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ORIGINAL ARTICLE

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Application of the E-nose machine system to detect adulterations in mixed edible oils using chemometrics methods

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Abstract

Foodstuff adulteration involves addition of any low-cost substances to the high-price materials to reduce the content of the expensive components, and hence decrease the production cost and reach to the maximum profit. An electronic nose was used in this study to detect the adulterations in mixed edible oils. The acidity, peroxide, anisidine, and Totox values of the edible oil samples were measured according to the official American Oil Chemist Society (AOCS) standard. The results were analyzed by Cluster analysis (CA), principle component analysis (PCA), principal component regression (PCR), linear discriminant analysis (LDA), and artificial neural network (ANN) methods with accuracy of 95, 98, 98, 88, and 97.3%, respectively. According to the results, the ANN method with structure of 8-7-5 showed the highest accuracy in classification of oil adulteration. Its correct classification ratio, mean square errors, and correlation (*r*) were 97.3%, .117211, and .0963, respectively. The results also indicated that the proposed method can be used as an alternative of the official AOCS methods to innovatively detect the edible oil adulteration with high accuracy and speed.

Practical applications

Lipid oxidation is one of the major causes of food spoilage especially in those containing oil. AOCS has developed various methods to evaluate the oxidation status of the oil assets. However, these chemical tests are time-consuming, destructive, and costly and require several glassware and reagents. E-nose could be used for real-time monitoring of the volatile components of the food to evaluate different features of the product. Generally, E-nose evaluates mixture of smells released form a sample and is a reliable, nondestructive, cost-effective, and portable method with high feasibility and speed as well as simple use. CA, PCA, and ANN methods were also applied for qualitative differentiation of different adulteration percentages in oxidized and nonoxidized oils.

1 | INTRODUCTION

Regarding high rate of adulteration in food products, development of fast analytical methods to detect adulteration and verify the food product authenticity is of crucial importance (Peris & Escuder-Gilabert, 2016). The consumers' preference for use of a specific type of edible oil may be attributed to its aroma, taste, and nutritional values. Regarding the serious health-threatening concerns, validation of the edible oil is one of the major issues in food product analysis (Xu, Yu, Liu, & Zhang, 2016).

Lipid oxidation is one of the major causes of food spoilage especially in those containing oil (Yang, Han, & Noh, 2000). Therefore, this parameter has been considered as one of the important qualitative

criteria in food industry. Oxidation may occur from processing to storage of the edible oil. In addition to production of peroxides, aldehydes, ketones, acids, and other small molecules, it can decrease the quality of the food products. Oxidation degree can be influenced by storage condition. When the oil is exposed to light and high temperature, its oxidation will be increased (Xu et al., 2016).

American oil chemists' society (AOCS) has developed various methods to evaluate the oxidation status of the oil, for example, to assess peroxide value (PV), acidity value (AV), Anisidine value (AnV), and Totox value. PV and AV have been widely employed in edible oil industry and food processing. These chemical tests are not difficult; however, they are time-consuming, destructive as mentioned earlier. These methods also impose potential risks on human and environment health due to their solvent wastes (Armenta, Garrigues, & de la Guardia, 2007).

Electronic nose includes a series of electrochemical sensors, which can detect simple or complicated smells (Gardner & Bartlett, 1994). Digital outputs of the E-nose sensors should be analyzed to derive their useful information. Cluster analysis (CA), principle component analysis (PCA), linear discriminant analysis (LDA) and artificial neural network (ANN) are frequently used for this purpose (Majchrzak, Wojnowski, Dymerski, Gębicki, & Namieśnik, 2018). E-nose could be used for real time monitoring of the volatile components of food to evaluate different features of the product. 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 (Loutfi, Coradeschi, Mani, Shankar, & Rayappan, 2015; Tian, Wang, & Cui, 2013). Linear discriminant analysis, artificial neural networks, and support vector machines are among the methods most usually used in connection with E-noses (Majchrzak et al., 2018).

