www.international-agrophysics.org

Non-destructive test to detect adulteration of rice using gas sensors coupled with chemometrics methods

*Vali Rasooli Sharabiani*¹, *Ali Khorramifar*¹, *Hamed Karami*²⁽¹⁰⁾*, *Jesús Lozano*³, *Sylwester Tabor*⁴, *Yousef Darvishi*⁵, *and Marek Gancarz*^{4,6}⁽¹⁰⁾*

¹Department of Biosystems Engineering, University of Mohaghegh Ardabili, Ardabil 56199-11367, Iran ²Department of Petroleum Engineering, Knowledge University, Erbil 44001, Iraq

³Department of Electric Technology, Electronics and Automation, University of Extremadura,

Avda. de Elvas S/n, 06006, Badajoz, Spain

⁴Faculty of Production and Power Engineering, University of Agriculture in Kraków, Balicka 116B, 30-149 Kraków, Poland ⁵Department of Biosystems Engineering, University of Tehran, Tehran 11365-4117, Iran

⁶Institute of Agrophysics, Polish Academy of Sciences, Doświadczalna 4, 20-290 Lublin, Poland

Received March 31, 2023; accepted May 9, 2023

Abstract. In order to accurately determine and evaluate the odour of rice, it is necessary to identify the substances that affect that odour and to develop methods to determine their amounts. For more than three decades, researchers have been studying the factors that produce and influence the aroma of rice. An electronic nose can be used to detect the volatile compounds of rice, while an olfactory machine is capable of classifying and detecting the variety, origin, and storage time of rice with a high degree of efficiency. This study aimed to investigate the efficacy of electronic noses and other chemometric methods such as principal component analysis, linear discriminant analysis, and the Artificial Neural Network as a cost-effective, rapid, and non-destructive method for the detection of pure and adulterated rice varieties. Therefore, an electronic nose equipped with nine metal oxide semiconductor sensors with low power consumption was used. The results showed that the amount of variance accounted for by PC1 and PC4 was 98% for the samples used. Also, the classification accuracy of the linear discriminant analysis and Artificial Neural Network methods were 100%, respectively. The Support Vector Machines method (including Nu-SVM and C-SVM) was also used, which, in all its functions except the polynomial function, produced 100% accuracy in terms of training and validation.

K e y w o r d s: adulterated rice, electronic nose, classification, Artificial Neural Networks

INTRODUCTION

Rice (Oryza sativa L.), which belongs to the family Oryzeae, is an annual plant which is herbaceous, erect, superficially rooted, strong, and white (Xu et al., 2014; Rasooli Sharabiani and Khorramifar, 2022; Yinian et al., 2022). Rice is a staple food for about 2.5 billion people around the world and provides nearly 20% of the required energy and 15% of the protein requirements of these people (Qamar et al., 2013; Li et al., 2022). In general terms, tropical and subtropical countries such as Burma, Thailand, Vietnam, Laos, Indonesia, the Philippines, Pakistan, India, the United States, Japan, Italy, Egypt, China, Brazil, Cuba, Mexico, and Australia are the largest rice producers in the world. The Sadri, Tarom and Hashemi varieties may be considered to be the best indigenous varieties of Iran. In addition, the high-yielding varieties of Iran are Caspian, Speedroad, Sahel, Kadous, Shafaq, Darfak, Gohar, and Neda (Rice Research Institute of Iran website).

In order to accurately determine and evaluate the odour of rice, it is critical to identify the compounds responsible for the odour as well as developing methods to determine

^{© 2023} Institute of Agrophysics, Polish Academy of Sciences



^{*}Corresponding author e-mail: hamed.karami@knu.edu.iq, m.gancarz@urk.edu.pl

their amounts. The first studies concerning the factors that produce and influence rice aroma were conducted more than three decades ago. Several studies have been conducted to identify the volatile components of rice and to determine the main causes of odour production using more efficient and rapid methods. There are more than 100 known compounds in rice, but only a few of them are essential for aroma formation (Crowhurst and Creed, 2001; Grimm *et al.*, 2001; Fukai and Tukada, 2006; Ghiasvand *et al.*, 2007; Gancarz *et al.*, 2022).

The electronic nose can only detect the volatile compounds in rice, these have been used in extensive studies to identify and classify food and agricultural products. Zheng et al. (2009) used an electronic nose to identify four varieties of polished rice: Mahatma Brown, Riceland Milled, Thailand Jasmine, and Zatarain's Parboiled. In their study, they found that the rice could be identified and recognized using their electronic nose, but they reported that the principal component analysis (PCA) failed to distinguish the Zatarain's Parboiled variety from the other three varieties. Furthermore, Hu et al. (2011) used electronic noses and PCA to identify volatile gas components, non-aromatic and aromatic rice varieties. They considered the PCA method to be acceptable. In addition, Huichun et al. (2012) used an electronic nose to identify four rice varieties and reported that Fengliangyou 4 and Zajiao 838 overlapped in the PCA method. Khorramifar et al. (2021) investigated the potential of the olfactory machine to identify potato varieties. According to their study, potato varieties may be recognized with a high degree of accuracy using an electronic nose and PCA (Khorramifar et al., 2021). They also reported that potato varieties can be identified with 100% accuracy using an electronic nose, linear discriminant analysis (LDA) and Artificial Neural Network (ANNs). Cevoli et al. (2011) used an olfactory machine to classify cheeses at different stages of storage and reported that classification accuracy was 100% using an ANN. Some studies have investigated the use of an electronic nose to evaluate aromas, for example: sunflower and corn oils were detected with a 95% accuracy using electronic noses (Mildner-Szkudlarz and Jeleń, 2008). Other applications of the olfactory device include making a quality determination after the completion of the cucumber harvest using an electronic nose (Yin et al., 2017), and determining the quality of honey (Zhang et al., 2012), the amount and degree of mould growing on corn (Arendse et al., 2021), identification and classification of different grape cultivars (Afkari-Sayyah et al., 2021), identification of the chemical compounds of potatoes (Khorramifar and Rasekh, 2022) and examining the quality indicators and the degree of ripening of peaches (Karoui and Blecker, 2011). By using an electronic nose and GC-MS experiments, Zhou et al. (2019) identified Chinese Maca at the macroscopic and microscopic levels and concluded that the odour of Maca may be directly correlated with its chemical composition.

