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Preliminary study non-destructive sorting techniques for pepper (*Capsicum annuum L.*) using odor parameter

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ABSTRACT

Almost all fruits and vegetables sold in modern society are sorted and labeled, making it easier for customers to recognize the quality of the product, leading to more regular distribution and supply. Consequently, it facilitates the initial packaging and transportation of the product, and farmers will benefit from the added value. Therefore, it is necessary to develop sorting via affordable machines and easy to operate at the current technology level. Since electronic nose technology is new-emerging, it can be used in food quality control systems. In this study, the variety Padrón (*Capsicum annuum* L.) was evaluated. PCA, LDA, SVM and ANN methods were used to classify sweet and hot peppers. According to PCA, 98% of the variance in the data was detected by the first three components. SVM, ANN, and LDA all showed 100% accuracy in classification. The amounts of capsaicin in two types of sweet and hot peppers were predicted well and with high accuracy by three different methods: MLR, PCR, and PLSR. With this method, it is possible to reliably separate sweet and hot peppers based on odor parameters, and it is also possible to develop sorting machines according to the characteristics of odor.

1. Introduction

Pepper (*Capsicum annuum* L.) is one of the most consumed vegetables in the world, containing a large amount of vitamins C and A, as well as minerals. Therefore, the consumption of about 60–80 g of pepper per day can provide 100 and 25% of the recommended daily amount of vitamin C and A, respectively. In addition, this horticultural product contains considerable levels of other health-promoting substances with antioxidant activity, including carotenoids, flavonoids, and other polyphenols (Palma, Terán, Contreras-Ruiz, Rodríguez-Ruiz, & Corpas, 2020).

There is a great variety of peppers, differing essentially in shape, size, thickness of the flesh (pericarp), and final color at the stages of ripeness. Depending on their capsaicin content, pepper fruits are classified as sweet or hot in terms of their cooking and food properties (Fratianni et al., 2020).

The real difference between sweet and hot peppers is therefore found entirely in the taste: on the on hand, hot peppers contain capsaicin, a pungent component that burns not only the tongue, but also the fingers. Their burning taste is so overwhelming few people notice their underlying flavors. On the other hand, sweet peppers, contains no capsaicin or very, very little of it, so richer, sweeter flavors come to the forefront. Capsaicin belongs to the genus Capsicum, which can cause pungency. These fruits are rated using the Scoville scale, which assigns a value to each variety. On this scale, the maximum value for the hottest pepper variety is about 106 × 3, and pure capsaicin is 16 × 106 (Kopta, Sekara, Pokluda, Ferby, & Caruso, 2020; Palma et al., 2020).

According to pharmacological research, capsaicinoids, especially

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capsaicins, have a variety of biological and physiological functions in vitro and therefore act as antioxidants, stimulants of energy metabolism, fat accumulating suppressors, and anti-inflammatory drugs (Liu et al., 2020).

Pepper fruits also have a characteristic ripening process determined by their color changing from green to red, yellow, orange or purple, depending on the variety. The process involves the breakdown of chlorophyll and the synthesis of new carotenoids and anthocyanins, the release of organic volatiles, the synthesis of new proteins and the breakdown of existing proteins, and the softening of the cell wall and so on (L. Zhang et al., 2018).

The quality of fresh pepper depends primarily on consumer acceptance, which is determined primarily by color, pungency, and aroma. Aroma plays an essential role in determining the sensory characteristics of these products. Volatile organic compounds (VOCs) are generally associated with the taste and aroma of foods and are important factors in assessing consumer acceptance or rejection. Consequently, food quality, originality, purity, and origin can be evaluated by determining VOC (Korkmaz, Hayaloglu, & Atasoy, 2017). It has been reported that the aroma of peppers is closely related to their volatile components (Buttery, Seifert, Guadagni, & Ling, 1969).

Agricultural product sorting is a post-harvest activity based on dimensions, shape, and color. The grading of agricultural products, especially fruits and vegetables, has become a global trade. It is important in several ways, such as to control pests and diseases during the post-harvest process, to create added value for the farmer, and to allow the consumer to make a choice. National and international standards must be met when preparing products for export. Sorting and packaging of agricultural products is one of the ways in which developed countries add value to their products and increase their competitiveness in global markets (Nalbandi, Seiiedlou, Beranki, & Farzand Ahmadi, 2021).

Almost all fruits are sold in international markets sorted and labeled, which makes it easier for customers to recognize the quality of the product and ensures more regular distribution and supply (Nalbandi et al., 2021).

Currently, pepper classification is increasing in importance owing to international markets offering a price advantage for high-quality products. A product's homogeneity and appearance have a significant positive effect on a consumer's decision to purchase it. For this reason, agricultural produce is categorized for the final consumer. Classifying peppers is a time-consuming, manual task. One method of doing this is using trained inspectors to select and sort chilis; however, this process is quite subjective (Cruz-Domínguez et al., 2021).

To classify sweet and hot peppers and meet standards, sorting must be unique and accurate, this process is a time-consuming, manual task. One method of doing this is using trained inspectors to select and sort chilis; however, this process is quite subjective (Cruz-Domínguez et al., 2021). Hence, this labor-intensive grading leads to bias due to human error and inconsistencies in classification. A technology for unambiguous and accurate classification of dried pepper quality is needed to minimize errors during sorting (Azis, Khuriyati, & Suyantohadi, 2021).

Traditional methods for determining the quality of fresh-cut vegetables are based on chemical, microbiological, physical, and sensory indicators such as phenolic compounds, mold and bacterial counts, texture, and color. Most conventional methods are time consuming and require qualified personnel. Gas chromatography-mass spectrometry (GC-MS) has also been used to analyze volatile compounds in food. However, rapid detection of volatile profiles is not feasible (Chen, Zhang, Bhandari, & Guo, 2018).

E-nose, not only mimics digitally the human olfaction but also is capable of detecting and classifying the toxic vapors through a complicated method. Electronic nose includes a series of electrochemical sensors, which can detect simple or complicated smells. Generally, E-nose evaluates a mixture of smells released from a sample and is a reliable, nondestructive, cost-effective, and portable method with high feasibility and speed as well as simple use (Karami, Rasekh, & Mirzaee-Ghaleh, 2020b). Using a computer system, the responses are collected and analyzed using multivariate data analysis methods (Karami, Rasekh, & Mirzaee–Ghaleh, 2020). For the analysis of sensor response data, there are several methods such as cluster analysis (CA), principal component analysis (PCA), linear discriminant analysis (LDA), etc., which are linear approaches. While fuzzy logic, artificial neural networks (ANN), and probabilistic neural networks (PNNs) are nonlinear methods (Loutfi, Coradeschi, Mani, Shankar, & Rayappan, 2015).

