grocers. Gillingham, UK
4	Cucina short grain	Cucina SG	QIN food centre, Gillingham, UK

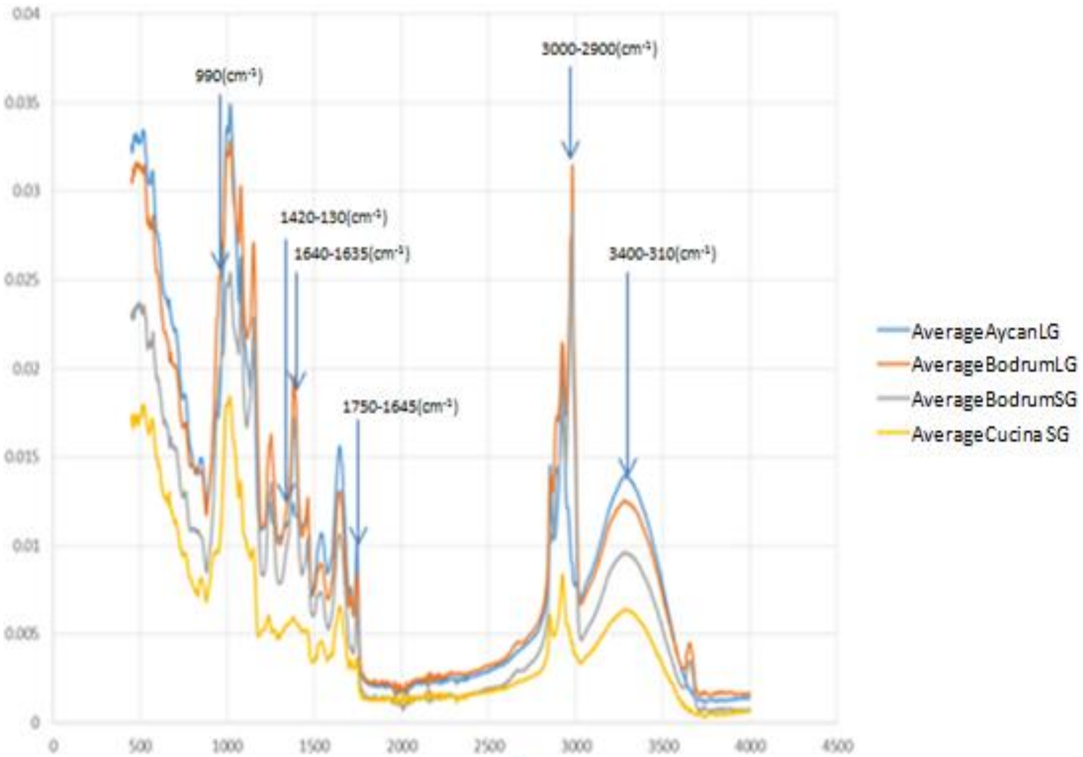

Figure.1: Spectral of the studied averaged rice varieties at 4000-500 cm^{-1} mid-IR range

Table 2: Main characteristic bands positions based on functional groups

S/N	Approx. band position(cm^{-1})	Functional group assignment
I	990(cm^{-1})	O=H deformation
2	1420-130(cm^{-1})	CH_2 and CH_3 bending vibrations
3	1640-1635(cm^{-1})	O-H Bending vibration
4	1750-1645(cm^{-1})	C=O stretching
5	3000-2900(cm^{-1})	C-H stretching
6	3400-310(cm^{-1})	O-H stretching

Table 2 shows the FTIR spectral of the rice varieties analyzed at wave number range 4000-450cm^{-1}. FTIR Spectroscopy is a substantial tool for identifying functional groups of samples (Daffalla et al., 2010) The main components of rice include starch, protein and lipids (Xinwei et al., 2013). The rice variety was classified and its various spectral components were associated with vibration and absorption of the chemical bonds in the rice constituents. This technique provides spectra with well-revolved bands that illustrates various FT-IR spectra absorbance. In this spectrum, the absorption peak was identified around 990cm^{-1} due to C=C stretching vibration. CH2-(methyl) and CH3-(methylene) groups bending vibration was detected around 1420-130cm^{-1} region. Large peak existed around 1640-1635cm^{-1} and was found to be O-H bending vibration. The peak large in 1645-1750cm^{-1} corresponds to C=O stretching. The peaks around 300-2900 was found to be C=H stretching vibration of alkyl groups. Broad peak of O-H stretching was detected at the peak of 3400-310cm^{-1}. The reason for this broadness is due to the fact that hydrogen is bonded to water and there is equally non hydrogen bond to water as the peak goes up and get broader. This equally resulted to over pairing of water. Differences were detected in the spectral contour between classes as well as slight shifting in the band positions. The differences discovered was that in some samples, the concentrations were higher than the other, these differences were found in peaks 1139, 1159,1255, 1163 2930, and 2990 respectively.