Application of the E-nose has drastically increased in the recent decade and has led to significant achievements in the food industry. Among these researches, evaluation of the edible oil authenticity to detect adulteration or spoilage can be mentioned (Aparicio, Rocha, Delgadillo, & Morales, 2000; Escuderos, García, Jiménez, & Horrillo, 2013; Gan, Tan, Man, NorAini, & Nazimah, 2005; Martın, Oliveros, Pavón, Pinto, & Cordero, 2001; Pacioni, Cerretani, Procida, & Cichelli, 2014). Moreover, E-nose was employed to detect oxidation in soy oil (Yang et al., 2000), oxidation degree of ultra-virgin olive oil (Cosio, Ballabio, Benedetti, & Gigliotti, 2007; Lerma-Garcia, Simo-Alfonso, Bendini, & Cerretani, 2009), auto-oxidation of canola oil (Mildner-Szkudlarz, Jeleń, & Zawirska-Wojtasiak, 2008), magnolia biondii pamp (Nie et al., 2020), camellia oil authentication (Shi, Wu, Jin, & Wang, 2020), detection and discrimination of plant oil scents and their mixtures (Okur et al., 2020), and edible olive oil characterization and shelf life assessment (Buratti, Malegori, Benedetti, Oliveri, & Giovanelli, 2018).

Zhu et al. used a new method in 2016 to qualitatively analyze the edible oil oxidation by E-nose. They employed an E-nose in combination with CA, PCA, and LDA methods to detect the oxidized and nonoxidized oils which resulted in accuracies of 95.8%, 98.9%, and 100%, respectively (Xu et al., 2016).

According to the literature review, no study has used E-nose technique to detect adulteration in oxidized and nonoxidized edible oil. This study employed an E-nose to evaluate the possibility of adulteration in oxidized and nonoxidized oils, and different adulteration percentages were prepared and assessed. The model performance was assessed by official AOCS method. CA, PCA, and ANN methods were also applied for qualitative differentiation of different adulteration percentage in oxidized and nonoxidized oils.

2 | MATERIALS AND METHODS

2.1 | Sample preparation

First, liquid mixed edible oils (sunflower, canola, and soy) with new production data and expiry dates were prepared from local market in Kermanshah. The samples were kept in a dry and dark place at room temperature (to minimize the physical and chemical changes) until the tests were conducted. Then, five oil samples were prepared using fresh and oxidized oils. The first sample included the fresh oil; while the second one contained 25% adulteration (75% fresh oil + and 25% oxidized oil). The third sample contained 50:50 fresh and oxidized oils. The fourth one included 75% oxidized oil, while the fifth one fully included the oxidized oil (100%). Then, 20 ml of each sample was transferred to a 50 ml glass container at ambient temperature (23 ± 2°C). The samples were equilibrated to the headspace for 50 min in a capped vessel. On total, five types of oil with 15 replicates for each sample were used.

2.2 | Electronic nose

In this study, the electronic nose fabricated in Razi University (Ayari, Mirzaee-Ghaleh, Rabbani, & Heidarbeigi, 2018b) was employed to detect adulteration in edible oil. The employed system included two sections: hardware and software. The hardware section encompassed data collection system, sensors, sensors chamber, sampling chamber, voltage supply, joints and accessories, electric valves, air pump, and filter. The applied E-nose is schematically illustrated in Figure 1. The sensor array used in this study was composed of eight metal oxide semiconductor (MOS) sensors whose features are listed in Table 1 (Ayari, Mirzaee-Ghaleh, Rabbani, & Heidarbeigi, 2018a).

Sampling process involved three stages: baseline correction, sample smell injection, measuring, and cleaning the sensor chamber with fresh air. Regarding the unique schedule of E-nose in each of these stages for each application, these stages will be re-scheduled by changing the application. In this study, the proper schedule was obtained after several tests and investigation of the response of the sensors. In the baseline correction stage, oxygen was passed over the sensors for 200 s until the array response reached to equilibrium. Upon injection of the sample smell to the sensors chamber, the output voltage of each sensor will be changed depending on the sensor type and sensitivity. This stage often lasts for 150 s. In the last stage,