Electronic noses are an effective method for measuring the degree of ripeness and other quality indicators of fruits and vegetables. Recently, these sensors have been investigated for their ability to detect the volatile odor associated with fruit ripening during storage (Gomez, Wang, Hu, & Pereira, 2007). The electronic tool was used to identify volatile components of fruits and vegetables, including mango (Lebrun, Plotto, Goodner, Ducamp, & Baldwin, 2008), tomato (Gomez, Wang, Hu, & Pereira, 2008), potato (Khorramifar, Rasekh, Karami, Malaga-Toboła, & Gancarz, 2021; Rutolo, Clarkson, & Covington, 2018), apple (Ezhilan, Nesakumar, Jayanth Babu, Srinandan, & Rayappan, 2018), peach (Benedetti, Buratti, Spinardi, Mannino, & Mignani, 2008), tea (Borah et al., 2008), green bell pepper (Chen et al., 2018), broccoli (Ezhilan, Nesakumar, Babu, Srinandan, & Rayappan, 2019), coffee (Gonzalez Viejo, Tongson, & Fuentes, 2021), and saffron (Heidarbeigi et al., 2015).

According to today's standards, capsaicin is one of the determinants of pepper pungency, which is directly related to the odor of the sample. Because it is important to distinguish hot peppers from sweet ones, we used an electronic nose to distinguish sweet peppers from hot peppers in this study. Research has shown that the electronic nose is able to discriminate between VOCs products. As this technology is emerging and has high accuracy, it can be used in food quality control systems. The purpose of this study is to provide some base research for further investigations on practical developments in large-scale hot and sweet pepper classification. Thus, the predominant contribution of this study is to present a new alternative for classifying peppers based on hot and sweet by combining E-nose with chemometrics methods. Capsaicin index will also be used to model the spiciness and sweetness of peppers. The findings will benefit the field of agriculture by exploring new ways to classify hot and sweet peppers. To the best of our knowledge, such a study has not been conducted in this field to date. This approach represents an innovative, feasible, and economical alternative for farmers who require efficient pepper classification on a daily basis.

2. Materials and methods

2.1. Sample preparation

The variety used in this study was Padrón, a very popular species in Spain (Fig. 1). The green fruits showed no signs of ripening or discoloration and remained completely green.

The peppers weighed an average of 12 ± 2 g when fresh. The weights for the sweet and spicy varieties were determined by weighing 30 fruits each. The fruits to be examined were first evaluated by electronic nose, since it is a non-destructive method. Then, they were prepared for the study of capsaicin content. Hence, the pericarp (when the seeds and placenta were discarded) was removed (Fig. 1B), cut into small cubes (approximately 3–5 mm), frozen under liquid nitrogen, and kept at -80 °C. Biochemical parameters were determined three repetitions on 30 sweet and 30 spicy peppers.

2.2. Non-destructive evaluation method by electronic nose

The experiments were performed using an olfactory device fabricated in the Department of Biosystems Engineering, Mohaghegh Ardabili University (Rasekh, Karami, Wilson, & Gancarz, 2021b) (Fig. 2). This device consists of 9 metal oxide sensors for odor measurement (Rasekh, Karami, Wilson, & Gancarz, 2021a). The names of the sensors

Fig. 1. Representative pictures of plant materials used in this work. (a) Fruits from the Padrón varieties with different shape. (b) Different parts of the pepper fruit.

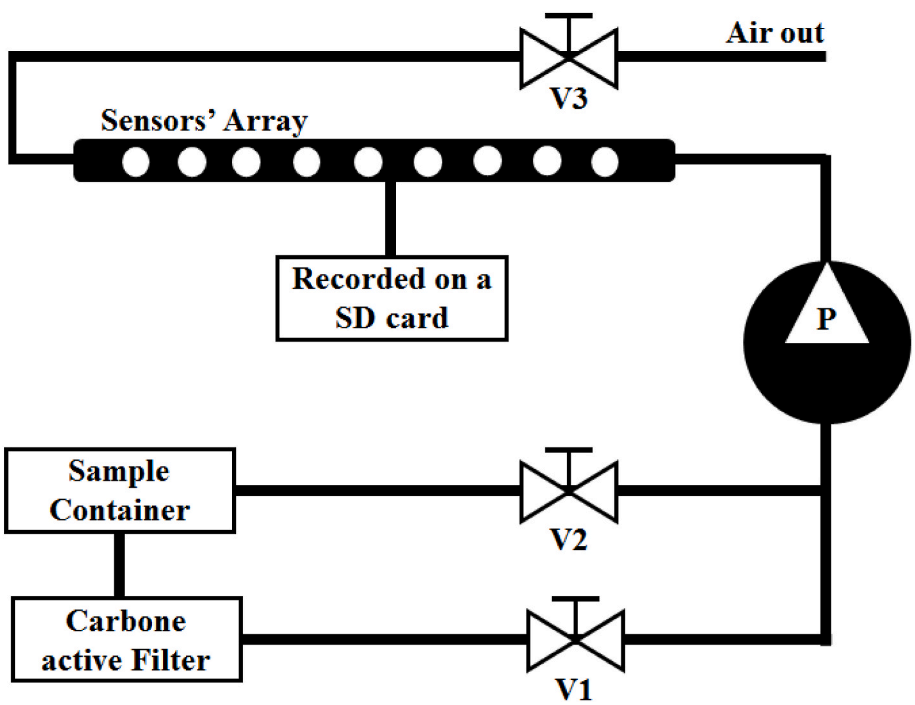

Fig. 2. Functional block diagram of the designed E-nose system.

(in order, with primary VOCs detected) are as follows: TGS813 (aliphatic alkanes), TGS822 (organic solvents), TGS2620 (alcohols, organic solvents), MQ3 (alcohols), MQ4 (urban gases and methane), MQ8 (hydrogen), MQ9 (carbon monoxide and combustible gases), MQ135 (ammonia, benzene, sulfides), and MQ136 (sulfur dioxide).

