Non-destructive Detection of the Freshness of Garlic Powder Using Near-infrared (NIR) Spectroscopy and Chemometrics Techniques

Reza Mohammadigol[1*] and Reza Shahhoseini[2]

[1] *Department of Biosystem Mechanics Engineering, Arak University, Arak, Iran, P.O.Box: 38156-8-8349*
[2] *Department of Medicinal Plants, Arak University, Arak, Iran, P.O.Box: 38156-8-8349*

* Corresponding author: Email: r-mohammadigol@araku.ac.ir

ABSTRACT

Garlic (*Allium sativum* L.) is a valuable medicinal plant that is widely used in pharmaceutical, food, cosmetic, and hygiene industries due to the various products it contains in the form of extracts and powders. Non-destructive and rapid methods for assessing food quality are of interest to industries and research. In the present study, the garlic powder was determined by spectrometry in the range of 936 to 1660 nm and chemometric techniques. For this purpose, 120 spectra were recorded from the prepared samples of garlic powders during the storage period of 3, 90, and 360 days. The effects of SNV, MSC, D1+SG, and D2+SG preprocessing methods on the performance of ANN, SVM, and KNN classifiers were investigated. The principal component analysis (PCA) technique was used to reduce the spectral variables, and the first 4 principal components (PCs) were considered as the input of the models. The D1+SG preprocessing showed the greatest effect on the identification of the spectra of the garlic powder samples. Results showed that the highest classification accuracy of 96.88% was achieved in all the 3 classifiers. The results of the present study confirm the feasibility of using the near-infrared (NIR) technique and chemometrics for the rapid identification of the freshness of garlic powder.

Keywords: Freshness, Garlic powder, Near-infrared, Nondestructive, Spectroscopy

Abbreviations

A	Absorbance
ANN	Artificial Neural Networks;
D1	First Derivative;
D2	Second Derivative;
FTIR	Fourier Transform Infra-Red
KNN	k-Nearest Neighbors;
LS-SVM	Least-Squares Support Vector Machines
MIR	Mid-Infrared Radiation
MSC	Multiplicative Scatter Correction;
N	Total number of confusion matrix samples
NIR	Near Infrared Radiation
PC	Principle Component;
PC1	First Principle Component;
PC2	Second Principle Component;
PC3	Third Principle Component;
PCA	Principle Components Analysis;
PCR	Principle Component Regression
PLSR	Partial Least Squares Regression
R	Reflectance
SG	Savitzky-Golay;
SNV	Standard Normal Variate;
SVM	Support Vector Machine
TC	Number of correctly classified samples
Vis	Visible

INTRODUCTION

Allium sativum L. belonging to the *Liliaceae* family, is a valuable medicinal plant that is widely used in various pharmaceutical, food, cosmetic and, hygienic industries [1, 2]. The most important medicinal organ of this species is bulblet, which is used as fresh and dried, extract, oil, slice, and powder [3]. Garlic powder is one of the most important spice, which has great commercial importance and is widely used in the food and pharmaceutical industries [4]. This valuable plant grows all around the world and is considered as one of the most important plants among onion species [5]. Garlic contains compounds such as carbohydrates, starch, protein, vitamins, minerals, and mucilage [6, 2], as well as various organosulfur and amino acid compounds [7]. These compounds have antibacterial, antioxidant, anticancer, immunomodulatory, and many other therapeutic properties. These functions are influenced by the conditions and storage time of garlic powder and extract. [8, 9, 10, 11, 12, 13].

The development and progress of optical equipment has led to the reduction of dimensions and the number of components of optical systems. Therefore, the cost of using them is decreasing [14]. In Vis-NIR spectroscopy, spectroscopic modes include reflectance, transmittance, transeflectance, and intractance, where the light source and receiver change position relative to each other [15]. The best spectroscopic method is related to the characteristics of the investigated materials; for example, the transmission or transmission-reflection mode is the best choice for liquid samples, and the reflection mode is mainly used for powders [16].