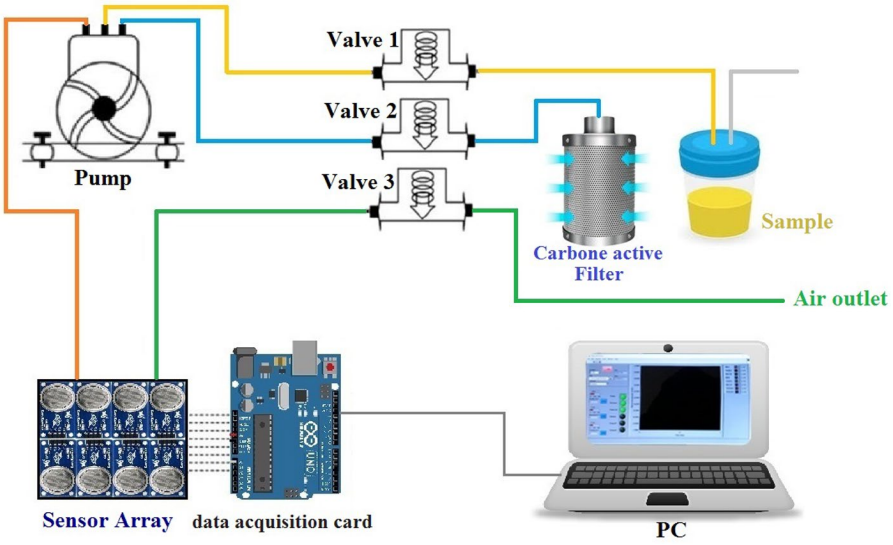

FIGURE 1 Schematic of olfactory system used

TABLE 1 The used sensors in electronic nose

Sensor type	Main applications	Typical detection ranges (ppm)
MQ3	Alcohol	10–300
TGS822	Steam organic solvents	50–5,000
MQ-136	Sulfur dioxide (SO2)	1–200
MQ-9	CO and combustible gas	Co 10–1,000, Cg 100–10,000
TGS813	CH4, C3H8, C4H10	500–10,000
MQ135	Steam ammonia, benzene, sulfide	10–10,000
TGS2602	Sulfide hydrogen sulfide, ammonia, toluene	1–30
TGS2620	Alcohol, steam organic solvents	50–5,000

fresh air was again passed over the sensors for 200 s to return the sensor's response to the baseline and prepare the system for the subsequent test.

The sensor's responses were recorded and saved by a data collection system connected to a computer (NI USB 6009) which used a graphic link programmed by LABVIEW 2013 software.

2.3 | Feature extraction

The first step in data analysis is the pre-processing of the obtained signals to extract the data from the sensors response, improve the quality of the created database and prepare the data for the pattern analysis and detection stage (Pearce, Schiffman, & Nagle, 2003). Various methods (i.e., discriminant, relative and fractional) have been developed for baseline correction, which can be employed depending on the type of applied sensors, sensor application and the researchers' preference (Arshak, Moore, Lyons, Harris, & Clifford, 2004). Here, the fractional method was employed to correct the baseline. This method can also be used for data normalization and it has been widely employed for MOS sensors (Pearce et al., 2003):

$$Y_s(t) = \frac{x_s(t) - x_s(o)}{x_s(o)} \quad (1)$$

In which $Y_s(t)$ is the normalized response, $x_s(o)$ denotes the baseline and $x_s(t)$ represents the sensor response.

2.4 | Data analysis methods

To analyze the pre-processed data, CA, PCA, PCR, LDA, and ANN methods were applied. Cluster method is a classification method to allocate the similar entities and objects to the groups or clusters. Considering a series of objects and some of their similarity values, their ranking in the classification clusters or groups could be defined, CA is a technique aimed to divide the data to specific groups based on their similarity or distance (Huang, Guo, Qiu, & Chen, 2007). The results of a hierarchical clustering method are often represented as a dendrogram (Haddi et al., 2013). In this research, Ward's method (with the help of square Euclidian distance) was used to determine the membership cluster based on the nearest centroid ordering method.

Principle component analysis is a nonmonitored pattern detection method with a perpendicular linear transform, which transform the data to the new coordination system in such a way that the largest variance will be placed on the first axis, the second largest one will be placed on the second axis and so on. In this way, the data of a series could be simply visualized. Analysis of the major components could reduce the data dimension. In this way, the components of the data set with the highest impact on the variance will be preserved. This method has been widely employed to represent the E-nose response to simple and complicated smells and

can provide some qualitative information for pattern detection (Ghasemi-Varnamkhasti, Mohtasebi, Siadat, Ahmadi, & Razavi, 2015; Ye et al., 2011). In principal components regression, we use PCA to decompose the independent (x) variables into an orthogonal basis and select a subset of those components as the variables to predict (y). The model performance can be evaluated by R^2 and *RMSE* (Karami, Kaveh, Mirzaee-Ghaleh, & Taghinezhad, 2018; Kaveh, Karami, & Jahanbakhshi, 2020):

$$R^2 = 1 - \frac{\sum_{i=1}^{N} (S_k - T_k)^2}{\sum_{i=1}^{N} (S_k - T_m)^2} \quad (2)$$

$$RMSE = \frac{1}{N} \sum_{i=1}^{N} |S_k - T_k| \quad (3)$$

where, S_k, T_k, and T_m are measured, predicted, and average predicted.