We prepared 60 samples to discriminate between hot and sweet peppers. Samples of each pepper were placed in a 50 mL sample chamber. The electronic nose operates in three stages. The first and last each require 100 s to clean the sensor housing and achieve the baseline response of the sensor. Before sampling, the sensors were cleaned with air (oxygen). In the last phase of cleaning, oxygen is again passed through the sensors and the odor inside the sample chamber is expelled by the pump. In the second phase, the odor evaluation stage, a diaphragm pump removes the sample odor and blows it onto the sensors. During this phase, the output voltage of each sensor changes according to its type and sensitivity level, which was also considered as 100 s. The volume of the sensor chamber containing the sensor array was 1414 cm^3. The inlet flow into the sensor chamber was 1.5 L per minute and the sampling chamber volume was 50 cm^3. Sensors within the sensor array respond differently to sample aromas (VOC emissions) from different volatile sample types. The trained system records the voltage response of the sensors. A fractional method was used to preprocess the obtained signals following the experiments. The room temperature was controlled at (20 ± 0.5 °C) during sample preparation and detection to help minimize changes in carrier input-air relative humidity prior to being filtered by the activated-charcoal carbon. At the end, the preprocessed data were evaluated and analyzed using chemometric methods (PCA, CA, LDA, SVM, ANN, PLSR, PCR and MLR) (Karami, Rasekh, & Mirzaee-Ghaleh, 2021; Rasekh & Karami, 2021a).

2.3. Chemometrics methods

Principal component analysis (PCA) is a multivariate statistical analysis method that can transform data into a new coordinate system. In other words, it can convert multivariate information into multiple synthetic variables. PC was used to determine patterns in the dataset and identify outliers by visual inspection. LDA, SVM, and ANN were used to classify sweet and hot peppers. All these methods were performed on electronic nose output data.

Linear detection analysis (LDA) is a statistical method to find a linear combination of features that can best distinguish two or more objects (McLachlan, 2004). To optimize the discrimination between groups, the LDA method maximizes the within-group variance while minimizing the within-group variance (Karami, Rasekh, & Mirzaee-Ghaleh, 2020a). In addition, Support Vector Machine (SVM) was used to classify linear and nonlinear data. C-SVM and Nu-SVM are used in this method to classify the data. In both cases, the difference is how to select the Nu, C and γ parameters to minimize the error function and express the problem as an optimization problem. Data with linear distribution was selected to obtain a high confidence margin (Karami et al., 2020b).

An artificial neural network (ANN) is made up of layers of process elements called neurons, consisting of three layers: an input layer, a hidden layer, and an output layer. Hidden layers may be increased as needed (Karami et al., 2020a; Rasekh & Karami, 2021b).

The amount of capsaicin was predicted using PLSR, PCR, and MLR. A multivariate statistical analysis method known as PLSR is suitable for solving prediction problems. Calibration models (PLSR), a Y reference, were developed to investigate the possibility of predicting chemical parameters using EN signals. Matrix X was taken as the E-nose signal and matrix Y as the capsaicin parameter (Abu-Khalaf, 2021). As with PCR, PLS is used to create models based on orthogonal reciprocal factors. The PLS method generates these factors in a different way than the PCR method. In the PCR method, the principal component is the matrix of variables, while in the PLS method, the relationship between the variables and the matrices of the dependent variables is considered. According to the PLS method, each factor describes the maximum covariance between the variables and the dependent variables. Covariance combines the high variance of the variable matrix with a high correlation of the desired trait (Szulczyński, Rybarczyk, & Gębicki, 2018). To evaluate the accuracy of the PLSR and PCR models, the following parameters were used: Correlation coefficient in the calibration set (R2cal), correlation coefficient in the validation set (R2val), root mean square error of the calibration set (RMSEcal), and root mean square error of the validation set (RMSEval). The PLS model can be considered an acceptable model if the number of PCs is low, and there are low values of RMSE and high values of R2. Also, the distance between the two sets is high (i.e., calibration and validation). Once the number of optimal PCs (C) was determined, their values were used to build the MLR model. The multiple linear regression (MLR) method was used to build predictive models for capsaicin content in sweet and hot peppers.

2.4. Determination of capsaicin by high-performance liquid chromatography-electrospray mass spectrometry (HPLC-ES/MS)

First, the samples were ground to powder under N_2 liquid. The plant material (0.5 g powder) was suspended in 2 mL acetonitrile (AcN) containing 100 ppm of N - [(3,4-dimethoxyphenyl) methyl] -4-methyl-octanamide (DMBMO). The mixtures were incubated as follows: 1 h at room temperature and in the dark with constant shaking, 65 °C and darkness for 1 h and brief shaking every 15 min, and 1 h at room temperature in the dark. Samples were then centrifuged at 16,000×g at room temperature for 15 min. The supernatant was passed through 0.22 μm polyvinylidene fluoride filters and used for HPLC-ESI/MS analysis by multiple reaction monitoring (MRM). An XBridge 2.1 × 10 mm pre-column and an XBridge 2.1 × 100 mm C18 3.5 μm column (Waters Corporation, Milford, MA, USA) were connected to an HPLC Allience 2695 system with a triple quadrupole mass micro API. Both were provided by Waters Company. Chromatography was performed at a flow rate of 0.3 mL/min at 35 °C for the column and 5 °C for the automatic injector; then 5 μL per sample was injected. The gradient used was: 6 min with AcN: H2O (60:40) containing 0.1% (v/v) formic acid, 10 + 5 min with AcN: H2O (90:10); and 20 + 4 min with AcN: H2O (60:40).

A standard curve was established with pure capsaicin (Cayman Chemical, Ann Arbor, MI, USA). Under these conditions, capsaicin had a retention time of 1.88 min. Capsaicinoids concentration were measured in micrograms per gram fresh weight (FW) (Kopta et al., 2020; Palma et al., 2020).

3. Results and discussion

In this study, peppers of Padron varieties with spicy and sweet taste were investigated. Therefore, we measured the capsaicin content in the pericarps. Table 1 shows the capsaicin content for both sweet and spicy Padrón cultivars. Sweet and spicy cultivars were considered to have capsaicin less and greater than 5 (μg/g) fresh weight, respectively.

3.1. PCA results

Fig. 3 presents the results obtained by the PCA method for 2 group of peppers. The PCA diagram shows the total variance of the data for 2 group of peppers as PC-1 (90%), and PC-2 (6%). Therefore, the first two main components formed 96% of the total variance of normalized data. According to Fig. 3, The hot peppers can be observed on the right side are highlighted in red, while the sweet peppers is presented on the left side of the graph are highlighted in blue, making the two groups of peppers completely distinct. Thus, the e-nose well responded to the smell of the hot and sweet peppers. An electronic nose with 12-MOS-based gas sensors have been used to classify the quality of 3 Indonesia black tea. The experimental results showed that all three samples almost have the same aroma when observed from the sensor response. The results of the PC-1 and PC-2 components accounted for 80.3% and 15.3% of the variance, respectively (Lelono, Triyana, Hartati, & Istiyanto, 2016). Additionally, an electronic nose was also used to predict rapeseed quality with detection accuracy of 100% (Gancarz et al., 2017), coffee bean roasting with detection accuracy of 91.68% (Gancarz et al., 2022) and to detect early signs of soft-rot infection in potatoes, with 100% detection accuracy (Rutolo et al., 2018).

