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Rapid detection of adulteration in red dates (*Ziziphus jujuba* mill.) powder by Fourier-transform infrared spectroscopy combined with chemometrics analysis

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Abstract. Food adulteration presents a major challenge in the food industry, impacting product quality and consumer trust. This study investigates the use of Fourier Transform Infrared (FTIR) spectroscopy combined with chemometric methods, Principal Component Analysis (PCA) and Partial Least Squares-Discriminant Analysis (PLS-DA), for detecting cornstarch and powdered sugar adulterants in *Ziziphus jujuba* Mill. fruit powder. The PCA model effectively separated pure and adulterated jujube powders, clustering samples by adulterant type and concentration. Brands A, B, and E of the retail jujube powder samples were identified as likely adulterated with corn starch, while Brands C and D showed minimal adulteration. PLS-DA further differentiated adulteration levels, suggesting high corn starch adulteration levels in Brand A, B, and E samples. A Partial Least Squares Regression (PLSR) model yielded high accuracy (R^2 = 0.9859) and precision, with low error rates (RMSEE = 5.50% and RMSECV = 9.16%), supporting the model's robustness in adulteration prediction. Our findings highlight FTIR spectroscopy coupled with chemometric modelling as an efficient, reliable tool for rapid adulteration detection in jujube powder. This approach offers significant potential for ensuring product authenticity and quality control in functional food products.

1 Introduction

Food fraud, encompassing a wide range of deceptive practices within the food supply chain, incurs substantial economic losses, estimated at $30-40 billion annually [1]. One of the most common types of food fraud is food adulteration. It is the act of intentionally degrading food quality by adding or substituting food ingredients with undisclosed replacements, or by

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removing an essential ingredient. This pervasive issue manifests in diverse forms, as evidenced by the adulteration of honey with sugar [2], the substitution of cheaper oils for olive oil [3], and illegal dye and chemical use in spices [4]. Such practices intentionally incorporate low-cost fillers like cornstarch and powdered sugar, diminishing the product's quality, safety, and economic worth. The potential health risks associated with food fraud necessitate a paradigm shift. Global estimates suggest that approximately 22% of the food supply is tainted each year, resulting in health issues for nearly 57% of consumers [5].

Ziziphus jujuba Mill., commonly referred to as red date, Chinese date, or jujube, has been held in high esteem for centuries due to its medicinal and nutritional properties [6]. Jujube is utilised in various culinary applications and beverages as a natural sweetener as it lends its unique flavours to recipes. Adulteration of *Ziziphus jujuba* Mill. fruit powder represents a pressing concern that erodes consumer trust and jeopardises public health. Detection and prevention of adulteration in jujube fruit powder is paramount to maintaining the integrity of the industry and safeguarding consumer well-being. Traditional methods for identifying adulteration can be time-consuming, costly, and may lack the requisite sensitivity and specificity [7]. This research aims to answer whether FTIR spectroscopy, in conjunction with chemometrics analysis using PCA and PLS-DA can efficiently detect adulteration in *Ziziphus jujuba* Mill. fruit powder.

2 Materials and Methods

2.1 Sample preparation

The jujube fruits originated from Xinjiang, China were bought from a local market. The fruits were washed to remove any dirt or dust. The fruits were dried, cut into half and the pit was removed. The fruit pulps were evenly distributed on a metal plate covered with aluminium foil with holes and stored in an ultra-low temperature freezer at -80 °C overnight. The frozen fruit pulps were freeze-dried at -105 °C. The fruit pulps were blended, and the powder was freeze-dried. The final product was ground and sieved. The pure jujube powder was stored in a zip lock bag at -80 °C until further analysis.

Adulterated jujube powder was prepared by blending it with corn starch and powdered sugar in varying percentages. First, granulated sugar of 95 g was mixed with 5 g of corn starch and blended to obtain powdered sugar. Adulterated samples containing 2%, 6%, 10%, 20%, 30% and 100% (w/w) of corn starch (CS) as well as 6%, 15%, 30%, and 100% (w/w) of powdered sugar (PS) were prepared. A total mass of 5g for each adulterated sample were mixed in 15 mL centrifuge tubes and vortexed to homogenize. A total of 12 series of samples were prepared, each with three replicates (training data, n = 36). In addition to sample for model building, triplicates of five retail samples (Brand A, B, C, D, E) were collected (testing data, n = 15) from online retailers.