Artificial neural network is a neural network, which encompasses three layers: input, output, and hidden layers. Each unit in the hidden layer and the output layer acts like a perceptron the only difference is the application of the threshold function instead of sigmoid function. The units in the input layer are only responsible for distribution of the input values to the subsequent layer; $E = \frac{1}{N} \sum_{i=1}^{N} |S_k - T_k|$ hence, they do not conduct any calculations (Haykin, 1999). In this study, the multi-layer Perceptron algorithm with back error-propagation was employed to classify the edible oils and detect adulteration. The hidden layer included several neurons, which indicate the nonlinearity of the network. An ANN with one hidden layer possessing the activation function of tangent hyperbolic was employed. The number of neurons in the hidden layer was determined by trial and error. Depending on the states (original and fake oils), the output layer indicates the prediction (desired) values. The performance of the designed networks was evaluated by mean square error (MSE) and correlation coefficient (r) (Kaveh, Chayjan, & Khezri, 2018). To train the network, the number of neurons in the hidden layer and MSE were changed. The data were divided into three groups training subset (60%), validation (20%), and test (20%).

Linear differentiation analysis (LDA) creates a linear combination of the features resulting in classification. This function increases the inter-group variance to intra-group variance ratio. Three methods including mahalanobis, quadratic, and linear are used for data classification by LDA approach. CA, PCA, PCR, and LDA methods were implemented by UnscramblerX10.4 to differ the authentic edible oil from the fake ones.

2.5 | Chemical analysis of the oils

Lipid oxidation is a dynamic equilibrium process in which the hydroperoxides are the key mediators in controlling the auto-oxidation progress. Hydro-peroxide can continue to produce the oxidation secondary products and degrade (Shahidi & Zhong, 2005). Chemical analysis includes measurement of different parameters, which will be discussed below. AV and PV measurements were conducted according to the official AOCS methods (American Oil Chemists' Society (AOCS), 2003). AV or the free fatty acid value (w_{FFA}) indicates the level of free fatty acid in the oil in the form of oleic acid (%); while PV indicates hydro-peroxide level (meq O_2/kg) which can be formed through oxidation during the storage process. AnV can be used to assess the aldehyde content (especially unsaturated α and β aldehydes) (Semb, 2012). Totox index can be also calculated by the following equation (Shahidi & Wanasundara, 2002):

$$Totox = 2 \times (PV) + AnV \quad (5)$$

According to AOCS standards, the oils with PV ≤ 10 meq/kg and AV ≤ 0.6 mg/g are defined as the nonoxidized oils, while those having PV 10 meq/kg and AV > 0.6 mg/g are considered as the oxidized ones (Xu et al., 2016). Chemical analyses were conducted in three replicates for each sample. All the experiments were carried out in Mahidasht Kermanshah Vegetable Oil Agricultural Industrial. The statistical analyses were conducted using a completely randomized factorial test. Analysis of variance was performed in factorial experiment in Randomized complete block design. Comparison of mean and main effects of interaction was performed by Duncan's multiple range test and MSTAT-C statistical software.

3 | RESULTS AND DISCUSSIONS

Voltage responses of the sensors were measured in 15 replicates for all the samples (fresh, oxidized oil, and those containing different levels of adulteration (25%, 50% and 75%). Finally, the responses of the sensor arrays were recorded for 75 samples. Maximum response of each sample was extracted as the descriptor of the obtained signals. Then, a 75 × 8 feature matrix (obtained from the samples) was used as the input for the data analysis. The responses of the applied sensors to different levels of adulteration in the edible oil are represented in Figure 2. The difference in the output responses of the sensors in the measurement stage can be observed in the mentioned figure.

3.1 | CA method results

Hierarchical CA method was used to classify 75 edible oil samples based on the responses of the eight-sensor array using squared Euclidean as the similarity distance and Ward's clustering method as the amalgamation rule. Dendrogram of CA method is shown in Figure 3. As this figure suggests, the edible oil samples were divided into two cluster and five groups with distance of 4.3. The first cluster included two groups of nonoxidized oils (fresh and 25% adulteration); while the three oxidized oils (50%–75% adulteration and oxidized sample) were placed in the second cluster. Therefore, CA method could offer an initial classification; although the group divisions were different in the different distances. Xu et al. (2016) classified the oxidized and nonoxidized oils with the inter-group distance of 5.01.