The sensors respond to the odor of the samples, as shown in Fig. 4. The highest sensor intensity in response to volatiles (VOCs) was recorded by gas sensors MQ135, MQ4, MQ9, and TGS822, while the lowest sensor intensity was observed by MQ3. Comparing Fig. 4A and B, it is clear that the MQ135 sensor responded equally in both samples, while

Table 1
Content of capsaicin in pericarp.

	Capsaicin (μg/g FW[a])		
	Min	Max	Average
Sweet	1.50	2.25	1.947
Hot	6.40	10.10	8.248

[a] FW, fresh weight.

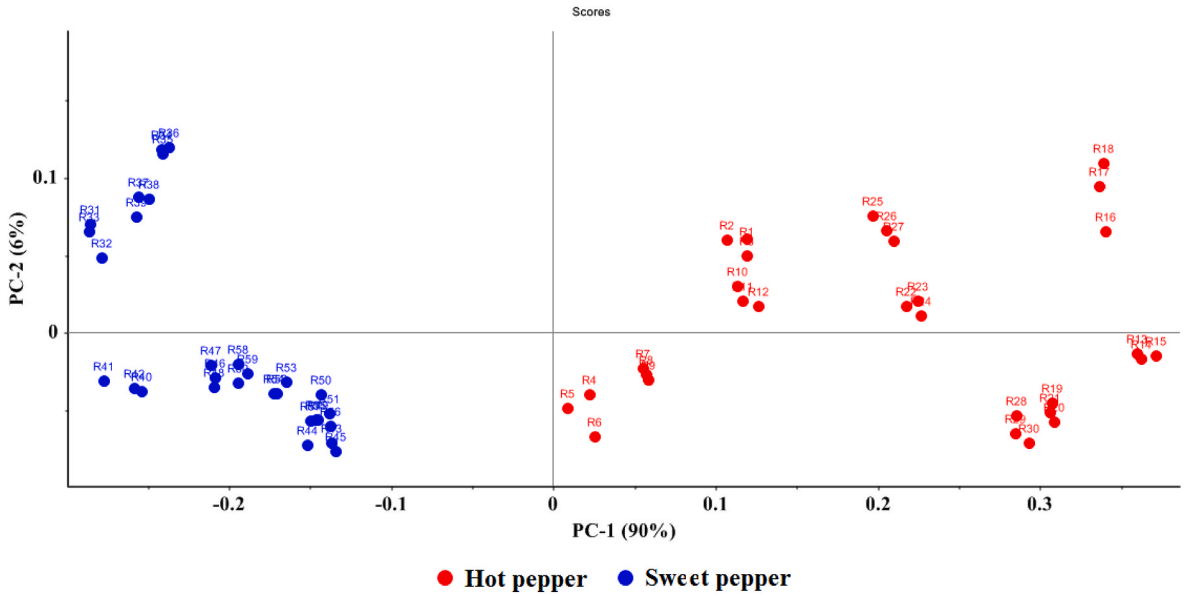

Fig. 3. Results of PCA scatter obtained from E-nose for classification Hot and Sweet pepper.

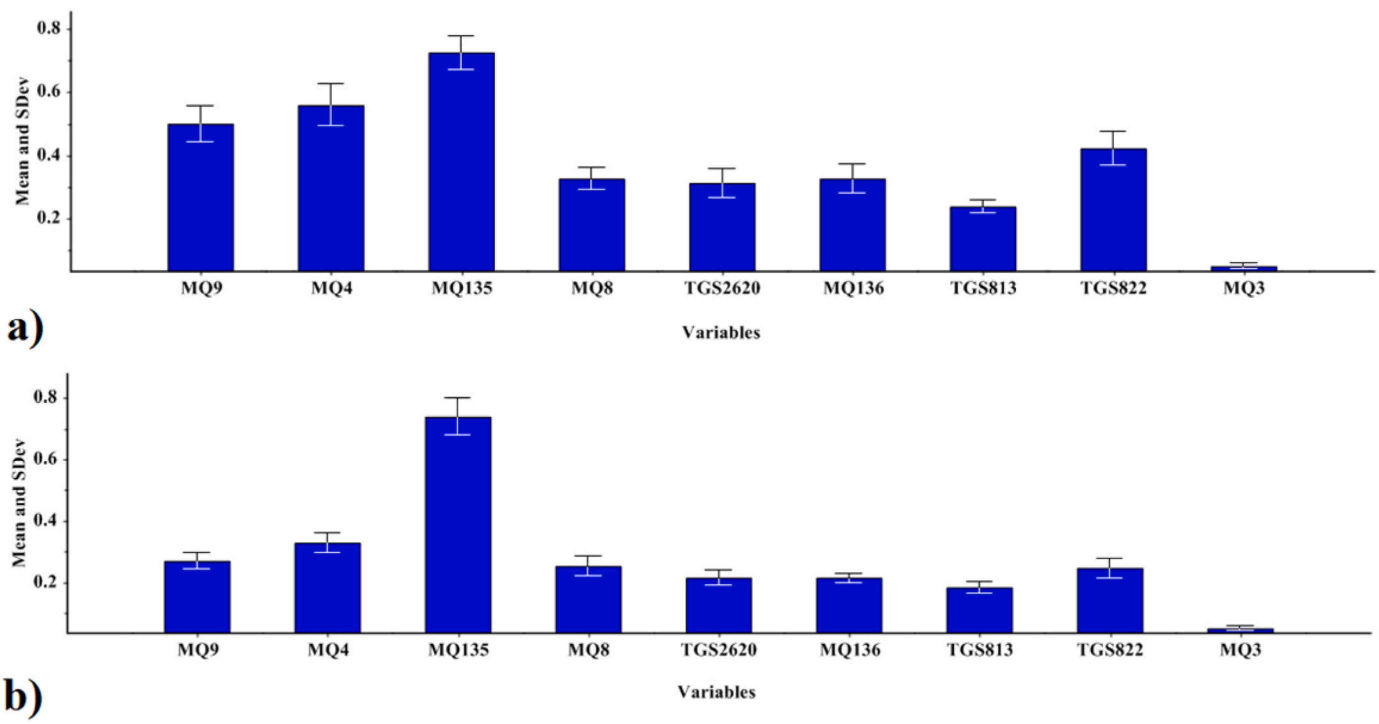

Fig. 4. Example of e-nose sensor array output response, indicated by individual sensor responses to a) hot pepper and b) sweet pepper sample VOC emissions in headspace, to form a bar graph smell print pattern.

the other sensors, with the exception of the MQ3 sensor, responded differently in both samples. In other words, they responded more strongly to spicy samples than to sweet ones, which this can justify the why these samples were classified with such high accuracy. Therefore, it can be argued that the MQ3 sensors, which are mainly for detecting the smell of alcohol with the lowest response and the MQ135 sensors, which are mainly for detecting the smell of ammonia, benzene, and sulfides with the highest response do not play an important role in classifying peppers. A good understanding of the most important and least important variables can help reduce the complexity of the device (sensors) and reduce calculations and overfitting in the analysis phase, and reduce manufacturing costs (Rasekh et al., 2021b; Rasekh & Karami, 2021b).