Therefore, an olfactory machine may be highly effective in terms of classifying and recognizing cultivars, their origin and storage time. Olfactory machines are unique in that they have a different structure and approach than other methods (image processing, neural networks, etc.), they are flexible, and are compatible with most agricultural products based on their odours (Karami et al., 2020b; 2020c). Various researches have been attempting to distinguish between fraud and authenticity in agricultural and horticultural products. Other methods used for this purpose include vibration spectroscopy, infrared spectroscopy, Raman spectroscopy, fluorescence spectroscopy and hyperspectral imaging (Arendse et al., 2021; Karoui and Blecker, 2011). For example, in a study by Korifi et al. (2011) using NIR spectroscopy and the PLS-DA method, virgin olive oil fraud was detected with a 92.3% accuracy (Korifi et al., 2011). Furthermore, Xie et al. (2008) were able to detect bayberry juice fraud with a 97.62% accuracy using NIR spectroscopy and an artificial neural network (Xie et al., 2008). In another study, a combination of Fourier transform infrared (FT-IR) spectroscopy and PCA was used to detect counterfeit pomegranate juice concentrate through the addition of different concentrations of grape juice concentrate and a 99% accuracy was reported (Vardin et al., 2008). In another study, olive oil fraud was studied using Raman spectroscopy and chemometrics methods, and the researchers were able to detect product fraud with an accuracy and error $R^2 = 0.505-0.982$, RMSEP = 0.0485-0.176 (Li *et al.*, 2018). In a study that focused on discrimination between Shaoxing wines and other Chinese rice wines using NIR and chemometric methods, the accuracy of the PCA method was reported to be about 93% (Shen et al., 2012).

In addition, various techniques are used to detect volatile organic compounds (VOC), including: a) non-separative mass spectrometry (Casas-Ferreira *et al.*, 2019; Żytek *et al.*, 2023), b) chromatographic separation (Frigerio *et al.*, 2019), c) micro gas chromatograph (Wang *et al.*, 2019), d) solid-phase microextraction (Kong *et al.*, 2020; Rusinek *et al.*, 2022).

The aroma of the "Pandan" rice leaves is a distinctive feature and is used to distinguish the quality of the rice. The quality determines whether it has a certain degree of cleanliness and purity (Cheaupun *et al.*, 2003).

Most consumers prefer aromatic rice because of its good quality, including its tenderness, shape, colour, aroma, and taste (Choudhury *et al.*, 2001). Due to its popularity and quality, aromatic rice is used for celebrations and special occasions. Several factors affect the quality of aromatic rice, including the location of its cultivation, climatic conditions, genetics, and postharvest treatment (Champagne, 2008). The quality of the rice is influenced by postharvest practices such as storage conditions and duration, the drying method used, the enrichment process, and the packaging material. If the influencing factors such as storage conditions and duration, as well as the temperature and humidity are controlled, the potentially harmful effects of these factors on rice quality such as taste and odour can be minimized (Wongpornchai et al., 2004). In the rice industry, quality control, mislabelling, sorting, and adulteration are major issues in different rice varieties. Therefore, the rice industry uses standard grades based on market criteria to identify the rice grain. The most common means of evaluating the quality of aromatic rice are human expert panels who distinguish the rice based on its aromatic characteristics (Fitzgerald et al., 2009). However, this method has drawbacks, such as the many years of training required and the potential fatigue of panel members as the number of samples increases causing less accurate results (Karami et al., 2020d; Noorsal, 2005). An analysis using GC-MS can also be used to evaluate the quality of the aromatic rice samples, but this is a complex and expensive method (Abdullah et al., 2015; Karami et al., 2020a).

During the processing of the rice grain, several inspection steps may be performed to determine the quality and type of rice seed. Therefore, evaluating the purity of the seed varieties is more difficult and complicated than evaluating other factors such as aroma, taste, size, colour, and cleanness. This problem may be overcome by using a nondestructive and faster method for rice evaluation and easy handling (Abdullah *et al.*, 2016).

Due to the rapid and outstanding advances in computer and sensor technology, the application of a bionic electronic nose, which includes a gas-sensitive semiconductor sensor and a pattern recognition system, provides a new means for rapid classification and variety recognition (Karami *et al.*, 2021; Rasekh and Karami, 2021a). In addition, electronic nose technology has provided a non-invasive, rapid method for the classification and recognition of paddy rice (Hu *et al.*, 2011; Huichun *et al.*, 2012; Zheng *et al.*, 2009). Pattern recognition methods include Neural Networks (NN) (Llobet *et al.*, 1999; Rasekh and Karami, 2021b), principal component analysis (PCA) (Capone *et al.*, 2001; Tatli *et al.*, 2022), and linear diagnostic analysis (LDA) (Aghili *et al.*, 2022; Hai and Wang, 2006).

As mentioned earlier, studies have been conducted concerning the detection and differentiation of rice cultivars using electronic noses, in the particular case of distinguishing pure cultivars from counterfeit ones, it may best stated that it is generally useful and can be very useful. The aim of this study was to evaluate the ability and accuracy of an electronic nose using chemometrics (PCA, LDA and Support Vector Machines-SVM) and artificial neural networks (ANN) to distinguish pure rice cultivar (Hashemi variety) from 3 gross cultivars (80% pure + 20% non-original) so that a safe, rapid and non-destructive method may be introduced for the benefit of consumers (in order to help them to choose the right product).

This paper presents an effective approach for the detection of adulterated and pure rice based on chemometrics methods using an MOS-based E-nose. The goal was to achieve a suitable, accurate and rapid (non-destructive) method to identify genuine and fake rice using electronic nose and chemometric techniques and artificial neural networks. This study makes the following contributions:

1. Firstly, samples of the original rice and three types of fake rice were prepared for testing, and the results of analysing the characteristics of the VOCs were comprehensively and rapidly evaluated using the electronic nose.