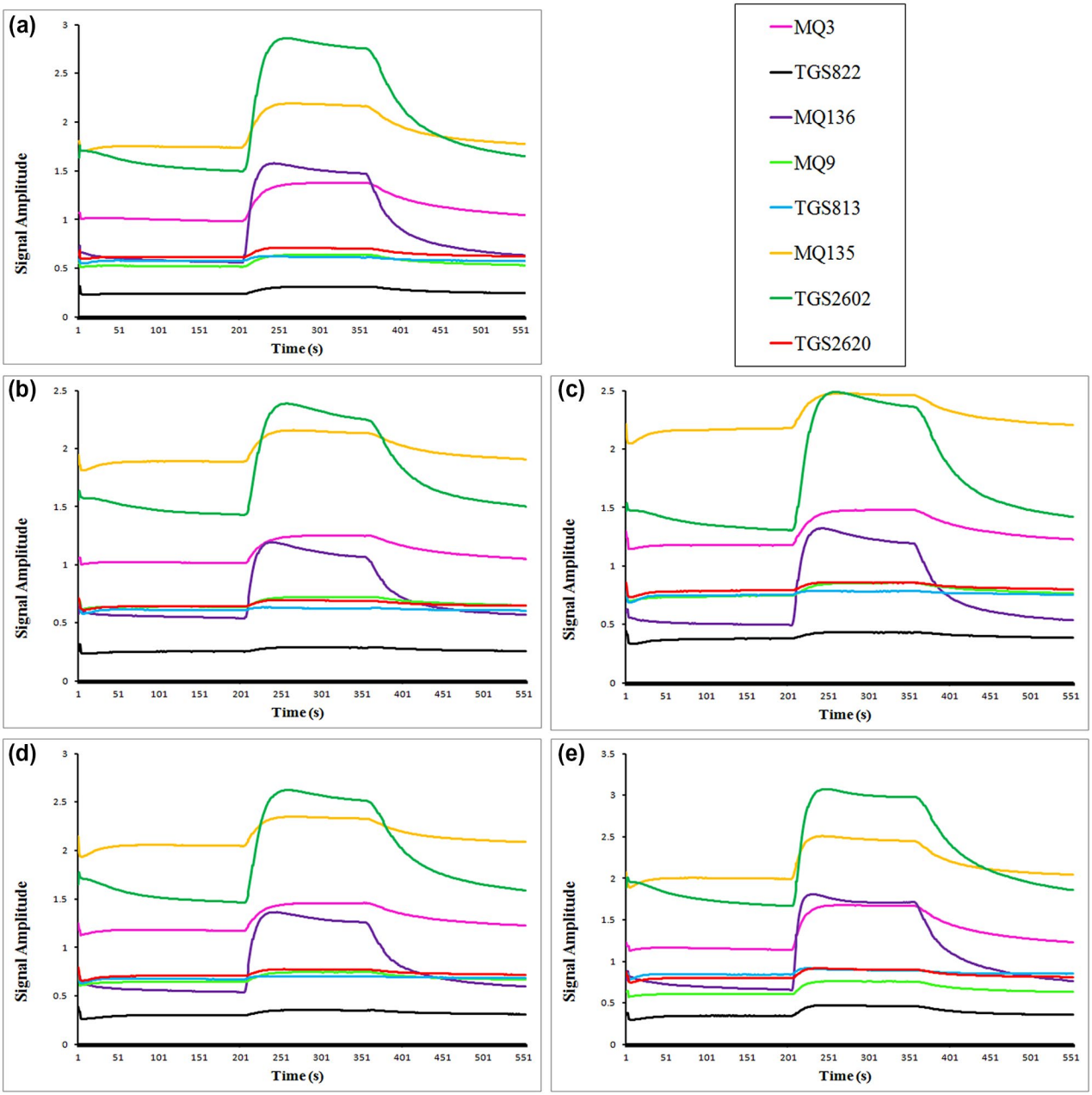

FIGURE 2 The responses of the electronic nose system to Different levels of adulteration on edible oils: (a) Fresh oil, (b) 25% adulterated, (c) 50% adulterated, (d) 75% adulterated, (e) Oxidized

3.2 | PCA method results

To detect adulteration in the edible oil samples, PCA method was also applied. Score diagram of the two major components is represented in Figure 4. This diagram is generally used to classify the separate data clusters to identify their pattern (Pearce et al., 2003). The first two major components described 98% variance of the data set (PC1 = 94% and PC2 = 4%) for differentiating the different levels of adulteration. According to the score diagram, the samples with different levels of adulteration were relatively different although 75% and oxidized oil sample somewhat overlapped with each other.