3.2. CA results

Clustering analysis is a machine learning method known as unsupervised learning. Using Ward's dendrogram method, clustering can be observed more clearly between closely spaced samples. To perform this analysis, the output signal of the sensors was analyzed by The Unscrambler software. The dendrogram classified 60 pepper samples into 2 clusters according to the squared Euclidean distance. As shown in Fig. 5, the hot samples were in the first cluster with a relative distance of 3.8

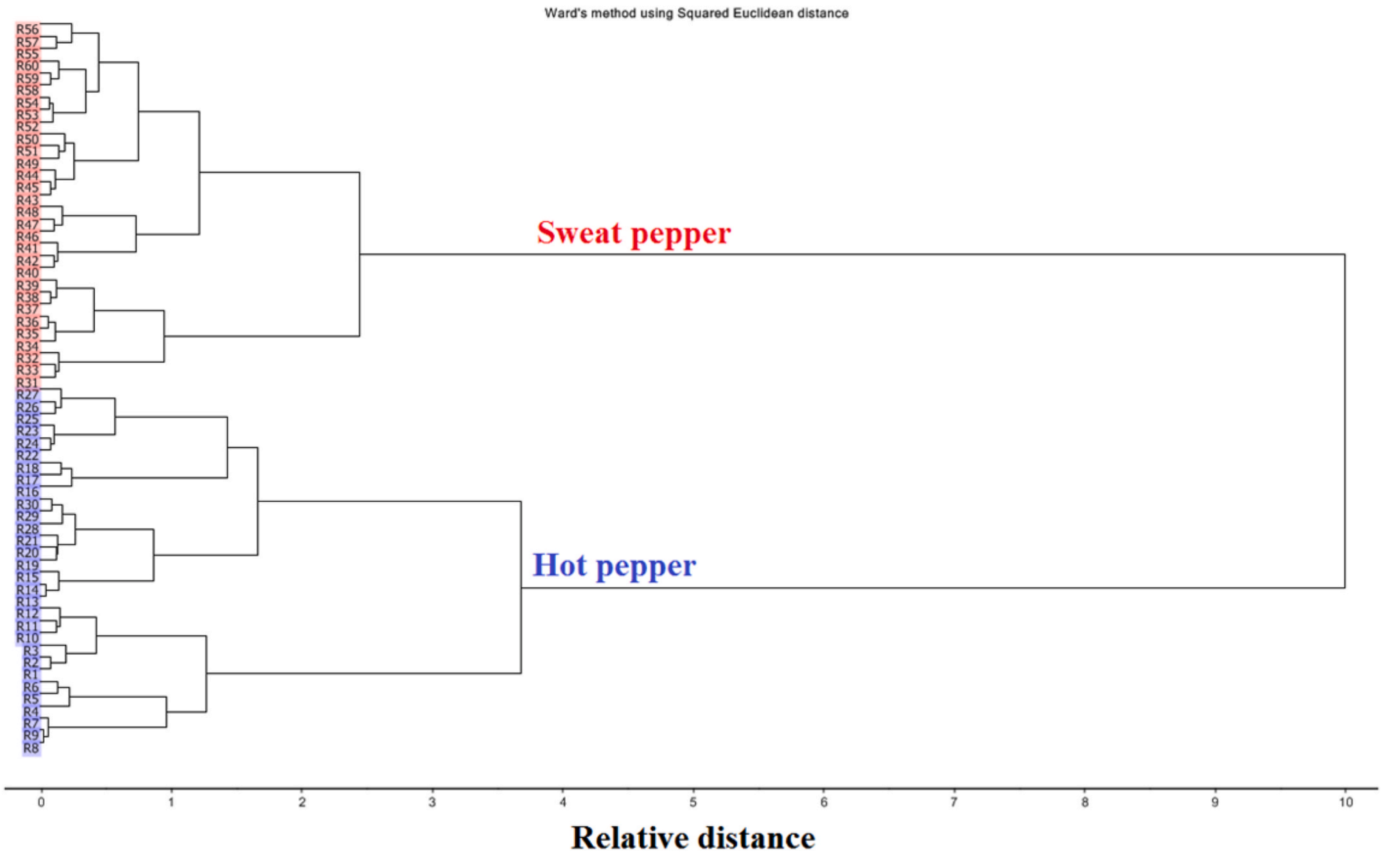

Figure 5. CA dendrogram obtained from E-nose data for Hot and Sweet pepper.