2. Then, according to the response of the sensor array of the electronic nose system, four pattern recognition methods – PCA, LDA, SVM and ANN-were used to identify and classify the gas samples.

3. A comprehensive study concerning the detection of adulterated and pure rice is presented, thereby demonstrating the high degree of accuracy of the proposed chemometrics methods. It was found that by using these methods, it is possible to distinguish whether rice is genuine or fake with a high degree of accuracy. The findings of this study will provide a reference to related research to be conducted at some future date.

MATERIALS AND METHODS

Firstly, four rice varieties from the Rice Research Institute of Iran were prepared. The four varieties included one high-quality variety named Hashemi and three lowquality varieties named Neda, Khazar, and Sahel. It is noteworthy that there are two types of Hashemi rice: the hot and cold types, which are similar in appearance, but the cold type is superior in terms of ease of cooking and taste. In this study, the cold type of Hashemi variety was used. Thus, in the experiments, one original rice variety (cold Hashemi type) and three non-original or adulterated varieties were prepared (a mixture of the Khazar, Neda and Sahel varieties with the Hashemi variety), so that the adulterated varieties each contained 80% Hashemi variety and 20% low-quality varieties (The weight amount was equal to 160 grams of the Hashemi variety + 40 g of the low-quality variety).

After the varieties were prepared and mixed, the samples were placed in a closed container (the sample container) for 1 hour in order to saturate the container with the rice odour, and then the sample containers were used for data collection with an electronic nose.

In this study, an electronic nose was used, it was manufactured in the Department of Biosystems Engineering, in the University of Mohaghegh Ardabili (Fig. 1).

In this device, nine metal oxide semiconductor (MOS) sensors with a low power consumption were used, these are among the most common sensors available. The specifications of the sensors are given in Table 1.

Data were collected by connecting the sample container to the electronic nose. Data collection began by passing clean air through the sensor chamber for 150 s to clear the sensors of odours and other gasses. The sample odour was

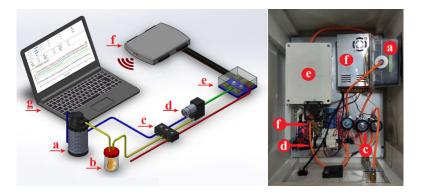


Fig. 1. Schematic of an artificial olfactory (e-nose) system, the components of this system consist of the following parts (listed in the order and direction of airflow): (a) air filter (activated charcoal to remove ambient-air VOC hydrocarbons), (b) sample headspace chamber, (c) solenoid air valves, (d) diaphragm pump, (e) e-nose sensor array chamber, (f) data acquisition recorder and wireless transmission card, and (g) personal computer (PC). Adapted from Karami *et al.* (2020b).

 Table 1. Sensor types, the gas detection ranges, and the known chemical sensitivity of the tin oxide MOS sensors within the electronic nose sensor array

Row	Sensor name	Main applications (Gas detector)			
1	MQ9	CO ₂ and combustible gas			
2	MQ8	Hydrogen			
3	MQ136	Sulphur dioxide (SO ₂)			
4	MQ135	Steam ammonia, benzene, sulphide			
5	TGS2620	Alcohol, steam organic solvents			
6	TGS813	CH_4, C_3H_8, C_4H_{10}			
7	TGS822	Steam organic solvents			
8	MQ4	Urban gases and methane			
9	MQ3	Alcohol			

then drawn out of the sample chamber by the pump for 150 s and directed to the sensors. Fresh air was then injected into the sensor chamber for 150 s to prepare the instrument for the replication and subsequent experiments (Karami *et al.*, 2020c). For each sample, 22 replicates were performed.

In these steps, the output voltage of the sensors was changed by exposure to the gases emitted by the sample (rice aroma) and the odour responses were recorded on data acquisition cards. The sensor signals were recorded and stored at 1-second intervals. The baseline correction method was a fractional one in which noise and possible deviations were eliminated, then, the sensor responses were normalized and made dimensionless based on following equation (Capone *et al.*, 2001):

$$Y_{s}(t) = \frac{X_{s}(t) - X_{s}(0)}{X_{s}(0)}$$

where: $Y_s(t)$ is the normalized response, $X_s(0)$ is the baseline and $X_s(t)$ is the sensor response. Chemometrics and principal component analysis (PCA) were used to determine the outputs of the sensors and reduce the data dimension. In the next step, the LDA and ANN methods were used to classify the four rice varieties.

Principal component analysis is one of the simplest multivariate methods and is usually used unsupervised to cluster data by group. It usually reduces the dimension of the data, and the best results are obtained when the data are negatively or positively significantly correlated. Noorsal (2005) reported that this technique has been widely used in processing electronic nose data. Another advantage of PCA is that this technique reduces the size of the multidimensional data by removing additions without losing important information.

The most commonly supervised technique for classifying samples into predetermined classes is linear detection analysis (LDA). This technique selects independent data variables to recognize the sample that follows a normal distribution. Based on classification functions (van Ek and Trim, 1998), the LDA is the line at which the variance between the groups is maximized, while the variance within the groups is minimized.

The SVM method was first introduced by Vapnik (2000) has been further developed in recent years. Various studies have been reported which indicate that an SVM is usually more effective than other classification algorithms. In the last decade, this method has been used as an important learning technique to solve classification and regression problems in various fields.

In addition, ANN and pattern recognition were used to identify the similarities and differences between the pure and adulterated rice varieties. Based on the nine sensors, nine neurons were considered for the input layer. The hidden layer was evaluated according to the optimal number of neurons, and the four output neurons were evaluated according to the number of output classes (four rice varieties). The logarithmic sigmoid transfer function and Lunberg-Marquardt learning method were used to train the network. The errors level was also calculated using the mean square error. All data were randomly selected for learning (70%), testing (15%), and validation (15%). The training data was provided to the network during the training period and the network was adjusted according to their errors. Validation was used to measure the generalization of the network and the completion of the training. Testing the data did not affect training and therefore provided an independent indication of network performance during and after training (Bieganowski *et al.*, 2018).

RESULTS AND DISCUSSION

A spider web graph was used to observe the differences in patterns (fingerprints) between the rice varieties. The average output data from the electronic nose sensors during the 150 s of sample measurement were normalized. They were then plotted as a spider web graph using equation (Fig. 2). According to this diagram, it may be seen that two sensors, MQ135 and TGS813, play a particularly decisive role in the identification.