Daszykowski *et al*. (2023) investigated the rapid and non-destructive detection and measurement of adulteration of garlic powder (corn starch and corn flour) by modeling NIR reflectance spectra [17]. They prepared different mixtures of garlic powder with starch and corn flour and performed spectroscopy in the range of 4000 to 100000 cm^{-1}. Their results showed that the NIR spectroscopy can be used to predict the level of adulteration in garlic powder. Also, the PLSR method was superior to the PCR model according to the model evaluation indicators.

The possibility of detecting the presence of corn starch in garlic powder with FTIR spectroscopy and PLSR model was studied by Lohumi *et al*. (2015). Reflectance spectra were used in the range of 650-4000 cm^{-1}. They concluded that non-destructive detection of corn starch in garlic powder is possible [18]. Wang *et al*. (2019) examined the potential of spectroscopic techniques (NIR and MIR) and chemometrics in determining whether strawberry powders were prepared from stored fruit (0, 2, 4, 15, 20, and 27 days) or fresh fruit. The separation rate of 100% was obtained based on the evaluation of 111 samples using PLSR and LS-SVM models, which indicated the great potential of this method [19]. Due to the high consumption of garlic powder in food and other industries, no research has been reported on measuring the freshness of this widely used product with non-destructive methods, including near infrared spectroscopy (936-1660 nm). According to the increasing trend of making internal and external optical spectroscopic instruments, the present study was conducted to improve the evaluation techniques of food powders.

MATERIAL AND METHODS

Preparation of Samples

The required samples were obtained from garlic (white garlic - a landrace native from Arak, harvesting in early August) grown in the climatic conditions of Markazi Province, Arak city (latitude 34°04′N, longitude 49°40′E, and altitude 1743 m), and propagated with uniform healthy cloves free from diseases and pests. At each stage, after peeling and separating the bulblets from each other, slices with a thickness of 2-3 mm were prepared. After drying in the shade (temperature of 25-30 °C for a week) and away from direct light, the dried slices were powdered with a laboratory mill (cradle- Ts 1300). All the powders were passed through a 50 mesh sieve and were prepared in three periods of 3 days (A_1), 90 days (A_2), and 360 days (A_3) using laboratory mill. From the beginning, all the slices were powdered and samples were taken from the initial powder in three time intervals. The powders were stored in a zipped aluminum envelope in the refrigerator until the test

Spectroscopy

Diffuse reflectance spectra were obtained by irradiating light at an angle of 45° [20]. A Portable Flame-NIR spectrometer (Ocean Optics Company, USA) was used in a wavelength range of 936-1660 nm (Table 1). Before starting the spectroscopy, the light source was kept on for more than half an hour in order to remove the

non-uniformity and noises caused by the heating and heat of the light source. After this step, the absorption spectra were drawn in the software according to the existing relationship (A=Log 1/R) from the reflection spectra.

QP400 VIS-NIR optical fibers were used to transmit and receive light. The fibers were placed in a fixed position relative to each other (angle of 45°), and each spectrum was obtained from the average of 4 scans. A total of 120 reflection spectra were taken from the samples. Before spectroscopy and after taking 10 spectra, the standard background and white light (barium sulfate) were removed and stored again. An aluminum probe was used to fix the angle and distance of the fibers to the powder surface when taking the spectrum. The corresponding diagram is shown in Fig. 1.