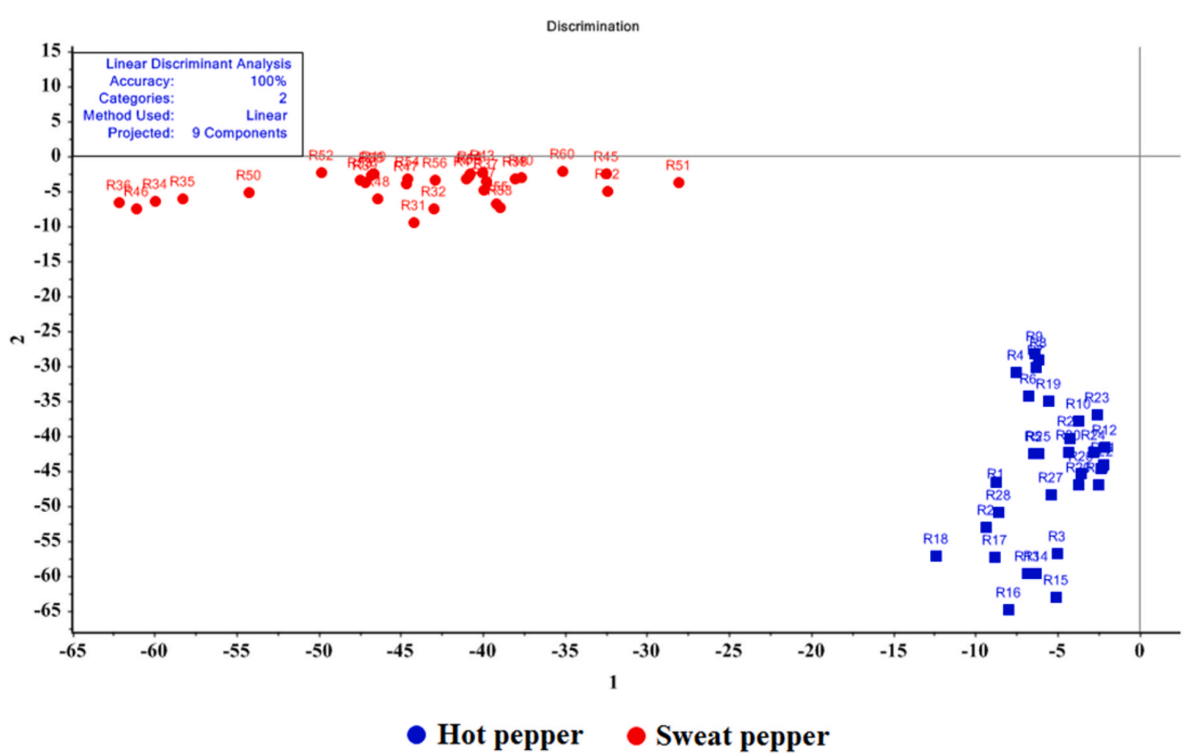

Fig. 6. Results of LDA method for 2 group of peppers.

and the sweet peppers were in the second cluster with a relative distance of 2.4. All the 60 samples were correctly assigned to the two groups.

3.3. LDA results

The classification results of the 2 group of peppers on the coordinates based on first linear discriminant (LD1) and second linear discriminant (LD2) are shown in Fig. 6 as score plots. The model inputs were obtained from 9 metal oxide sensors; the weight of the model inputs was one. This method showed 100% accuracy for 2 group of peppers. The purpose of this method was to determine the difference between sweet pepper and hot pepper. Tatli, Mirzaee-Ghaleh, Rabbani, Karami, and Wilson (2022), Classified cucumber fruits based on the amount of urea fertilizer used in five treatments by LDA method with 92% accuracy. In another study, E-Nose was used to identify counterfeit labels of virgin olive oil, which resulted in more than 95% classification accuracy for LDA method (Cerrato Oliveros et al., 2002). Khorramifar et al. (2022) Obtained 92% accuracy from e-nose to identify and classify five grape cultivars based on VOC emission by LDA method.

3.4. SVM results

C-SVM and Nu-SVM methods were employed to classify 2 group of peppers. The parameters γ, Nu, and C were validated by trial and error through minimization. 70% of the data were used for training while 30% of them were utilized for testing. The input weights were equal to one for all data. Four functions of linear, sigmoid, radial, and polynomial were used to classify 2 group of peppers. The results of the SVM method are shown in Table 2. According to the results obtained for classify 2 group of peppers, all models showed 100% accuracy for training and validation (Table 2). Ghasemi-Varnamkhasti, Mohammad-Razdari, Yoosefian, Izadi, and Rabiei (2019) to describe the freshness of strawberries in polymer packaging using the Nu-SVM method with radial base function, they reported 85.2% and 55.6% accuracy for training and validation. Gorji-Chakespari, Nikbakht, Sefidkon, Ghasemi-Varnamkhasti, and Valero (2017) Reported the Damask rose essential oil classification was reported with 99% accuracy.

3.5. ANN results

Table 3 presents the statistical data for the ANN model developed based on the e-nose signals as input (number of sensors) and group of the peppers (hot and sweet) as targets; these neurons were considered 9 for input layer and 2 for output layer, respectively. Of the total data, 60, 20, and 20% were used for training, validation, and testing, respectively. The results are shown in Table 3. The developed models were evaluated in terms of correct classification rate (CCR) and root mean square error (RMSE). The accuracy of the artificial neural network method was very high, that is, its accuracy was 100% for classify 2 group of peppers. All topologies used provided 100% accuracy train and test.

Overall, it can be concluded that all the models used for the classification of sweet peppers of the spicy type were 100% accurate due to the clear division between pepper groups. The result of the experiment is quite logical, because hot peppers seem to have a stronger aroma than sweet ones, and this intensity of aroma can be easily detected by an electronic nose. Jana et al. (2011) used E-nose with PCA, LDA and ANN to detect non-aromatic and aromatic rice. The accuracy of the results obtained by these methods was 96.5%, 80%, and 93% respectively. The results of this study showed high accuracy, maybe due to the presence of different VOCs emitted from peppers. B. Zhou, Wang, and Qi (2012) used e-nose to distinguish between grain types of wheat. They used several statistical methods. PCA had an accuracy of 99.7%, while LDA accuracy was 97.2%. The accuracy of classification using BPNN model for training and testing the data set was 100% and 90%, respectively. An e-nose was employed for the rapid identification of quality grades of green tea for the two neural networks BPNN and PNN, the classification success rates was 100% and 98.7% for the training set, respectively and these were, respectively, 88% and 85.3% for the testing sets (Yu, Wang, Yao, Zhang, & Yu, 2008). The results of hot and sweet pepper classification using ANN in this study were consistent with those of other researchers (Alphus Dan Wilson, 2012; Alphus D.; Rusinek, Jeleń, Malaga-Toboła, Molenda, & Gancarz, 2020; Rusinek, Kmiecik, et al., 2020; Wilson, 2013). In another study, an e-nasal system was used to extract tea flavour characteristics and classify black tea quality based on these characteristics. Using chemometric methods, the features extracted from a sensor array with ten different metal oxide gas sensors were used to classify five quality groups of black tea. The results showed that ANN perform best with an overall classification accuracy of 88%. Following that, the LDA and SVM methods also had accuracies of 78% and 67%, respectively. Overall, the performance of the e-nose system was found to be adequate in classifying Iranian black tea (Payman, Bakhshipour Ziaratgahi, & Sanaeifar, 2019).

The researchers evaluated the freshness of broccoli using four different techniques: e-nose, bacterial culture test, gas chromatography-mass spectrometry (GC-MC), and Fourier transform infrared (FTIR) spectroscopy. PCA methods and cluster analysis offered acceptable results (Ezhilan et al., 2019). The results of this study were consistent with the findings of Hidayat et al. (2019) who used an e-nose and ANN to determine the quality of coffee beans and reported an accuracy of 99%.

3.6. Prediction of capsaicin amount in the hot and sweet peppers based on PLSR and PCR methods

The relationship between E-nose signals and the prediction of Capsaicin indices was described by PCR and PLSR models. The performance of these models for Capsaicin was evaluated using RMSE and R^2.

Table 3
Artificial neural network results.