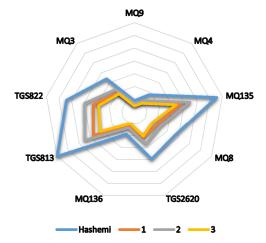


Fig. 2. Spider web graph of the VOCs in rice cultivars.

The graph shows the difference between the response patterns of the sensors for each rice variety. As may be observed from Fig. 2, there are significant similarities in the fingerprints of the different rice varieties, so all varieties showed the same pattern with different values. The variety of Hashemi showed the strongest odour among all of the rice varieties.

According to the scores graph (Fig. 3), the total variance of the data was equal to PC-1 (98%) and PC-4 (0%), respectively, and the first two principal components accounted for 98% of the total variance of the normalized data. When the total variance is greater than 90%, it means that the first two principal components can explain the total variance of the data set (Khorramifar et al., 2021). As may be observed in this figure, the Hashemi variety (a) on the left side of the graph is easily distinguished from the three fake varieties (b, c, d) by the PCA method. Hence, it may be concluded that the e-nose was good at detecting rice fragrances and distinguishing between the pure and impure varieties, which proves the high degree of precision of the device in detecting different fragrances. The results are consistent with those of Xu et al. (2014) who studied the classification of six rice varieties. According to their results, the PCA had an accuracy of 99.5% (Xu et al., 2014). Other researchers also studied potential canola oil fraud with Fourier transform MIR spectroscopy and were able to detect it with a 99% accuracy using the PCA method (Li et al., 2015) the results were consistent with those of our study. The results of our research were much better than the results produced by Georgouli et al. (2017), who, by applying the PCA method and using Raman spectroscopy detected the counterfeit canola oil with a 56.6% accuracy. The results of the PCA method used in the Hun et al. (2016) research to detect adulteration in oil were very similar to the results produced by the PCA method in our research. They identified adulteration in the oil with hyperspectral imaging and the results of their research showed that the accuracy of the PCA method is 99% (Han et al., 2016).

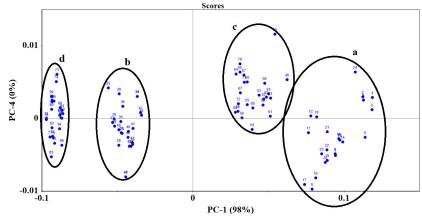


Fig. 3. Two-dimensional PCA plot used to identify four rice cultivars with data collected using an electronic nose: a) Hashemi, b) Hashemi + Neda, c) Hashemi + Khazar and d) Hashemi + Sahel.

The correlation loading plot shows the relationships between all of the variables. The loading plot (Fig. 4) illustrates the relative contribution of the sensors to each principal component. The inner and outer ellipses represent 50 and 100% of the total variance of the data, respectively. The higher the loading coefficient of a sensor, the greater the role of that sensor in terms of identification and classification. Thus, the sensor results located in the outer ellipse more significantly affected the classification of the data (Khorramifar *et al.*, 2021). It may be observed from the figure that all of the sensors played an important role in the identification of rice varieties.

The TGS822 sensor (used to detect Steam organic solvent gases), MQ9 (used to detect carbon dioxide and flammable gases) and MQ3 (used to detect alcohol, methane, and natural gases) played minor roles as compared to the other sensors. It is possible to reduce expenditure and save costs by removing these two sensors from the odour device for detecting original and adulterated rice. Also, the sensor of MQ135, MQ8 and TGS813 have the most roles compared to the other sensors.

The LDA and ANN methods have been used to identify and distinguish the pure and mixed varieties based on the output response of the sensors. Unlike PCA, the LDA method may be used to optimize the resolution between classes based on extracted multisensor information. Therefore, this method was used to recognize four rice varieties (1 pure

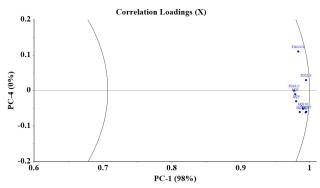


Fig. 4. Loading plot for PCA analysis to identify four rice cultivars.

and high-quality variety and 3 counterfeit varieties) based on the output response of the sensors. The recognition rate of the varieties was 100% (Fig. 5). The results of our study were similar to the results produced by the study of Shen et al. (2016). They examined the freshness of the orange juice using an electronic nose and FT-IR spectroscopy and stated that the accuracy of the LDA method for detecting freshness in orange juice using FT- IR spectroscopy is equal to 87.5% and, when using an electronic nose, 91.7% (Shen et al., 2016). In addition, in another study, researchers using Raman spectroscopy were able to detect olive oil fraud using the LDA method with an accuracy of $R^2 = 0.912$ -0.994 (Lerma-García et al., 2010) had a method accuracy that was close to the results of our research. The researchers identified the authenticity and counterfeiting of coffee with 100% accuracy by applying FT-IR spectroscopy using PCA and LDA methods (Reis et al., 2013), the results of which were similar to the results produced by our study. Also, Jana et al. (2011) used an electronic nose and LDA to distinguish between aromatic and non-aromatic rice, the accuracy of their results was equal to 80% which was less accurate than our research.

The SVM model is based on the theory of statistical learning and mathematical optimization, this uses the principle of minimizing structural error and leads to a generally optimal solution. In this study, two methods, C-SVM and Nu-SVM, were used to classify the samples. The parameters of Nu, C and y were validated using trial and error for minimizing. 70% of the data were used for training and the remaining 30% were applied as a test dataset. The input weights for all data were 1. The 4 functions, linear, sigmoidal, radial and polynomial were applied. The results of the SVM method are summarized in Table 2. According to the obtained results, all models except for the polynomial ones had a 100% accuracy for the training and validation sets. In general, it may be stated that the SVM method offers a high degree of accuracy using linear, sigmoidal and radial functions. In research conducted by Khorramifar et al. (2022) this method was used to identify grape varieties with leaf smell, which produced good results (with almost a 90%

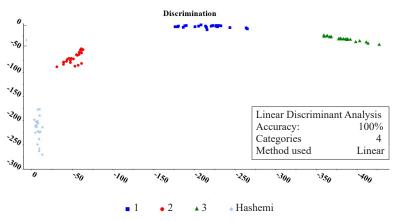


Fig. 5. LDA analysis was used to identify four rice cultivars.