Table 1 Characteristics of flame-NIR spectrometer

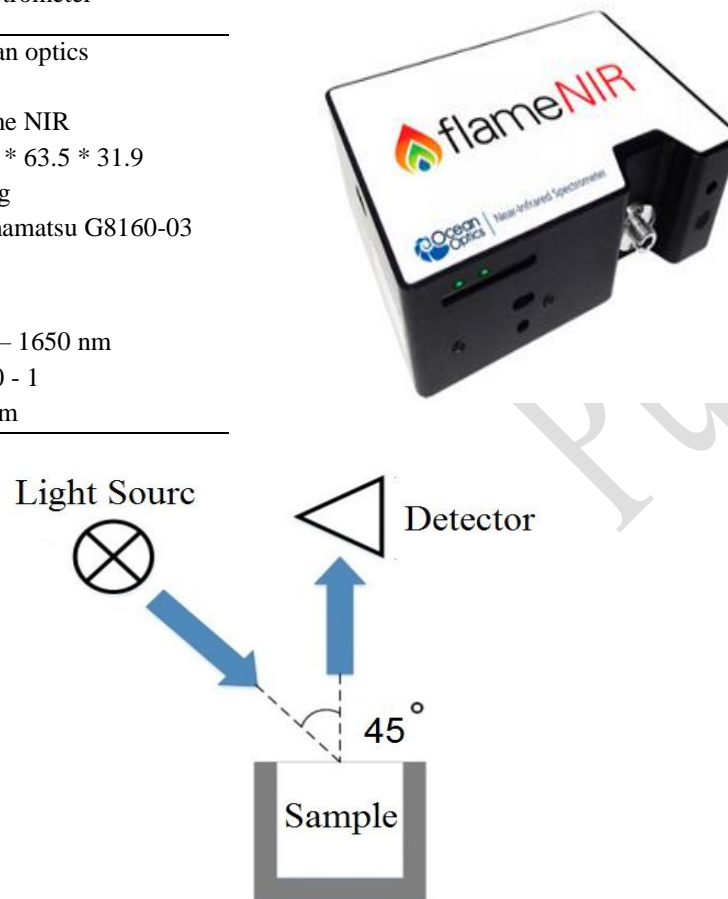| Characteristics	Spectrometer
Manufacturing company	Ocean optics
Model	Flame NIR
Dimensions	88.9 * 63.5 * 31.9
Weight	265 g
Detector	Hamamatsu G8160-03
Pixel number	128
Working range	936 – 1650 nm
Signal to noise ratio	6000 - 1
Wavelength separation	10 nm

Fig. 1 Schematic diagram of spectral acquisition

Chemometrics – Preprocessing

Raw NIR spectra contain significant noise due to the variation of particle size, issues related to the light source and receiver, and other unwanted factors. Therefore, different preprocessing methods are used to extract chemical information from spectral data [21]. Unfortunately, there is no specific guide in choosing preprocessing methods [17]. Several common preprocessing methods were used in this research. Preprocessing techniques of SNV and MSC are employed to remove the effects caused by the difference in particle size and the change in the distance between the light source and the surface of the sample [22, 23, 24]. The derivation of the spectra leads to the enhancement of the peak points and the noises, so usually after taking the derivative, smoothing is done [25]. The Savitzky-Golay smoothing method is one of the common methods used after derivation. In the current research, the effect of the first and second derivatives on the spectral data was investigated, and smoothing was performed using the SG method.

Principal component analysis (PCA)

Use of principal component analysis technique creates new variables, each of which is a linear combination of several main independent variables. The new reduced variables are the principal components, and the first principal component covers the highest variance, and the second principal component covers the data that is not present in the first component, and this process is repeated in the subsequent components as well [26]. The first to fourth principal components formed the input of the classifiers in this research.

Classifiers

Classification models have been used in various research fields [27, 28, 29, 30]. In the present study, the potential of ANN, SVM, and KNN models was evaluated in the separation of powders based on spectrum. It is necessary to validate the created models, so about 25% of the spectra (32 spectra) were randomly considered for validation before modeling by the software, and the calibration of the models was performed with the remaining spectra (88 spectra). The overall accuracy index (%) of the validation samples (Equation 1) was used to evaluate the classifiers.

Where TC is the number of correctly classified samples and N is the total number of confusion matrix samples of the validation data set. Ocean view 1.6.3 was used for spectra acquisition, and unscramble X10.4 was employed for preprocessing methods. IBM Modeler 18 was used for principal components extraction and classification.