Correlation Coefficient Table

Using the wave number (4000-450 cm^{-1}), the relationship between four sets of rice was matched (4 rows and 4 columns). The results (table 3) are delivered in a tabular format and display the highest relationship of 0.992 detected for the absorbance of Aycan LG and Cusina SG in the first row, in the second row, 0.995 R^2 for Bodrum LG and Bodrum Short Grain. Third row R^2 0.995 for Bodrum SG and Bodrum LG, fourth row R^2 0.992 for Cusina SG and Aycan Long Grain. This means that the varieties are highly correlated. The value of 1.00 was seen on the transverse of each pole because (a variable will usually possess a perfect positive correlation with itself). This result is in line with the view given by Yan et al., (2005) that mid and NIR spectroscopy are able to offer worthy estimates with a R^2 value higher than 0.99. Although the degree of the resemblance has a definite range, for instance, Pearson's correlation coefficient lies at either -1 or 1 while its square lies between 0 and 1.

In reality, however, the highest connection is not usually achieved and the dispersal of values could be more steady. Thus, an R^2 value of 0.99 usually does not mean a match in most cases. This may only be achieved with an initial understanding of the distribution table, contrary to how a specific outcome is judged (Li et al., 2005). When the distribution of a resemblance measure was extracted, a broader distribution of spectral connection of differences was observed in rice. This is represented in the table below.

Table 3: Correlation Coefficients of average FTIR spectra among Aycan long grain, Bodrum long grain, Bodrum short grain and Cusina short grain

	AVR Aycan-LG	AVR Bodrum-LG	AVR Bodrum-SG	AVR Cusina-SG
AVR Aycan-LG	**1.000**	0.937	0.910	0.992
AVR Bodrum-LG	0.937	**1.000**	0.995	0.927
AVR Bodrum-SG	0.910	0.995	**1.000**	0.892
AVR Cusina-SG	0.992	0.927	0.892	**1.000**