2.2 Fourier Transform Infrared Spectroscopy Measurement

The adulterated samples and the retail samples were scanned using Perkin Elmer Spectrum 100 FT-IR. A total of 8 scans with 4 cm^{-1} resolution from 650 to 4000 cm^{-1} were acquired for each spectrum. Spectrum pre-processing was done to eliminate the instability in IR spectra due to measurement errors and inconsistent compression [8]. Derivative baseline correction, Savitzky-Golay smoothing, and Standard Normal Variate (SNV) normalization was carried out to eliminate scattering using the Perkin Elmer Spectrum Software Version 10.6.1.

2.3 Chemometric Analysis and Model Validation

SIMCA-P version 14.1 (Umetrics, Umeå, Sweden) was employed for chemometric modelling. FT-IR spectra in Microsoft Excel (.xls) format was imported into the software for analysis. All spectral data were mean centred, UV scaled, and auto-fitted before principal component analysis (PCA) and partial least squares discrimination analysis (PLS-DA) were performed. The performance of PLS-DA models was observed through R^2X, R^2Y, Q^2 values and permutation tests. Multivariate calibration analysis was performed using PLS model. The model was evaluated using coefficient determination (R^2), root mean square error of estimation (RMSEE), and root mean square error of cross validation (RMSECV) values [9].

3 Results and Discussion

To get an overview of the data set, PCA was applied to extract meaningful principal components (PCs). The PCA model demonstrated R^2 of 0.972 and Q^2 of 0.907 (Figure 1), indicating a good ability to differentiate the corn starch (lower left quadrant) and powdered sugar (upper left quadrant) adulterants from the pure jujube powder (upper right quadrant). The retail samples, Brands C and D clustered with pure jujube, while Brands A, B, and E clustered with corn starch. This indicated that Brands A, B, and E jujube powders were possibly adulterated with corn starch while Brand C and D jujube powders were not adulterated or contains lower levels of adulterant. The high sugar content of jujube fruit and its tendency to absorb moisture often led to caking or agglomeration [10], which may impact consumer acceptance due to its visual appearance. To improve the appearance of jujube powder, anti-caking agents such as starch, talc, and flour are sometimes added, along with artificial colours or dyes to enhance consumer appeal. Starch is a commonly used adulterant in food products due to its affordability, minimal health impact, and effectiveness as an anti-caking agent [10].

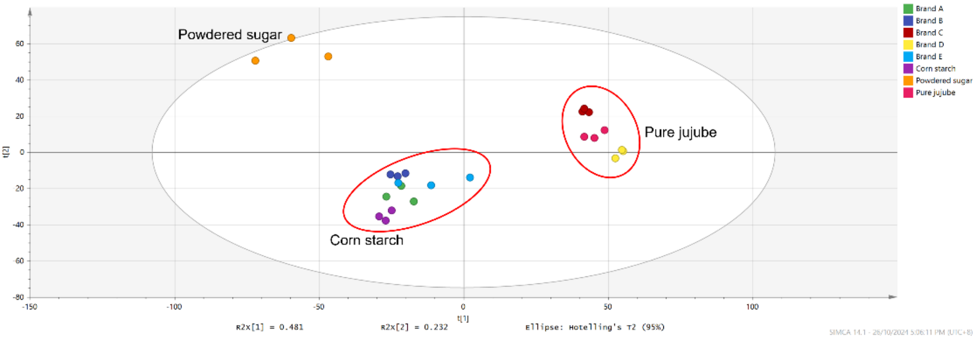

Fig. 1. PCA score plot of different brand of retail jujube powders with pure jujube powder, corn starch and powdered sugar.