The role of each sensor in differentiating the samples can be studied by Loading diagram (Ghasemi-Varnamkhasti et al., 2015). For this purpose, the sensors were visualized in the loading diagram with their specific coefficients (Figure 5). Higher loading of a sensor on a major component (more proximity to the outer circle) reflects its higher role in detection and differentiation of the samples. According to the loading results, the sensors with the lowest impact of the detection and differentiation can be eliminated. This can reduce the complexity of the data analysis and also decline the construction cost of the sensor array (Ghasemi-Varnamkhasti et al., 2015). The loading diagram of the two major components is depicted in Figure 5. Accordingly, TGS2602 and MQ136 had the highest loading coefficients and hence played the most significant roles in the samples differentiations. Despite their high loading coefficients, as these coefficients were close to each other, it can be concluded that the two sensors had similar impacts on

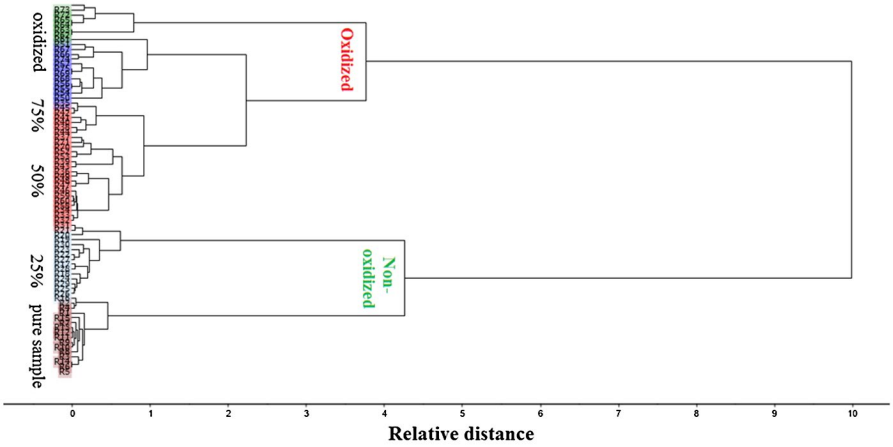

FIGURE 3 CA dendrogram responds to Pure and adulterated oil samples

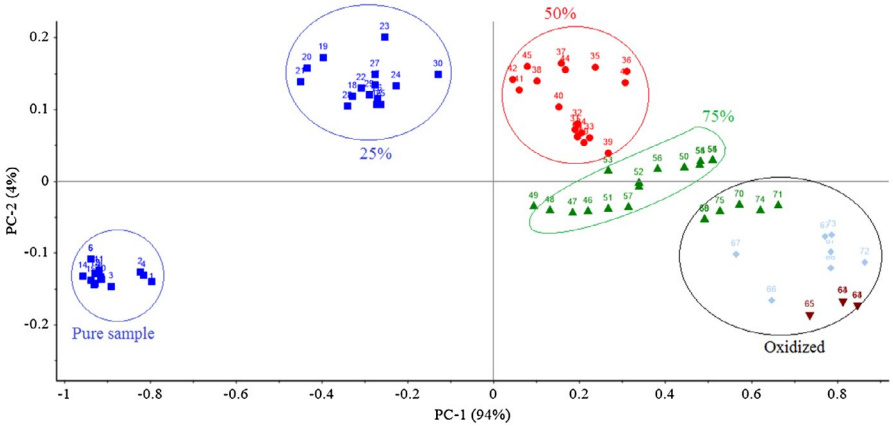

FIGURE 4 Score plot PCA analysis for different levels of adulteration

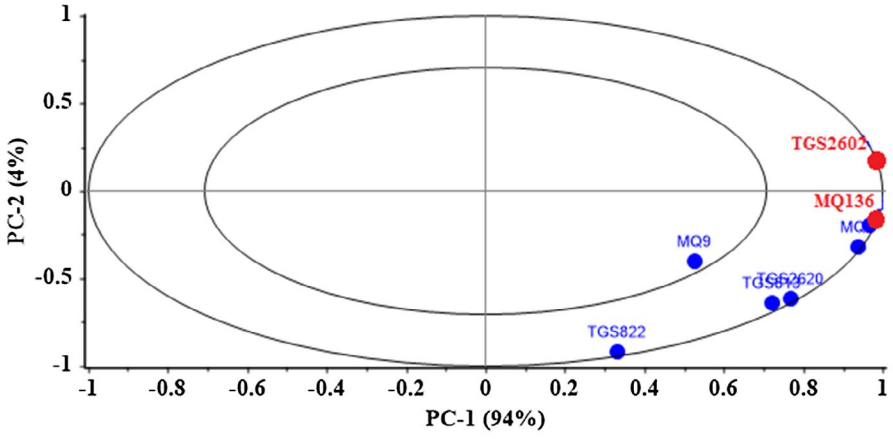

FIGURE 5 Loading plot for PCA analysis for different levels of adulteration

pattern identification. Hence, for the sake of simplicity, one of them can be used, as the figure suggests, MQ9 sensor had the lowest loading coefficient and exhibited the lowest differentiation capacity.