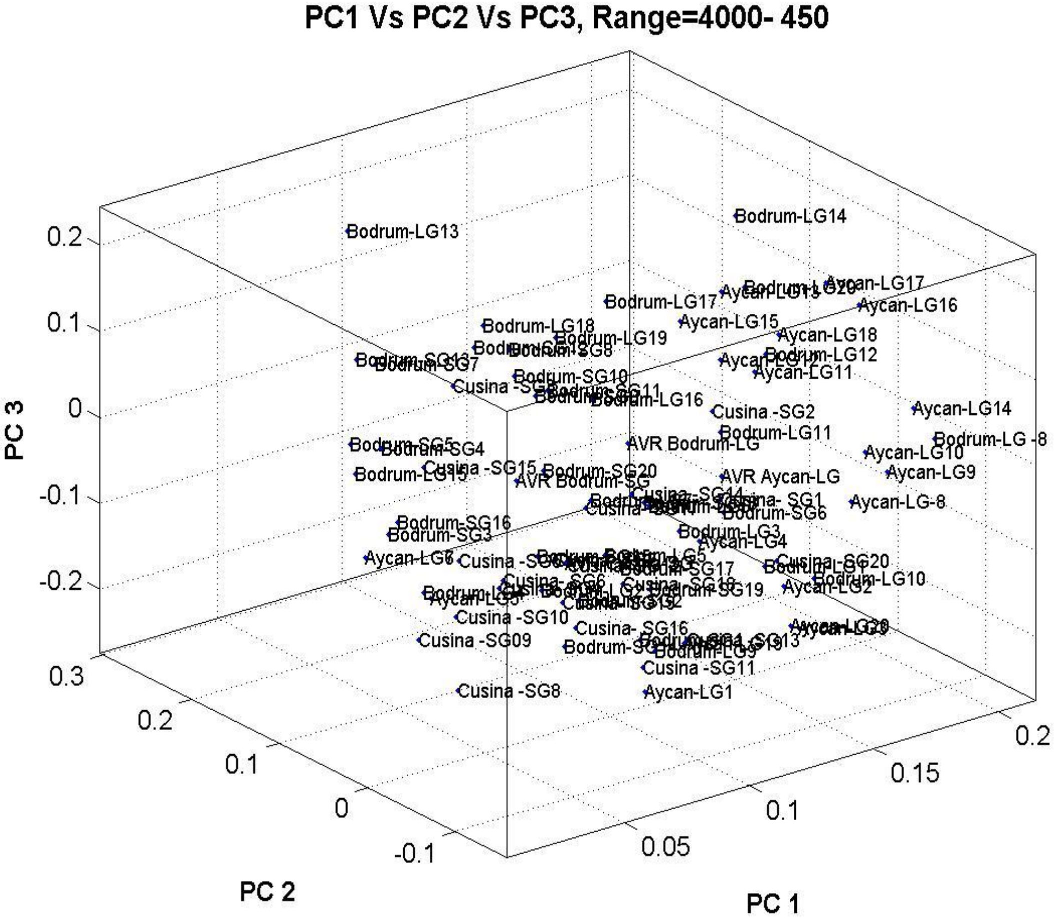

Figure 2. PCA score plot for classification of rice varieties PC1 vs. PC2 vs PC3

Classification with Principal Component Analysis

The main objective of applying PCA was to compress variables into a lesser number of principal constituents that capture the highest bulk of differences found in the data. This largely decreases the length of data by giving way for successful imaging and organization and regression of multivariate set of data (Terouzi et al., 2013). The FTIR spectra which were modelled at finger print region of 4000-450cm^{-1} for 80 samples of rice varieties were analyzed by PCA. This was done to distinguish between the four varieties: Aycan long grain, cusina long grain, Bodrum short and long grain. The application of PCs (PC1, PC2 and PC3) to the data matrix shows that there is no clear separation between the four varieties. As shown in the diagram above (Figure 2), it was expected that a clear clustering of each of the varieties would have been observed by leaving the outlier. The cluster of the rice varieties were not totally separated or recovered into clusters in the PC plot. This therefore means that PCA was effective in the classification of these rice varieties however outliers were observed. It is worthy of note that the finding of this work does not disprove the efficay of PCA classification for rice sample. Rubi and Rurit, (2009), successfully classified four varieties of basmati rice using using PCA. It could then be said that, the parameter is not sensitive enough to produce the desired clustering or the same variety were branded and packaged for sale.