Another PCA model was conducted to include only the corn starch series with different levels of corn starch adulteration. The PCA model showed R^2 of 0.981 and Q^2 of 0.936 (Figure 2a). No outliers were observed, suggesting that all the samples are representative of the population. The PCA score plot demonstrated that Brands A, B, and E were separated from Brands C and D by PC1. It was noted that Brands A, B and E form a cluster with the adulterant, corn starch on the right quadrants. This indicated that these three brands shared very similar chemical properties or bonding that transmitted the FTIR light similar to that of corn starch, potentially due to the higher concentration of corn starch in the three jujube powder samples. However, Brands C and D were closely associated with pure jujube powder in the left quadrants, suggesting that these two brands have very similar properties with the pure jujube. Besides, the PCA showed that Brands C and D were separated by PC2, in which Brand C clustered with pure jujube, as well as 2% and 10% corn starch, while Brand D clustered with 6% and 20% corn starch. This suggested that Brands C and D jujube powders may be adulterated with moderate level of corn starch, but the level of adulteration is uncertain. PLS-DA was further used for the discrimination of pure and adulterated jujube powders.

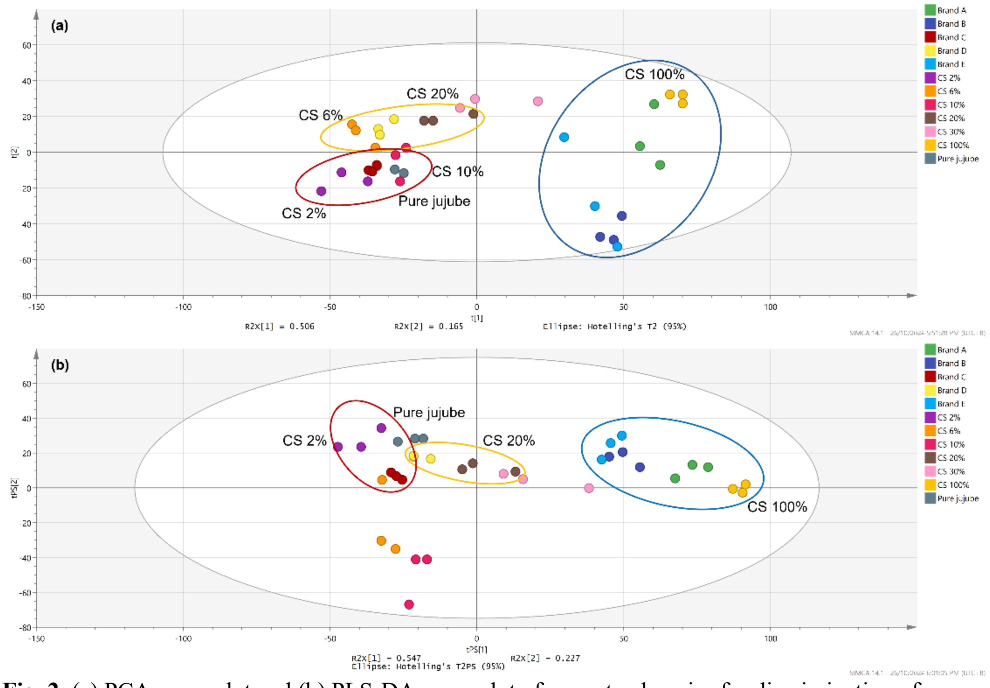

Fig. 2. (a) PCA score plot and (b) PLS-DA score plot of corn starch series for discrimination of pure and adulterated jujube powders. CS, corn starch.

A classification model was built using PLS-DA in order to evaluate the possibility of predicting the level of corn starch adulteration. PLS-DA is a supervised method that uses class labels to maximize the separation between classes [11], in which each Y variable corresponds to a different level of adulteration ranging from 0% to 100%. PLS-DA score plot (Figure 2b) shows that 93% of the variability in the data was accounted for using the first four principal components, indicating a good level of explanation for further analysis. The PLS-DA model also presenting a goodness-of-fit value of $R^2X = 0.977$, $R^2Y = 0.92$, and a goodness-of-prediction value of $Q^2 = 0.738$. A Q^2 value that is > 0.5 and < 0.9 is generally considered good and suggests that the model is not overfitted. Validation using the permutation test resulted in a Q^2 intercept value of zero and below zero indicating model validity. Figure 2b shows that Brand A jujube powder clustered closer to the 100% corn starch, while Brands B and E clustered nearer to 30% corn starch, indicating a higher level of corn starch adulteration in Brand A. Additionally, brand C and D were separated from Brands A, B and E by PC1, as observed in the PCA model. However, the PLS-DA model provides improved discrimination as compared to the PCA model; specifically, PC2 distinguished Brand D as clustering with the 20% corn starch, while Brand C clustered with 0% and 2% corn starch. The results demonstrated that the level of corn starch adulterant in the retail samples follows this order: Brand C (0-2%) < Brand D (~20%) < Brands A, B, and E (30-100%).