Kernel	C-SVM			Nu-SVM				
	С	γ	Train	Validation	Nu	γ	Train	Validation
Linear	100	1	100	100	0.225	1	100	100
Polynomial	10	10	93.75	93.75	0.01	1	100	97.92
Radial basis function	1	10	100	100	0.01	0.01	100	100
Sigmoid	1	10	100	100	0.255	0.01	100	100

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

Nu, C, γ – these are the dimensionless parameters of the model.

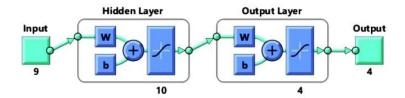


Fig. 6. Diagrams of the two-layer feedforward models with a tan-sigmoidal function in the hidden layer and a Softmax function in the output layer for electronic nose inputs.

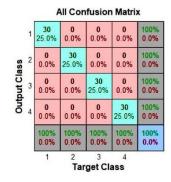


Fig. 7. ANN result used to identify four rice cultivars.

accuracy) (Khorramifar *et al.*, 2022). Also, this method was used to predict the amount of sugar and carbohydrates in potatoes, the results were very accurate (Khorramifar *et al.*, 2022). In other research, Kaur and Singh (2013) classified rice grains with a 90% accuracy using machine vision and the SVM method. It is clear that in the SVM method, the accuracy of the electronic nose device is much higher than that of the machine vision.

Also, in the case of the ANN method, nine neurons were considered for the input layer (corresponding to the output data with nine sensors) and four neurons were considered for the output layer (corresponding to the number of varieties). Topology 9-10-4 produced the highest degree of accuracy in recognizing rice varieties (Fig. 6), so its value was 100% (Fig. 7). Karami *et al.* (2020d) found similar results in their analysis concerning adulterated fruit juice. In a study conducted by Shi *et al.* (2018), a non-destructive prediction of the freshness of tilapia fish fillet during storage at different temperatures (0, 4, 7 and 10°C) was made by integrating the electronic nose and tongue with neural networks and they were able to detect the freshness rate of the sample with an error of about 5% (Shi *et al.*, 2018) it

is evident that the results of our study were better than the results of this study and the reason could be due to the differences in odour intensity and aroma in the samples of the two studies. Also, in the research of Jana *et al.* (2011), who used an electronic nose to distinguish between aromatic and non-aromatic rice, the accuracy of their ANN method was equal to 93%, which may be said to represent a high degree of accuracy.

Abdullah *et al.* (2015) identified and classified 17 rice samples into four categories using an olfactory machine. According to their results, the SVM method produced the highest degree of accuracy (100%) and was the best classification method for the various varieties, while the KNN method was second in classifying rice samples. Rahimzadeh *et al.* (2022) used the KNN method to recognize three rice varieties and the accuracy of their results was reported to be 100%. They stated that the KNN method performed better than the PCA and LDA methods in terms of accuracy.

Similarly, our results showed that the LDA method was less accurate than other methods such as ANN, KNN, SVM and PCA.

Lim *et al.* (2020) used an electronic nose to evaluate the quality of China commercial moxa floss and classified the degree of quality using the PCA method with an accuracy of 94.3%, which is consistent with the results of our study. In addition, they used the ANN method for classification with an accuracy of 85% which was actually less accurate than the same method used in our study (100%).

Liu *et al.* (2017) used multispectral imaging and chemometrics to detect sucrose adulteration in tomato paste. They reported that the accuracy of the PLS and BPNN methods (93%) was lower than that of the other two methods (LS-SVM and PCA). The accuracy of the LS-SVM and PCA methods was 96 and 98%, respectively. Therefore, the PCA method performed better than the others. In one study, Hidayat *et al.* (2019) used an electronic nose with chemometrics methods. They examined the quality of black tea. They also used the Radial SVM and LDA models for this purpose, which produced a lower degree of accuracy than the linear SVM model (Hidayat *et al.*, 2019).

In another study, Liu *et al.* (2018) classified various fragrances in terms of electronic nose responses (developed by the E.NOSE team in the University of Technology Sydney) by applying support vector machines and artificial neural networks (genetic algorithm). They found that they could achieve the highest degree of accuracy using the SVM method (86.04%) and that the accuracy of the neural network and the PCA + SVM methods were 51.37 and 63.47%, respectively (Liu *et al.*, 2018).

CONCLUSIONS

In this study, an electronic nose with nine metal oxide sensors was used to distinguish between the original and the mixed rice varieties.

1. Chemometric methods such as principal component analysis, linear discriminant analysis, Support Vector Machines and Artificial Neural Network were used for the qualitative and quantitative analysis of complex data with electronic sensor arrays. Principal component analysis was used to reduce the data and described the variance of the data set with two principal components PC1 and PC4 (98%) which provided a preliminary classification. In addition, linear discriminant analysis, SVM and ANN could be used to identify and accurately classify the pure and adulterated rice varieties with an accuracy of 100%, respectively.

2. Using an electronic nose, pure and impure rice varieties can be identified rapidly and non-destructively. Consumers, such as restaurants and hall owners, can use this method to identify rice varieties and select pure and high-quality varieties.

3. Moreover, the important difference between this study and previous works is that in the present study, two methods of chemometrics and artificial neural networks were used simultaneously to classify the samples.

Data availability statement: The datasets used and/ or analysed during the current study are available from the corresponding author if a reasonable request is made.

Conflicts of interest: The authors declare that there is no conflict of interest regarding the publication of this paper.

REFERENCES

- Abdullah A., Adom A., Shakaff A.M., Masnan M., Zakaria A., Rahim N., and Omar O., 2015. Classification of Malaysia aromatic rice using multivariate statistical analysis. Conf. Proc. AIP, AIP Publishing.
- Abdullah A., Rahim N., Masnan M., Sa'ad F., Zakaria A., Shakaff A., and Omar O., 2016. Rice and the electronic nose. In: Electronic Noses and Tongues in Food Science (Eds Victor R. Preedy, Maria Rodriguez Mendez). Elsevier, Academic Press.