RESULTS AND DISCUSSION

The total absorption spectra of powders and the average spectra of three types of powder freshness in the range of 936 to 1660 nm are shown in Figure 2. The similarity between the obtained spectra was very high, but the amount of absorption in some wavelengths was different. The obtained spectra had a very good conformation with the spectra reported by Daszykowski *et al.* [17].
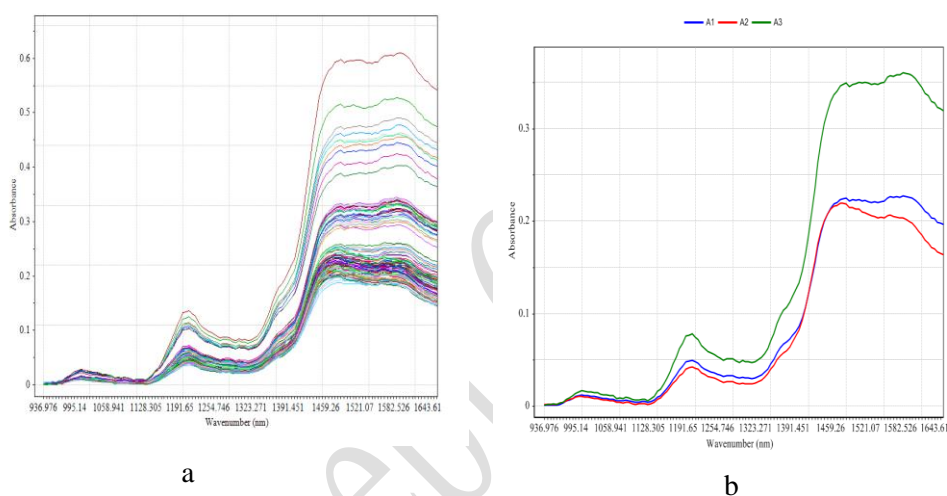

Fig. 2 All samples (garlic powders) spectra (a) and Mean spectra (b) of 3 days (A$_1$), 90 days (A$_2$), and 360 days (A$_3$)
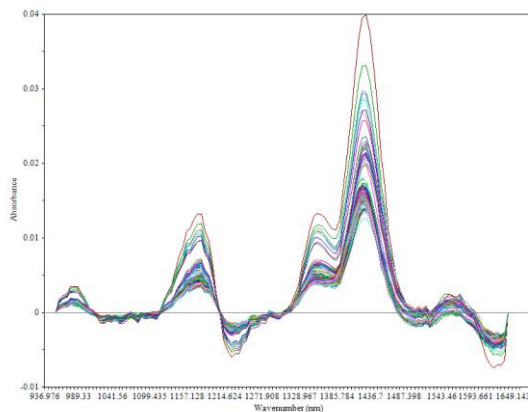