Figure 3a shows the PCA score plot of the powdered sugar adulteration series. The PCA model had R^2 of 0.961 and Q^2 of 0.913. The presence of pure powdered sugar adulterant as an outlier suggested that the retail jujube powders may not contain high level of sugar. Brands A, B and E clustered together and were positioned far from Brands C and D, which were clustered with the powdered sugar adulteration series in the right quadrants. Brand C clustered with 15% and 30% powdered sugar in the lower right quadrant and Brand D clustered with 0% and 6% powdered sugar in the upper right quadrant. The PCA model suggested that Brands C and D jujube powders may contain a moderate level of powdered sugar adulteration, which is 15-30% in Brand C and 0-6% in Brand D. However, the clustering pattern could also be attributed to compositional variations among the unknown jujube cultivars used in producing the powder. Additionally, the similarity between the sucrose found in commercial table sugar and the natural sucrose in jujubes [12] may have contributed to the observed clustering pattern. The PLS-DA model of the powdered sugar series (Figure 3b) explained only 88.5% of the variability in the X matrix, and the clustering pattern does not show any improved discrimination from that of the PCA model. The model was demonstrated to be weak and underfitted, owing to the low R^2Y value of 0.391. The low Q^2 value of 0.272 indicated that the PLS-DA model generated using the powdered sugar adulteration series has poor predictive performance and is likely not reliable.

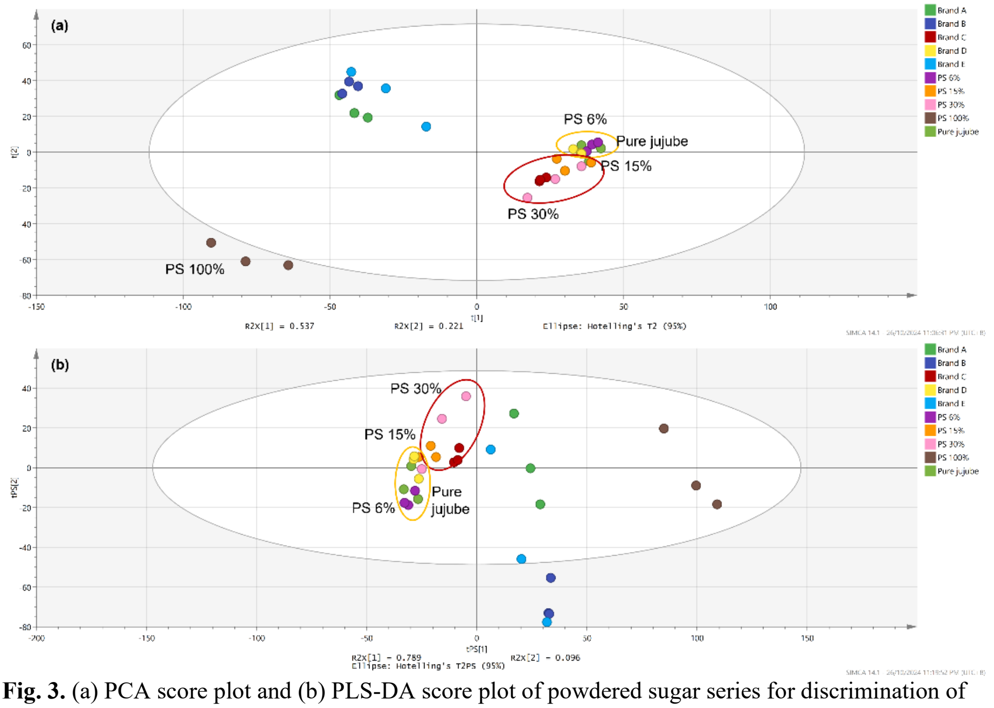

Fig. 3. (a) PCA score plot and (b) PLS-DA score plot of powdered sugar series for discrimination of pure and adulterated jujube powders. PS, powdered sugar.