- Afkari-Sayyah A.H., Khorramifar A., and Karami H., 2021. Identification and classification of different grape cultivars using cultivar leaves by electroni nose. J. Environ. Sci. Studies, 6(4), 4382-4389.
- Aghili N.S., Rasekh M., Karami H., Azizi V., and Gancarz M., 2022. Detection of fraud in sesame oil with the help of artificial intelligence combined with chemometrics methods and chemical compounds characterization by gas chromatography-mass spectrometry. LWT, 167, 113863. doi:https:// doi.org/10.1016/j.lwt.2022.113863
- Arendse E., Nieuwoudt H., Magwaza L.S., Nturambirwe J.F.I., Fawole O.A., and Opara U.L., 2021. Recent advancements on vibrational spectroscopic techniques for the detection of authenticity and adulteration in horticultural products with a specific focus on oils, juices and powders. Food Bioprocess Technol., 14(1), 1-22.
- Bieganowski A., Józefaciuk G., Bandura L., Guz Ł., Łagód G., and Franus W., 2018. Evaluation of hydrocarbon soil pollution using E-Nose. Sensors, 18(8), 2463. https://www. mdpi.com/1424-8220/18/8/2463
- Capone S., Epifani M., Quaranta F., Siciliano P., Taurino A., and Vasanelli L., 2001. Monitoring of rancidity of milk by means of an electronic nose and a dynamic PCA analysis. Sensors Actuators B: Chemical, 78(1-3), 174-179.
- Casas-Ferreira A.M., del Nogal-Sánchez M., Pérez-Pavón J.L., and Moreno-Cordero B., 2019. Non-separative mass spectrometry methods for non-invasive medical diagnostics based on volatile organic compounds: A review. Analytica Chimica Acta, 1045, 10-22.
- Cevoli C., Cerretani L., Gori A., Caboni M., Toschi T.G., and Fabbri A., 2011. Classification of Pecorino cheeses using electronic nose combined with artificial neural network and comparison with GC-MS analysis of volatile compounds. Food Chemistry, 129(3), 1315-1319.
- Champagne E.T., 2008. Rice aroma and flavor: a literature review. Cereal Chemistry, 85(4), 445-454.
- Cheaupun K., Wongpiyachon S., and Kongseree N., 2003. Improving Rice Grain Quality in Thailand Rice is Life. Proc.World Rice Research, Japan in Scientific Perspectives For The 21st Century, 20013, 248-249.
- Choudhury P., Kohli S., Srinivasan K., Mohapatra T., and Sharma R., 2001. Identification and classification of aromatic rices based on DNA fingerprinting. Euphytica, 118(3), 243-251.
- Crowhurst D.G., and Creed P.G., 2001. Effect of cooking method and variety on the sensory quality of rice. Food Service Technol., 1(3), 133-140.
- Devos M., Patte F., Rouault J., Laffort P., and van Gemert L.J. (Eds) 1990. Standardized human olfactory thresholds, Oxford University Press, Oxford.
- Fitzgerald M.A., McCouch S.R., and Hall R.D., 2009. Not just a grain of rice: the quest for quality. Trends Plant Sci., 14(3), 133-139.
- Frigerio G., Mercadante R., Polledri E., Missineo P., Campo L., and Fustinoni S., 2019. An LC-MS/MS method to profile urinary mercapturic acids, metabolites of electrophilic intermediates of occupational and environmental toxicants. J. Chromatography B, 1117, 66-76.

- Fukai Y. and Tukada K., 2006. Influence of pre-washing on quality of cooked rice maintained at a constant temterature (Influence of cooking conditions on quality of cooked rice, 1). J. Japanese Society Food Sci. Technol. (Japan), 587-591.
- Gancarz M., Dobrzański B. Jr., Malaga-Tobola U., Tabor S., Combrzyński M., Ćwikła D., Strobel W.R., Oniszczuk A., Karami H., Darvishi Y., Żytek A., Rusinek R., 2022. Impact of coffee bean roasting on the content of pyridines determined by analysis of volatile organic compounds. Molecules, 27(5), 1559. https://doi.org/10.3390/ molecules27051559
- Georgouli K., Del Rincon J.M., and Koidis A., 2017. Continuous statistical modelling for rapid detection of adulteration of extra virgin olive oil using mid infrared and Raman spectroscopic data. Food Chemistry, 217, 735-742.
- Ghiasvand A.R., Setkova L., and Pawliszyn J., 2007. Determination of flavour profile in Iranian fragrant rice samples using cold-fibre SPME-GC-TOF-MS. Flavour Fragrance J., 22(5), 377-391.
- Grimm C.C., Bergman C., Delgado J.T., and Bryant R., 2001. Screening for 2-acetyl-1-pyrroline in the headspace of rice using SPME/GC-MS. J. Agric. Food Chem., 49(1), 245-249.
- Hai Z., and Wang J., 2006. Electronic nose and data analysis for detection of maize oil adulteration in sesame oil. Sensors Actuators B: Chemical, 119(2), 449-455. doi:https://doi. org/10.1016/j.snb.2006.01.001
- Han Z., Wan J., Deng L., and Liu K., 2016. Oil Adulteration identification by hyperspectral imaging using QHM and ICA. PLoS One, 11(1), e0146547.
- Hidayat S.N., Triyana K., Fauzan I., Julian T., Lelono D., Yusuf Y., Ngadiman N., Veloso A.C.A., and Peres A.M., 2019. The electronic nose coupled with chemometric tools for discriminating the quality of black tea samples in situ. *Chemosensors*, 7(3), 29. https://doi.org/10.3390/ chemosensors7030029
- Hu G.X., Wang J., Wang J.J., and Wang X.L., 2011. Detection for rice odors and identification of varieties based on electronic nose technique. J. Zhejiang University (Agric. Life Sci.), 37(6), 670-676.
- Huichun Y., Zuozhou X., and Yong Y., 2012. The identification of rice varieties based on electronic nose. J. Chinese Cereals Oils Associ., 27, 105-109.
- Jana A., Bandyopadhyay R., Tudu B., Roy J.K., Bhattacharyya N., Adhikari B., Kundu Ch., and Mukherjee S., 2011. Classification of aromatic and non-aromatic rice using electronic nose and artificial neural network. IEEE Recent Advances in Intelligent Computational Systems. 10.1109/ RAICS.2011.6069320
- Karami H., Rasekh M., and Mirzaee-Ghaleh E., 2020a. Application of the E-nose machine system to detect adulterations in mixed edible oils using chemometrics methods. J. Food Proc. Preserv., 44(9), e14696. doi:https://doi. org/10.1111/jfpp.14696
- Karami H., Rasekh M., and Mirzaee-Ghaleh E., 2020b. Qualitative analysis of edible oil oxidation using an olfactory machine. J. Food Measurement Characterization, 14(5), 2600-2610.
- Karami H., Rasekh M., and Mirzaee-Ghaleh E., 2020c. Application of the E-nose machine system to detect adulterations in mixed edible oils using chemometrics methods. J. Food Processing Preservation, 44(9), e14696.