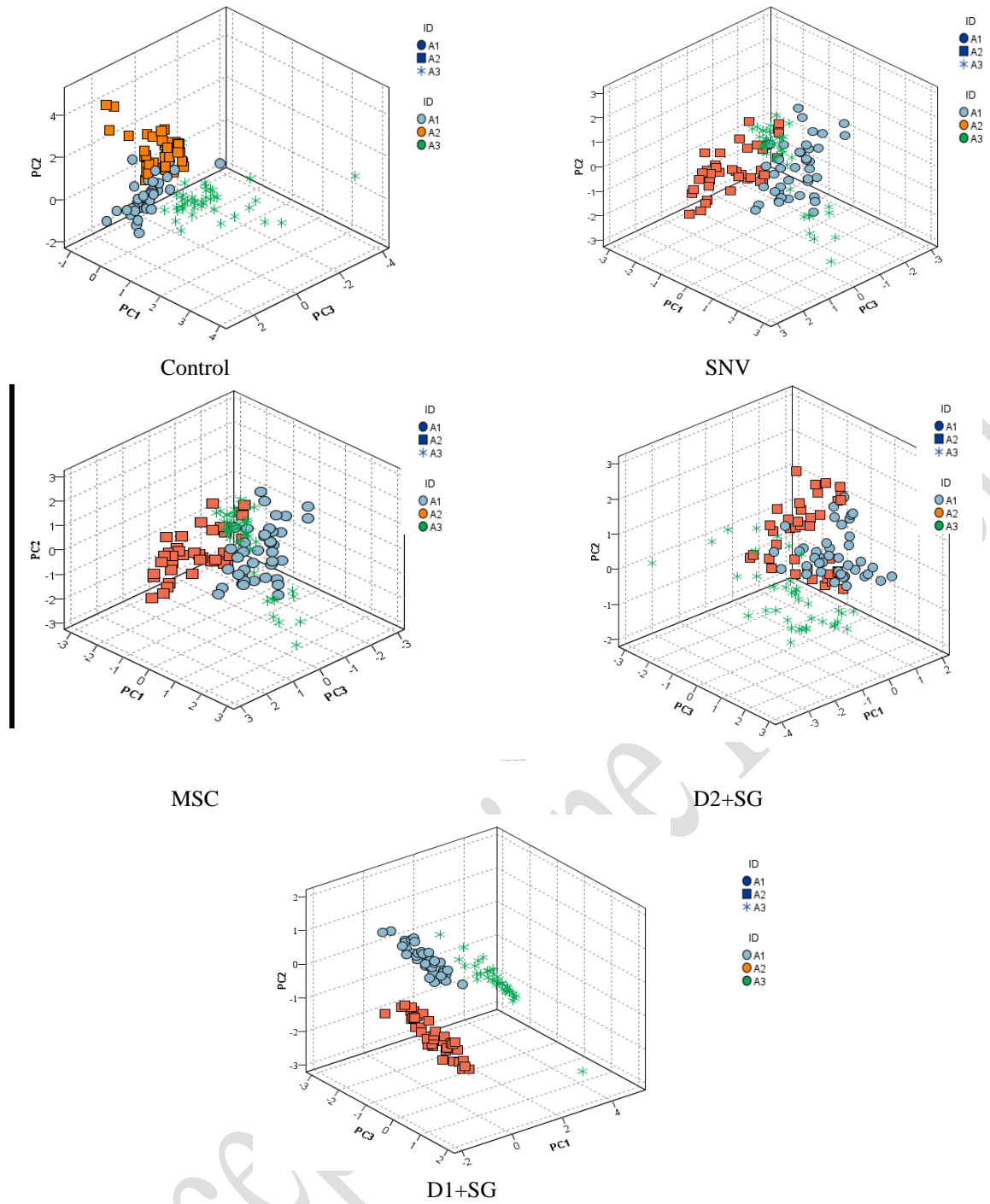**Fig. 3** The effect of D1+ SG preprocessing on all acquired spectra

Fig. 4 The effect of different preprocessing on the scattering plot of spectra (in PC_1, PC_2 and PC_3 coordinate)

Table 2 The overall accuracy (%) by classifiers in the training and testing samples based on different preprocessing methods

Spectral preprocessing	KNN		SVM		ANN	
	Train	Test	Train	Test	Train	Test
No Preprocessing	95.45	84.38	95.45	93.75	95.45	90.62
MSC	95.45	93.75	97.73	93.75	98.86	96.88
SNV	98.86	96.88	96.59	93.75	100	93.75
D1+SG	100	96.88	100	96.88	100	96.88
D2+SG	97.73	96.88	98.86	93.75	96.59	87.5

(Eq. 1)   Accuracy (%)= (TC/N)×100

Garlic contains some compounds including sulfur, flavonoids, allicin, amino acids, polyphenols, water-soluble compounds, and fats. The content of these compounds in garlic is relatively low, and therefore the interpretation of the spectra is complicated due to the possible overlap of the spectra of the mentioned compounds. The effective absorption bands found in the collected spectra (in the range of 936-1660 nm) were as follows: (1) 1120-1290 nm band caused by the second overtone of the C-H bond and (2) 1320-1520 nm band caused by the first overtone of the N-H bond and also the first overtone of the O-H bond [31]. The peak created at the wavelength of 1420 nm was reported to be caused by the first overtone of the O-H bond of water [32].