A calibration model for the relationship between observed and predicted values, as determined using multivariate calibration of the corn starch PLS model was performed. Results showed that PLS was successfully used to detect and predict the concentration of corn starch in jujube powder with high accuracy and good precision. The unknown sample of corn starch adulterated jujube powder could be predicted using the equation of y = x -

5.391×10^{-8} with the R^2 value of 0.9859. In addition, the Root Mean Square Error of Estimation (RMSEE) is low (5.50%), indicated that the model has a good fit to the training data. The calibration model was further evaluated using cross validation, and a low RMSECV (9.16%) was obtained. It can be summarized that multivariate calibration of PLS could be used as rapid and effective methods for authentication of jujube powder by detecting and predicting the concentration of corn starch with high accuracy and precision.

4 Conclusion

This study demonstrated the effectiveness of multivariate analysis, particularly PCA and PLS-DA, in detecting adulteration in retail jujube powders and distinguishing between authentic and adulterated samples. The PCA model successfully revealed clustering patterns that separated adulterated samples from pure jujube powders based on variations in their FTIR spectra, while PLS-DA offered enhanced discrimination and predictability of adulterant levels. Corn starch and powdered sugar adulterations were detected at varying concentrations across different brands, with PCA indicating moderate levels of adulteration for powdered sugar in Brands C and D and PLS-DA accurately estimating corn starch concentration ranges in all five samples. The calibration model developed showed high accuracy and precision, validating the model's robustness in predicting corn starch levels. These findings suggest that PLS-based multivariate calibration can serve as a rapid and reliable method for authenticating jujube powder quality and detecting adulterants, contributing to improved quality control in functional food products.

References

1. N.N. Ahmad, N.S. Khairatun, The understanding of food fraud among consumers in Klang Valley, Malaysia. JoSTE **2**, 31–40 (2021).
2. M.J. Walker, S. Cowen, K. Gray, P. Hancock, D.T. Burns, Honey authenticity: the opacity of analytical reports - part 1 defining the problem. NPJ Sci. Food **6**, 11 (2022).
3. P. Dais, E. Hatzakis, Quality assessment and authentication of virgin olive oil by NMR spectroscopy: a critical review. Anal. Chim. Acta **765**, 1–27 (2013).
4. C. Di Anibal, M.S. Rodriguez, L. Albertengo, UV-visible spectroscopy and multivariate classification as a screening tool to identify adulteration of culinary spices with Sudan I and blends of Sudan I + IV dyes. Food Anal. Methods **7**, 1090–1096 (2013).
5. S. Manasha, M. Janani, Food adulteration and its problems (intentional, accidental and natural food adulteration). Int. J. Res. Finance Manage. **6**, 131-140 (2016).
6. Y. Lu, T. Bao, J. Mo, J. Ni, W. Chen, Research advances in bioactive components and health benefits of jujube (*Ziziphus jujuba* Mill.) fruit. J. Zhejiang Univ. Sci. B **22**: 431-449 (2021).
7. B. Li, M. Yu, W. Xu, L. Chen, J. Han, Comparison of PCR techniques in adulteration identification of dairy products. Agriculture **13**, 1450 (2023).
8. Y. Jiao, Z. Li, X. Chen, S. Fei, Preprocessing methods for near-infrared spectrum calibration. J. Chemom. **34**, e3306 (2020).
9. K.E. Loh, Y.S. Chin, I.S. Ismail, H.Y.Tan, Rapid characterisation of xanthine oxidase inhibitors from the flowers of *Chrysanthemum morifolium* Ramat. using metabolomics approach. Phytochem Anal. 33:12-22 (2022).

10. X. Xia, F. Li, H. Ran, J. Zhao, X. Lei, L. Lei, J. Wen, G. Xiao, K. Zeng, J. Ming, Effect of jujube kernel powder addition on moisture absorption performance, color stability, texture properties and agglomeration characteristics of jujube powder. LWT, **174**, 114452 (2023).
11. M. Lasalvia, V. Capozzi, G.A. Perna, Comparison of PCA-LDA and PLS-DA techniques for classification of vibrational spectra. Appl. Sci. **12**, 5345 (2022).
12. Q. Zhang, L. Wang, Z. Wang, Z. Liu, Z. Zhao, G. Zhou, M. Liu, P. Liu, P. Variations of the nutritional composition of jujube fruit (*Ziziphus jujuba* Mill.) during maturation stages. Int. J.Food Prop. **23**, 1066–1081 (2020).