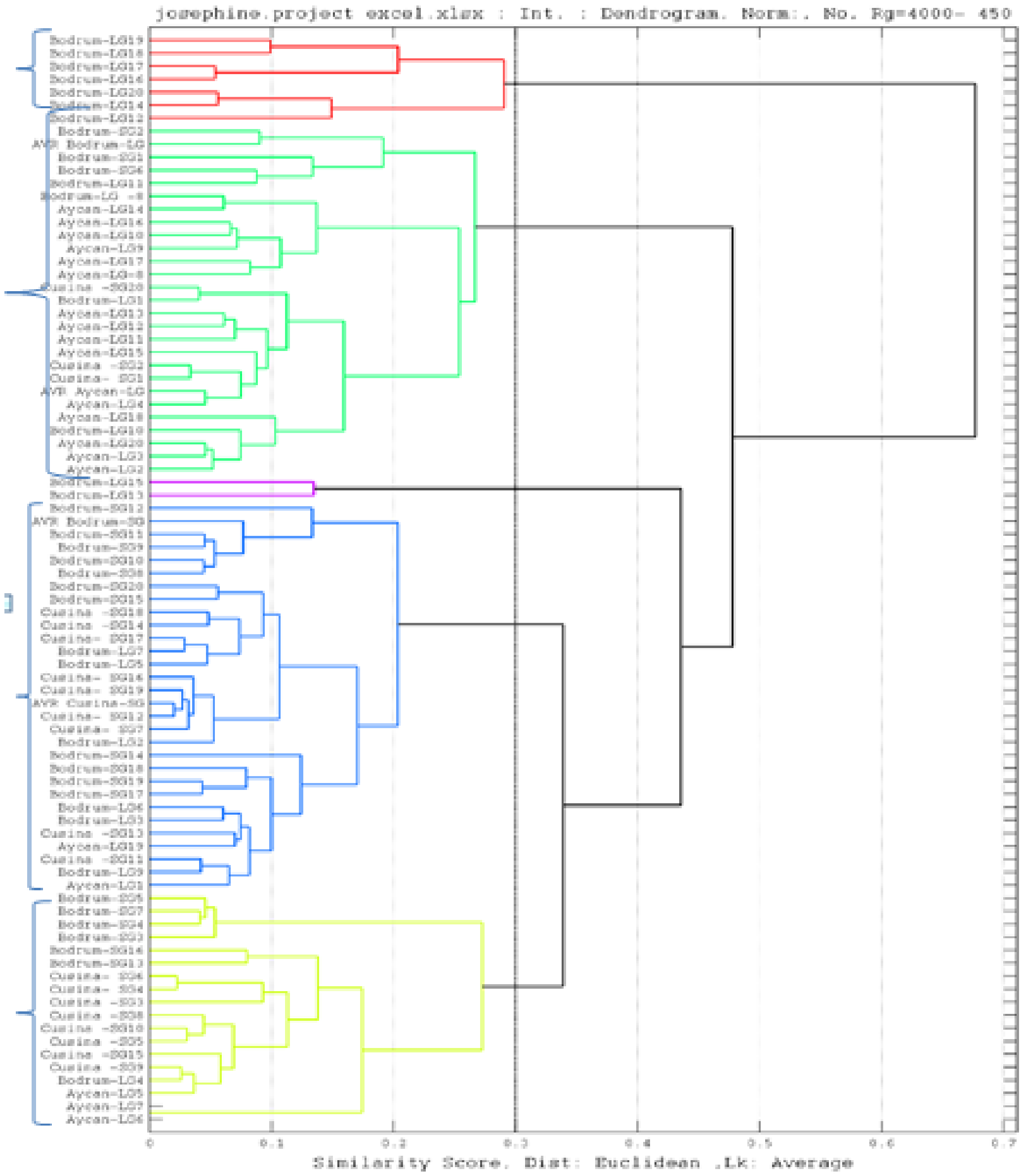

Figure 3: Classification of rice varieties using Hierarchical Cluster Analysis (HCA

HCA is said to be an unsupervised method applied in collecting data obtained from measured variables to demonstrate that regular clusters exist between the models under study. In this system, the initialization of class numbers is achieved (Obeidat et al., 2009). To see the relationship and be able to differentiate the rice varieties, hierachical cluster analysis was drawn using raw FTIR spectral profile recorded from the four varieties of rice samples. The model was developed using the wavenumber of 4000-450cm^{-1}. The spectral were then connected to one hierarchical grouping method, characterized by a denrogram. The resultant denrogram (figure 3) shows that the four distinctive clusters exist. It was expected that each of the varieties Brodrum Long Grain, Bodrum Short Grain, Aycan Long Grain, and Cusina Short Grain clustered together, interestingly samples were mixed up in each of the four clusters that is each variety were not completely separated into a different clusters. As in the case of group A (red color). some samples of bodrum LG where clearly separated but not all the 20 samples. In group B (green color) some samples of Aycan LG were clustered with mixtures of both Bodrum SH and LG and Cusina SH as well. In group C (blue color) Bodrum Short Grain were separated with mixtures of Aycan LG, Bodrum LG. In group D (grey color) samples of Cusina Short grain were separated with mixtures of Both Bodrum LG and Short with Aycan. HCA was efficient enough to classify these varierties however incomplete separation between the samples were observed. One of the objective of this study is to see the feasibility of classifying the rice varieties using HCA study. These findings suggest that the same rice varieties could have been mixed up with the others and packaged for sale. The primary component of rice include starch, protein and lipids. These components are definite regardless of the variety, be it short or long grain. This therefore makes it difficult for these varieties to be completely separated. The spectral data identified very minor differences which both the PCA and the HCA could not detect.

CONCLUSION

The data obtained from this work opens the possibility of classifying rice varieties. This study demonstrates that FTIR-ATR spectroscopy is a substantial tool in the classification of rice varieties. In practical, direct FTIR scanning of the rice samples without squashing makes the measurement convenient, easy and fast. The combination of experimental data along with chemometric approaches such as PCA and HCA were successful in the classification of the rice varieties studied, outliers were however observed. The results obtained from this study paves way for further research.

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Author contribution:
Josephine Ukomadu prepared the original draft, manuscript editing and data analysis. John Tetteh did the methodology and Data analysis, and Mustapa Gani wrote and edited.

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