To compare the effect of preprocessing methods on the separability of sample spectra from each other (Fig. 3), the distribution of sample spectra in the coordinates of the first, second, and third principal components (PCs) is shown in Fig. 4. The use of PCA method and dispersion in the coordinates of PCs have been reported in various researches [33,24, 26]. The graphs show that there was good separation, especially after D1+SG preprocessing.

Classification

After PCA, the first to fourth principal components were selected as the inputs of all classifiers. The results of model calibration and validation are shown in Table 2. The training and test data sets were equal in all the classifiers. The highest overall accuracy of the correct classification of the model test samples was 96.88% which was obtained in all classifiers and using D1+ SG [34].

CONCLUSION

The near-infrared spectra (936-1660 nm) acquired from garlic powder samples have shown a relatively small number of peaks, which are probably caused by the overlap of light absorption of overtones and the bonds of various substances in the powder. Examining the effect of SNV, MSC, D1+SG, and D2+SG preprocessing has shown that the highest separation accuracy was achieved in D1+SG. The highest overall accuracy of correct separation was 96.88% and this number was suitable for practical applications. The results of the present study indicated the potential of using the non-destructive test of NIR spectroscopy to evaluate the freshness of garlic powder. Conducting similar studies for different storage periods of garlic powder and other cultivars of garlic, as well as spectroscopy in the entire near-infrared range (up to 2500 nm) is suggested as further complementary studies.

Conflict of Interest

The authors declare that there is no conflict of interest.

REFERENCES

1. Tudu C.K., Dutta T., Ghorai M., Biswas P., Samanta D., Oleksak P., Dey A. Traditional uses, phytochemistry, pharmacology and toxicology of garlic (*Allium sativum*), a storehouse of diverse phytochemicals: A review of research from the last decade focusing on health and nutritional implications. Frontiers in Nutrition. 2022; 9: 1-19. https://doi.org/10.3389/fnut.2022.929554

2. Amarakoon S., Jayasekara D. A review on garlic (*Allium sativum* L.) as a functional food. J. Pharmacognosy and Phytochemistry. 2017; 6(6): 1777-1780.

3. Suleria H.R., Butt M.S., Khalid N., Sultan S., Raza A., Aleem M., Abbas M. Garlic (*Allium sativum*): diet based therapy of 21st century–a review. Asian Pacific J. Tropical Disease. 2015; 5(4): 271-278. https://doi.org/10.1016/S2222-1808(14)60782-9

4. Sharma G.P., Prasad S. Comparison of convective and microwave-convective drying of garlic: kinetics and energy consumption. J. Food Sci. Technol. 2002; 39 (6): 603-608.

5. Kamenetsky R. Garlic: Botany and Horticulture. In: Horticulture Reviews, Ed. Janick J. John Wiley and Sons Publishing, New Jersey, U.S.A. 2007; 33: 123-138. Doi:10.1002/9780470168011.ch2

6. El-Saber Batiha G., Magdy Beshbishy A.G., Wasef L., Elewa Y.H., Al-Sagan A., Abd El-Hack M.E., Prasad Devkota H. Chemical constituents and pharmacological activities of garlic (*Allium sativum* L.): A review. Nutrients. 2020; 12(3): 1-21. https://doi.org/10.3390/nu12030872

7. Martins N., Petropoulos S., Ferreira I.C. Chemical composition and bioactive compounds of garlic (*Allium sativum* L.) as affected by pre-and post-harvest conditions: A review. Food Chem. 2016; 211: 41-50. https://doi.org/10.1016/j.foodchem.2016.05.029

8. Zhu D., Sadat A., Joye I.J., Vega C., Rogers M.A. Scientific gastronomy: On the mechanism by which garlic juice and allicin (thio-2-propene-1-sulfinic acid S-allyl ester) stabilize meringues. Food Chem. 2024; 431: 1-12. https://doi.org/10.1016/j.foodchem.2023.137121