- Karami H., Rasekh M., and Mirzaee-Ghaleh E., 2020d. Comparison of chemometrics and AOCS official methods for predicting the shelf life of edible oil. Chemometrics Intelligent Laboratory Systems, 206, 104165. https://doi. org/10.1016/j.chemolab.2020.104165
- Karami H., Rasekh M., and Mirzaee-Ghaleh E., 2021. Identification of olfactory characteristics of edible oil during storage period using metal oxide semiconductor sensor signals and ANN methods. J. Food Proc. Preserv., 45(10), e15749. doi:https://doi.org/10.1111/jfpp.15749
- Karoui R., and Blecker C., 2011. Fluorescence spectroscopy measurement for quality assessment of food systems – a review. Food Bioprocess Technol., 4(3), 364-386.
- Kaur H., and Singh B., 2013. Classification and grading rice using multi-class SVM. Int. J. Scientific Research Publications, 3(4), 1-5.
- Khorramifar A., Karami H., Wilson A.D., Sayyah A.H.A., Shuba A., and Lozano J., 2022a. Grape cultivar identification and classification by machine olfaction analysis of leaf volatiles. Chemosensors, 10(4), 125. doi:https://doi. org/10.3390/chemosensors10040125
- Khorramifar A., Rasekh M., Karami H., Covington J.A., Derakhshani S.M., Ramos J., and Gancarz M., 2022b. Application of MOS gas sensors coupled with chemometrics methods to predict the amount of sugar and carbohydrates in potatoes. Molecules, 27(11), 3508.
- Khorramifar A., and Rasekh M., 2022. Changes in sugar and carbohydrate content of different potato cultivars during storage. J. Environ. Sci. Studies, 7(1), 4643-4650.
- Khorramifar A., Rasekh M., Karami H., Malaga-Tobola U., and Gancarz M., 2021. A machine learning method for classification and identification of potato cultivars based on the reaction of MOS type sensor-array. Sensors, 21(17), 5836. doi:https://doi.org/10.3390/s21175836
- Kong W.-L., Rui L., Ni H., and Wu X.-Q., 2020. Antifungal effects of volatile organic compounds produced by *Rahnella* aquatilis JZ-GX1 against Colletotrichum gloeosporioides in Liriodendron chinense× tulipifera. Frontiers in Microbiology, 11, 1114.
- Korifi R., Le Dréau Y., Molinet J., Artaud J., and Dupuy N., 2011. Composition and authentication of virgin olive oil from French PDO regions by chemometric treatment of Raman spectra. J. Raman Spectroscopy, 42(7), 1540-1547.
- Lerma-García M.J., Ramis-Ramos G., Herrero-Martínez J.M., and Simó-Alfonso E.F., 2010. Authentication of extra virgin olive oils by Fourier-transform infrared spectroscopy. Food Chemistry, 118(1), 78-83.
- Li B., Luo Y., Guo C., Yang Y., Yuan X., Xing M., Fan P., Shu C., Li F., Fu H., Yang Z., Chen Z., Ma J., Sun Y., and Sun Y., 2022. Effects of wheat straw returning and potassium application rates on the physicochemical properties and lodging resistance of different stem internodes in directseeded rice. Int. Agrophys., 36(4), 309-321. https://doi. org/10.31545/intagr/155271.
- Li B., Wang H., Zhao Q., Ouyang J., and Wu Y., 2015. Rapid detection of authenticity and adulteration of walnut oil by FTIR and fluorescence spectroscopy: A comparative study. Food Chemistry, 181, 25-30.
- Li Y., Fang T., Zhu S., Huang F., Chen Z., and Wang Y., 2018. Detection of olive oil adulteration with waste cooking oil

via Raman spectroscopy combined with iPLS and SiPLS. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 189, 37-43.