As the radar diagram of Figure 6 shows, oxidized oil and the one with 25% adulteration had the highest and lowest impact on the sensors, respectively. The highest response of the sensors was for TGS2602 related to smell of hydrogen sulfide, ammonia, and toluene as well as MQ136 related to sulfur dioxide (SO_2). MQ9, TGS822, and TGS813 had no role in the oils differentiation. Given the urge for reducing the fabrication cost of E-nose, these sensors can be eliminated. Ayari et al. (2018b) also reported similar results regarding the adulteration detection in animal oil and edible oil (Ayari et al., 2018a, 2018b).

FIGURE 6 Radar graph response of the sensors

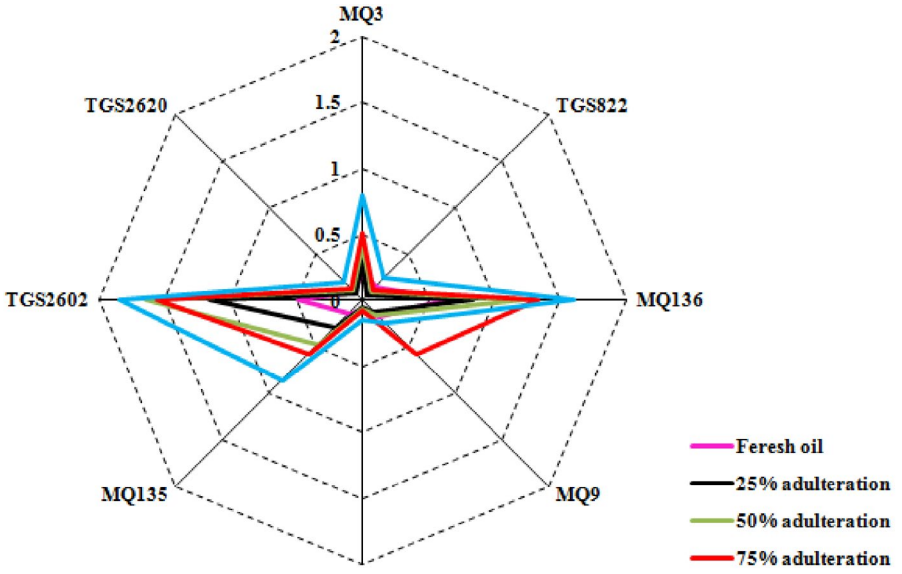

TABLE 2 Comparison of prediction and calibration results of PCR based on different data sets

		Calibration		Prediction	
	Sensor	R^2	RMSE	R^2	RMSE
Oil sample	MQ136	.99	.2749	.99	.2855
	TGS2602	.999	.0059	.999	.0058

3.3 | PCR method results

Prediction performance of PCR was estimated using the parameters obtained from the fitted equation; R^2 and RMSE between experimental and predicted values. Generally, the larger the R^2 and the lower the RMSE are, the better the prediction model is (Hong & Wang, 2014). Prediction and calibration results by PCR for TGS2602 and MQ136 sensor are shown in Table 2 and Figure 7. Hong and Wang (2014) in the detection of adulteration in cherry tomato juices based on electronic nose and tongue, obtained similar results.