9. Ravindra J., Yathisha U.G., Nanjappa D.P., Kalladka K., Dhakal R., Chakraborty A., Chakraborty. Allicin extracted from *Allium sativum* shows potent anti-cancer and antioxidant properties in zebrafish. Biomedicine and Pharmacotherapy. 2023; 169: 1-9. https://doi.org/10.1016/j.biopha.2023.115854

10. Salehi B., Zucca P., Orhan I.E., Azzini E., Adetunji C.O., Mohammed S.A., Ahmad Z. Allicin and health: A comprehensive review. Trends in Food Sci.Technol. 2019; 86: 502-516. https://doi.org/10.1016/j.tifs.2019.03.003

11. Naheed Z., Cheng Z., Wu C., Wen Y., Ding H. Total polyphenols, total flavonoids, allicin and antioxidant capacities in garlic scape cultivars during controlled atmosphere storage. Postharvest Biology and Technology. 2017; 131: 39-45. https://doi.org/10.1016/j.postharvbio.2017.05.002

12. Gonzalez, R.E., Burba, J.L., Camargo, A.B. A physiological indicator to estimate allicin content in garlic during storage. J. Food Biochemistry. 2013; 37(4): 449-455. https://doi.org/10.1111/j.1745-4514.2011.00647.x

13. Hughes J., Collin H.A., Tregova A., Tomsett A.B., Cosstick R., Jones M.G. Effect of low storage temperature on some of the flavour precursors in Garlic (*Allium Sativum*). Plant Foods for Human Nutrition. 2006; 61: 78-82. https://link.springer.com/article/10.1007/s11130-006-0018-4

14. Ambrose A., Cho B.K. A review of technologies for detection and measurement of adulterants in cereals and cereal products. Journal of Biosystems Engineering. 2014; 39(4): 357-365. http://dx.doi.org/10.5307/JBE.2014.39.4.357

15. Cortés V., BlascoJ., Aleixos N., Cubero S., Talens P. Monitoring strategies for quality control of agricultural products using visible and near-infrared spectroscopy: A review. Trends in Food Sci. Technol. 2019; 85: 138-148. https://doi.org/10.1016/j.tifs.2019.01.015

16. Sánchez-Paternina A., Román-Ospino A.D., Martínez M., Mercado J., Alonso C., Romañach R.J. Near infrared spectroscopic transmittance measurements for pharmaceutical powder mixtures. J. Pharmaceutical and Biomedical Analysis. 2016; 123: 120-127. https://doi.org/10.1016/j.jpba.2016.02.006

17. Daszykowski M., Kula M., Stanimirova I. Quantification and detection of ground garlic adulteration using fourier-transform near-infrared reflectance spectra. Foods. 2023; 12(18): 1-14. https://doi.org/10.3390/foods12183377

18. Lohumi S., Lee S., Cho B.K. Optimal variable selection for Fourier transform infrared spectroscopic analysis of starch-adulterated garlic powder. Sensors and Actuators B: Chem. 2015; 216: 622-628. https://doi.org/10.1016/j.snb.2015.04.060

19. Wang D., Wei W., Lai Y., Yang X., Li S., Jia L., Wu D. Comparing the potential of near-and mid-infrared spectroscopy in determining the freshness of strawberry powder from freshly available and stored strawberry. J. Analytical Methods in Chem. 2019; 2019: 1-10 https://doi.org/10.1155/2019/2360631

20. Rodríguez S.D., Rolandelli G., Buera M.P. Detection of quinoa flour adulteration by means of FT-MIR spectroscopy combined with chemometric methods. Food Chem. 2019; 274: 392-401. https://doi.org/10.1016/j.foodchem.2018.08.140

21. Kar S., Tudu B., Jana A., Bandyopadhyay R. FT-NIR spectroscopy coupled with multivariate analysis for detection of starch adulteration in turmeric powder. Food Additives and Contaminants Part A. 2019; 36(6): 863-875. https://doi.org/10.1080/19440049.2019.1600746