- Lim M.Y., Huang J., He F.-R., Zhao B.-X., Zou H.-Q., Yan Y.-H., ... Xie J.-J., 2020. Quality grade classification of China commercial moxa floss using electronic nose: A supervised learning approach. Medicine, 99(33).
- Liu C., Hao G., Su M., Chen Y., and Zheng L., 2017. Potential of multispectral imaging combined with chemometric methods for rapid detection of sucrose adulteration in tomato paste. J. Food Eng., 215, 78-83. doi:https://doi. org/10.1016/j.jfoodeng.2017.07.026
- Liu T., Zhang W., McLean P., Ueland M., Forbes S.L., and Su S.W., 2018. Electronic nose-based odor classification using genetic algorithms and fuzzy support vector machines. Int. J. Fuzzy Systems, 20(4), 1309-1320.
- Llobet E., Hines E.L., Gardner J.W., and Franco S., 1999. Non-destructive banana ripeness determination using a neural network-based electronic nose. Measurement Sci. Technol., 10(6), 538.
- Mildner-Szkudlarz S., and Jeleń H.H., 2008. The potential of different techniques for volatile compounds analysis coupled with PCA for the detection of the adulteration of olive oil with hazelnut oil. Food Chemistry, 110(3), 751-761.
- Noorsal E., 2005. Development of electronic nose system using quartz crystal microbalance odour sensor array. MSc. Thesis, Universiti Sains Malaysia.
- Qamar M., Siyah Poush M.R., and Hasibi P., 2013. Salinity tolerance assessment of rice sucrose transporter antisense lines (OsSUT1) at seedling stage (*Oryza sativa* var. TaiPai). Agricultural Biotechnology J., 5(3), 87-98.
- Rahimzadeh H., Sadeghi M., Mireei S.A., and Ghasemi-Varnamkhasti M., 2022. Unsupervised modelling of rice aroma change during ageing based on electronic nose coupled with bio-inspired algorithms. Biosystems Eng., 216, 132-146.
- Rasekh M., and Karami H., 2021a. Application of electronic nose with chemometrics methods to the detection of juices fraud. J. Food Proc. Preservation, 45(5), e15432. doi:https:// doi.org/10.1111/jfpp.15432
- Rasekh M., and Karami H., 2021b. E-nose coupled with an artificial neural network to detection of fraud in pure and industrial fruit juices. Int. J. Food Properties, 24(1), 592-602. doi:https://doi.org/10.1080/10942912.2021.1908354
- **Rasooli Sharabiani V., and Khorramifar A., 2022.** Recognition and classification of pure and adulterated rice using the electronic nose. J. Environ. Sci. Studies, 7(2), 4904-4910.
- Reis N., Franca A.S., and Oliveira L.S., 2013. Discrimination between roasted coffee, roasted corn and coffee husks by Diffuse Reflectance Infrared Fourier Transform Spectroscopy. LWT-Food Sci. Technol., 50(2), 715-722.
- Rusinek R., Dobrzański B., Jr., Oniszczuk A., Gawrysiak-Witulska M., Siger A., Karami H., Ptaszyńska A.A., Żytek A., Kapela K., and Gancarz M., 2022. How to identify roast defects in coffee beans based on the volatile compound profile. Molecules, 27, 8530. https://doi. org/10.3390/molecules27238530
- Shen F., Wu Q., Su A., Tang P., Shao X., and Liu B., 2016. Detection of adulteration in freshly squeezed orange juice by electronic nose and infrared spectroscopy. Czech J. Food Sci., 34(3), 224-232.

- Shen F., Yang D., Ying Y., Li B., Zheng Y., and Jiang T., 2012. Discrimination between Shaoxing wines and other Chinese rice wines by near-infrared spectroscopy and chemometrics. Food Bioprocess Technol, 5(2), 786-795.
- Shi C., Yang X., Han S., Fan B., Zhao Z., Wu X., and Qian J., 2018. Nondestructive prediction of tilapia fillet freshness during storage at different temperatures by integrating an electronic nose and tongue with radial basis function neural networks. Food Bioprocess Technol., 11(10), 1840-1852.
- Tatli S., Mirzaee-Ghaleh E., Rabbani H., Karami H., and Wilson A.D., 2022. Rapid detection of urea fertilizer effects on VOC emissions from cucumber fruits using a MOS E-Nose sensor array. Agronomy, 12(1), 35. doi:https://doi. org/10.3390/agronomy12010035
- van Ek J.A. and Trim J.L.M., 1998. Thresholds, 1990. Cambridge University Press.
- Vapnik V.N., 2000. The Nature of Statistical Learning Theory. Springer, Berlin.

http://dx.doi.org/10.1007/978-1-4757-3264-1

- Vardin H., Tay A., Ozen B., and Mauer L., 2008. Authentication of pomegranate juice concentrate using FTIR spectroscopy and chemometrics. Food Chemistry, 108(2), 742-748.
- Wang J., Nuñovero N., Nidetz R., Peterson S.J., Brookover B.M., Steinecker W.H., and Zellers E.T., 2019. Beltmounted micro-gas-chromatograph prototype for determining personal exposures to volatile-organic-compound mixture components. Analytical Chemistry, 91(7), 4747-4754.
- Wongpornchai S., Dumri K., Jongkaewwattana S., and Siri B., 2004. Effects of drying methods and storage time on the aroma and milling quality of rice (*Oryza sativa* L.) cv. Khao Dawk Mali 105. Food Chemistry, 87(3), 407-414.
- Xie L.-J., Ye X.-Q., Liu D.-H., and Ying Y.-B., 2008. Application of principal component-radial basis function neural networks (PC-RBFNN) for the detection of water-adulterated bayberry juice by near-infrared spectroscopy. J. Zhejiang University Science B, 9(12), 982-989.
- Xu S., Zhou Z., Lu H., Luo X., and Lan Y., 2014. Improved algorithms for the classification of rough rice using a bionic electronic nose based on PCA and the wilks distribution. Sensors, 14(3), 5486-5501.
- Yin Y., Hao Y., Yu H., Liu Y., and Hao F., 2017. Detection potential of multi-features representation of e-nose data in classification of moldy maize samples. Food Bioprocess Technol., 10(12), 2226-2239.
- Yinian L., Yulun C., Qishuo D., Ruiyin H., and Weimin D., 2022. Analysis of relationship between head rice yield and breaking force of Japonica rice grains at different maturity stages. Int. Agrophysics, 36(1), 1-11. https://doi.org/10.31545/intagr/145545
- Zhang H., Wang J., Ye S., and Chang M., 2012. Application of electronic nose and statistical analysis to predict quality indices of peach. Food Bioprocess Technol., 5(1), 65-72.
- Zheng X.-Z., Lan Y.-B., Zhu J.-M., Westbrook J., Hoffmann W., and Lacey R., 2009. Rapid identification of rice samples using an electronic nose. J. Bionic Engineering, 6(3), 290-297.
- Zhou Z., Kearnes S., Li L., Zare R.N., and Riley P., 2019. Optimization of molecules via deep reinforcement learning. Scientific reports, 9(1), 1-10.
- Żytek A., Rusinek R., Oniszczuk A., and Gancarz M., 2023. Effect of the consolidation level on organic volatile compound emissions from maize during storage. Materials, 16, 3066. https://doi.org/10.3390/ma16083066