Topology	Train		Test		CCR(%)[a]
	RMSE	R^2	RMSE	R^2	
9-2-2	2.67×10^{-14}	0.999	3.84×10^{-13}	0.999	100
9-3-2	1.68×10^{-15}	0.999	5.68×10^{-14}	0.999	100
9-4-2	5.40×10^{-11}	0.999	1.72×10^{-7}	0.999	100
9-5-2	3.44×10^{-11}	0.999	1.08×10^{-5}	0.999	100
9-6-2	1.98×10^{-14}	0.999	4.46×10^{-12}	0.999	100

[a] The value of CCR was obtained from the confusion matrix.

Table 2
Results and comparison of Nu-SVM and C-SVM models[a] subjected to the kernel functions.

Kernel function	C-SVM				Nu-SVM			
	C	γ	Train	Validation	Nu	γ	Train	Validation
linear	1	1	100	100	0.01	1	100	100
Polynomial	100	0.1	100	100	0.255	0.1	100	100
Radial basis function	1	1	100	100	0.255	0.01	100	100
sigmoid	100	0.01	100	100	0.255	0.01	100	100

[a] Statistical analysis models and parameters used for data analysis: Nu-SVM = Nu Support Vector Machine classification, and C-SVM = C Support Vector Machine classification. Coefficient parameter symbols: c = C-SVM penalty coefficient; Nu = Nu-SVM penalty coefficient; γ = core coefficient.

Table 4
PCR and PLSR models analysis results for predicting Capsaicin.

	Model	R^2_{cal}	R^2_{val}	$RMSE_{cal}$	$RMSE_{val}$	$Offset_{cal}$	$Offset_{val}$	Optimal factor
Sweet	PCR	0.865	0.768	0.077	0.101	0.262	0.416	6
	PLSR	0.907	0.860	0.063	0.085	0.179	0.241	6
Hot	PCR	0.951	0.905	0.230	0.333	0.399	0.600	7
	PLSR	0.951	0.896	0.230	0.344	0.399	0.415	7

The Root Mean Square Error Validation (RMSEval) of root was chosen as a numerical tool to select the optimal model (Table 4).

In our study, we found that the best model for the prediction of capsaicin was the PLSR method which showed more accuracy than PCR. Using the PLSR method for sweet peppers, the R^2 calibration and validation values were 0.907 and 0.860, respectively, and the RMSEcal and RMSEval values were 0.063 and 0.085, respectively. RMSEcal and RMSEval were calculated for hot peppers as 0.230 and 0.344, and with R^2cal and R^2val values of 0.951 and 0.896, respectively. As shown in Table 4, both the PLSR and PCR methods were more accurate in measuring capsaicin in hot peppers than in sweet ones. The PLSR and PCR regression models for capsaicin index are shown in Table 5. The models are obtained from Equation (1), where Y is the predicted value (capsaicin index), a0 is the constant coefficient of the equation (intercept), and C1 to Cn represent the optimal factors or coefficients of each predictor variable (sensor array).

$$Y = a_0 + C_1S_1 + C_2S_2 + \dots + C_nS_n \tag{1}$$

3.7. *Prediction of capsaicin amount in the hot and sweet peppers based on MLR*

MLR creates a model describing the relationship between sensor signals and capsaicin indices. The remaining variables are all significant at the 0.01 level. Then, different statistical methods were used to test the final equations for stability and validity. Four criteria were used to select the correct equation for further analysis, namely R^2, RMSE, F-statistic, and the number of descriptors in the model.

In this study, the Leverage Correction method was used, in contrast to the PCR and PLSR validation methods, which used cross-validation. For the best MLR models, the R^2 and F values are high, the standard error of prediction is low, the descriptors are minimal, and the predictive power is high. We used the optimal dataset from Table 4, which contained six PCs for sweet peppers and seven PCs for hot peppers, as input data (X) to build the prediction models. In the experiment, the training data set and the test data set were randomly selected. The correlation coefficient (R^2) and root mean square error (RMSE) between the experimental and the predicted values were used to evaluate the performance of the model.

The multiple linear regression (MLR) method is located between PLSR and PCR in terms of mean square error and was used to construct PCR and PLSR models. After analyzing and determining the optimal factors, the PCR and PLSR models were considered as independent variables and the MLR model was used. Correlation plots is shown in Fig. 7 as a visual method to evaluate the models fit with experimental data. Equations (2) and (3) represent the model obtained by MLR based on the optimal factors of PCR and PLSR for predicting the amount of Capsaicin in the sweet peppers:

$$\text{Capsaicin biased PCR} = 1.947 + 2.282 \times C_1 + 0.968 \times C_2 + 1.475 \times C_3 + 2.627 \times C_4 + 5.960 \times C_6 + 0.009 \tag{2}$$

C_5 is not significant at the 0.01 level, so are deleted in the model. Values obtained for the model; R2 = 0.784; RMSE = 0.099; F = 24.593; $P < 10^{-4}$.

$$\text{Capsaicin biased PLSR} = 1.947 + 2.355 \times C_1 + 2.120 \times C_2 + 1.812 \times C_3 + 3.976 \times C_5 + 0.006 \tag{3}$$

C_4, C_6 are not significant at the 0.01 level, so are deleted in the model. Values obtained for the model; $R^2 = 0.851$; RMSE = 0.082; F = 37.784; $P < 10^{-4}$.

Also equations (4) and (5) represent the model obtained by MLR based on the optimal factors of PCR and PLSR for predicting the amount of Capsaicin in the hot peppers:

$$\text{Capsaicin biased PCR} = 8.248 + 5.777 \times C_1 - 3.271 \times C_2 - 25.608 \times C_4 - 17.965 \times C_5 + 28.091 \times C_6 -34.223 \times C_7 + 0.009 \tag{4}$$

C_3 is not significant at the 0.01 level, so are deleted in the model. Values obtained for the model; $R^2 = 0.912$; RMSE = 0.315; F = 60.373; $P < 10^{-4}$.

$$\text{Capsaicin biased PLSR} = 8.247 + 6.084 \times C1 + 13.373 \times C2 + 16.717 \times C3 + 7.439 \times C4 + 13.826 \times C5 + 0.099 \tag{5}$$

C_6, C_7 are not significant at the 0.01 level, so are deleted in the model. Values obtained for the model; $R^2 = 0.912$; RMSE = 0.315; F = 61.900; $P < 10^{-4}$.

Fig. 7 shows the MLR prediction models for the predicting the amount of Capsaicin in the sweet and hot peppers.

The figures show a linear correlation between the sensors' responses and the Capsaicin index, so the model made with the optimal parameters of the PLSR method predicts the Capsaicin index of both sweet and hot peppers with high accuracy.