22. Nicolai B.M., Beullens K., Bobelyn E., Peirs A., Saeys W., Theron K.I., Lammertyn J. Nondestructive measurement of fruit and vegetable quality by means of NIR spectroscopy: A review. Postharvest Biology and Technol. 2007; 46(2): 99-118. https://doi.org/10.1016/j.postharvbio.2007.06.024

23. Jamshidi B., Minaei S., Mohajerani E., Ghassemian H. Reflectance Vis/NIR spectroscopy for nondestructive taste characterization of Valencia oranges. Computers and Electronics in Agriculture. 2012; 85: 64-69. https://doi.org/10.1016/j.compag.2012.03.008

24. Teye E., Amuah C.L., McGrath T., Elliott C. Innovative and rapid analysis for rice authenticity using hand-held NIR spectrometry and chemometrics. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2019; 217: 147-154. https://doi.org/10.1016/j.saa.2019.03.085

25. Ishikawa S.T., Gulick V.C. An automated mineral classifier using Raman spectra. Computers and Geosciences. 2013; 54: 259-268. https://doi.org/10.1016/j.cageo.2013.01.011

26. Callao M.P., Ruisánchez I. An overview of multivariate qualitative methods for food fraud detection. Food Control. 2018; 86: 283-293. https://doi.org/10.1016/j.foodcont.2017.11.034

27. Shafiee S., Minaei S. Combined data mining/NIR spectroscopy for purity assessment of lime juice. Infrared Physics and Technology. 2018; 91: 193-199. https://doi.org/10.1016/j.infrared.2018.04.012

28. Kafle G.K., Khot L R., Jarolmasjed S., Yongsheng S., Lewis K. Robustness of near infrared spectroscopy based spectral features for non-destructive bitter pit detection in honeycrisp apples. Postharvest Biology and Technology. 2016; 120: 188-192. https://doi.org/10.1016/j.postharvbio.2016.06.013

29. Amuah C.L., Teye E., Lamptey F.P., Nyandey K., Opoku-Ansah J., Adueming P.W. Feasibility study of the use of handheld NIR spectrometer for simultaneous authentication and quantification of quality parameters in intact pineapple fruits. J. Spectroscopy. 2019; 2: 1-9. https://doi.org/10.1155/2019/5975461

30. Kaiyan L., Chang L., Huiping S., Junhui W., Jiek C. Review on the Application of Machine Vision Algorithms in Fruit Grading Systems. Paper presented at the Emerging Trends in Intelligent and Interactive Systems and Applications: Proceedings of the 5th International Conference on Intelligent, Interactive Systems and Applications. 2021; 271-280. https://doi.org/10.1007/978-3-030-63784-2_34

31. Acri G., Testagrossa B., Vermiglio G. FT-NIR analysis of different garlic cultivars. J. Food Measurement and Characterization. 2016; 10: 127-136. https://doi.org/10.1007/s11694-015-9286-8

32. Wadood S.A., Guo B., Zhang X., Wei Y. Geographical origin discrimination of wheat kernel and white flour using near-infrared reflectance spectroscopy fingerprinting coupled with chemometrics. International J. Food Sci. Technol. 2019; 54(6): 2045-2054. https://doi.org/10.1111/ijfs.14105

33. Horn B., Esslinger S., Pfister M., Fauhl-Hassek C., Riedl J. Non-targeted detection of paprika adulteration using mid-infrared spectroscopy and one-class classification–Is it data preprocessing that makes the performance. Food Chem. 2018; 257:112-119. https://doi.org/10.1016/j.foodchem.2018.03.007

34. Wanitchang P., Terdwongworakul A., Wanitchang J., Nakawajana N. Non-destructive maturity classification of mango based on physical, mechanical and optical properties. J. Food Engineering. 2011; 05(3): 477-484. https://doi.org/10.1016/j.jfoodeng.2011.03.006