The results illustrated that the PCR and PLSR models were more accurate in predicting sugars and carbohy-drates than toughness parameter. Similar results have been reported for PLS models.Abu--Khalaf (2021), studied the quality parameters of olive oil using PLS models to analyze the chemical data and EN. The results illustrated that EN could model the acidity parameter with good performance. The correlation coefficients obtained for the PLS model for acidity were 0.87

Table 5
The regression coefficients estimated by MLR and PLS models.

	Model	a_0	C_1	C_2	C_3	C_4	C_5	C_6	C_7
Sweet	PCR	−0.398	−4.658	1.329	3.983	−1.300	2.076	0.131	–
	PLSR	−0.516	−7.438	1.222	3.647	−1.332	1.503	0.948	–
Hot	PCR	9.974	−11.309	6.164	0.279	−7.939	29.522	−0.279	−25.741
	PLSR	9.697	−11.439	6.075	0.130	−8.204	27.769	−1.355	−24.240

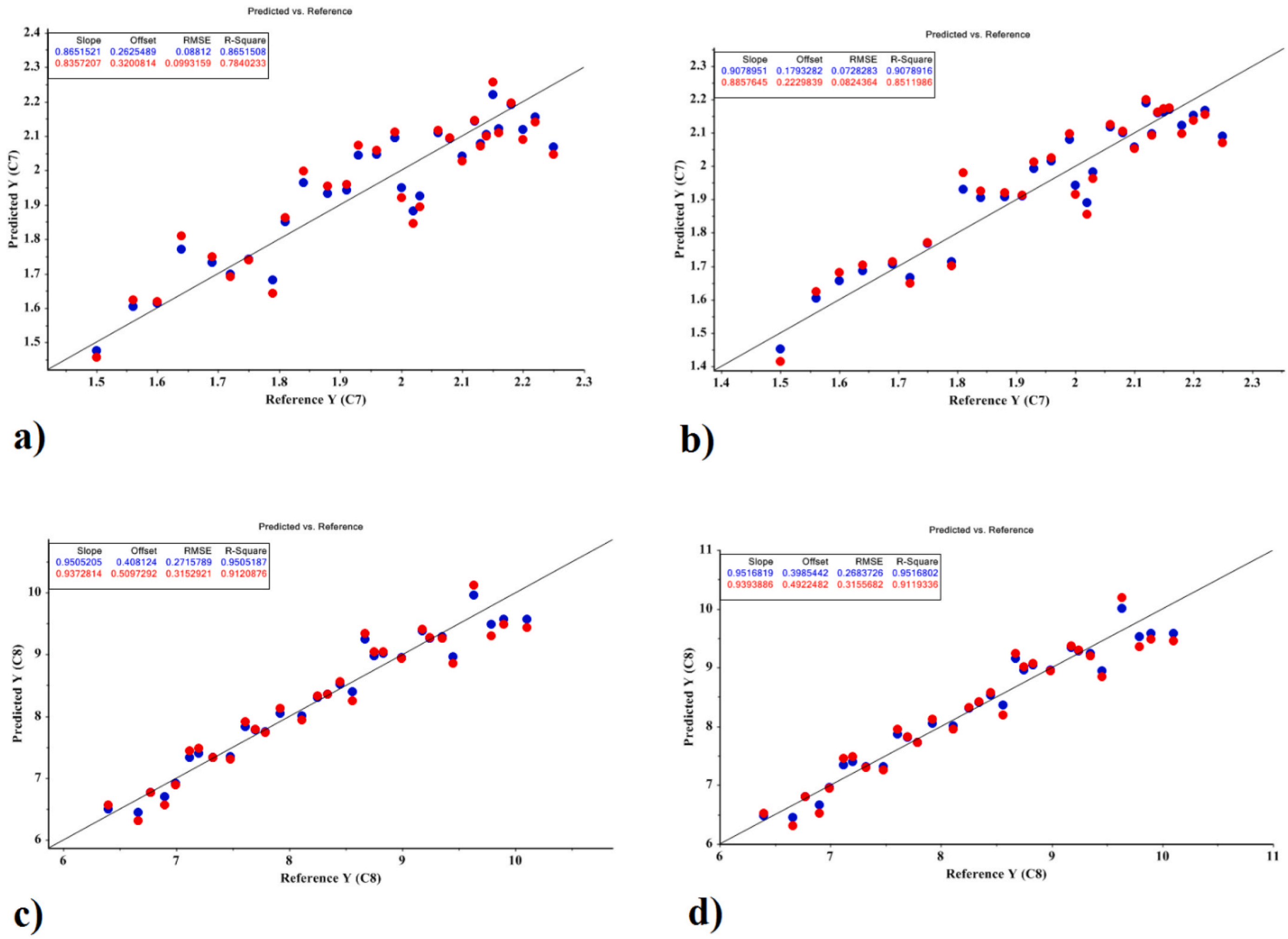

Fig. 7. MLR prediction models for predicting the amount of Capsaicin in the sweet and hot peppers based on a) PCR for sweet peppers, b) PLSR for sweet peppers, c) PCR for hot peppers, d) PLSR for hot peppers.

and 0.87 for the calibration and validation, respectively. X. Zhang et al. (2019) reported similar results using the PLSR method and electronic nose for grapes with R^2 of 0.93. In another study, using partial least squares spectroscopy and linear Discriminant analysis (PLS-LDA), similar results were obtained ($R^2 = 0.96$), which is in agreement with our results (Z. Zhou, Zeng, Li, & Zheng, 2015).

4. Conclusions

Using an e-nose in combination with machine learning can be a quick and cost-effective way to sort edible peppers. VOCs released by hot and sweet peppers differ significantly from each other, and this property can be used to develop nondestructive sorting machines as a reliable method. The development of a portable e-nose system with sensitive gas sensors and pattern recognition could provide a new approach to meet these requirements. In addition, it could offer several advantages over conventional methods so that this method is a cheap, fast and non-destructive technique, so it can be used not only for food quality control but also for production process control. As a result, the production performance is improved and the production process is better controlled, also provide a solution to the related challenges. Since the classification of hot and sweet pepper using an electronic nose has not yet been researched, the promising results of this study can be widely applied in the sorting industry. It is recommended that future studies focus on the reproducibility of electronic nasal systems developed in a wider range of peppers on the market.

CRediT authorship contribution statement

Mansour Rasekh: Formal analysis, Funding acquisition, Conceptualization, Project administration. **Hamed Karami:** Investigation, Conceptualization, Supervision, Methodology, Formal analysis, Software, Writing – original draft, Data curation, Writing – review & editing, Project administration. **Sigfredo Fuentes:** Writing – review & editing. **Mohammad Kaveh:** Data curation, Writing – review & editing. **Robert Rusinek:** Writing – review & editing. **Marek Gancarz:** Formal analysis, Funding acquisition, Data curation, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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