3.4 | LDA method results

Linear discriminant analysis diagram of the E-nose signals for detection of oil adulteration is shown in Figure 8 according to LDA-1 and LDA-2 components. The results indicated the accuracy of 85%.

As it can be seen, the fresh oil was well differentiated with three levels of adulterated and oxidized oil. Disturbance diagram and performance parameters of LDA method are listed in Tables 3 and 4. Table 4 gives the performance parameters of the classifier according to the aforementioned confusion matrix including precision, accuracy, specificity, sensitivity, and area under the curve for (1) fresh oil, (2) 25%, (3) 50%, (4) 75%, and (5) oxidized adulteration. The average per class for precision, accuracy, specificity, sensitivity, and area under the curve were 95.2, 89.7, 88, 97, and 92.5, respectively. Regarding the obtained results, the classification accuracy of fresh oil and 25% adulteration was 100%. Comparing this method with official AOCS method, it can be said that the chemical tests failed to detect adulteration at the level of 25%; E-nose, however, managed to detect this level of adulteration with accuracy of 100%. Addition of another food product to a substance (even in small amounts) will change its smell pattern. Given the high sensitivity of the sensors and their high differentiation ability, these sensors can detect the difference between the volatile substances passing on their surfaces (Bhattacharyya & Bandhopadhyay, 2010). Xu et al. (2016) applied LDA method and succeeded to classify the fresh and spoiled oils with precision of 100%. Nouri, Mohtasebi, and Jahanbakhshi (2019), to classify different percentages of cocoa in chocolate, they obtained a 100% detection accuracy. In addition, in another study, they found 100% accuracy in detecting the quality of pomegranate fruit infected with fungal disease (Nouri, Mohtasebi, & Rafiee, 2020). Mahmodi, Mostafaei, and Mirzaee-Ghaleh (2019), obtained 87.1% accuracy for classifying different fuels.

3.5 | ANN results

Perceptron neural network was employed to classify the five types of the fresh and spoiled oils as well as those containing 25%, 50%, and 75% adulteration. For this purpose, considering the number of available sensors, eight neurons were allocated to the input layer while five ones were considered for the output layer depending on the adulteration level. To train the network, the variation of the number of neurons in the hidden layer and the MSE were determined by trial and error. By training the network with different number of neurons in the hidden layer, an optimal network with seven neurons in the hidden layer was created. Therefore, the best ANN had the structure of 8-7-5, which showed the highest accuracy in classification of the adulteration in the oil. CCR, MSE, and *R*-values of the best structure were 97.3%, .0027003, and .0984, respectively (Table 5). These results were considerably higher than the results obtained by

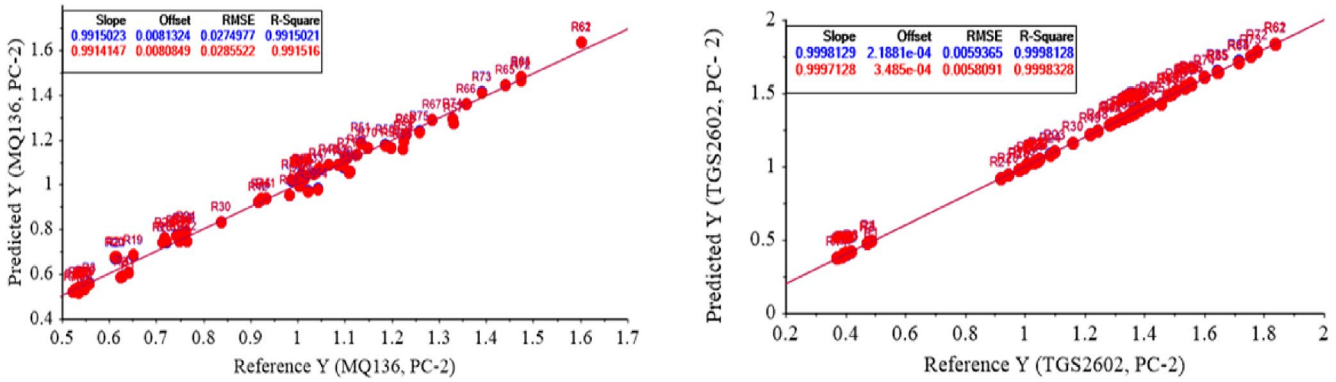

FIGURE 7 PCR results for different levels of adulteration (a) MQ136, (b) TGS2602

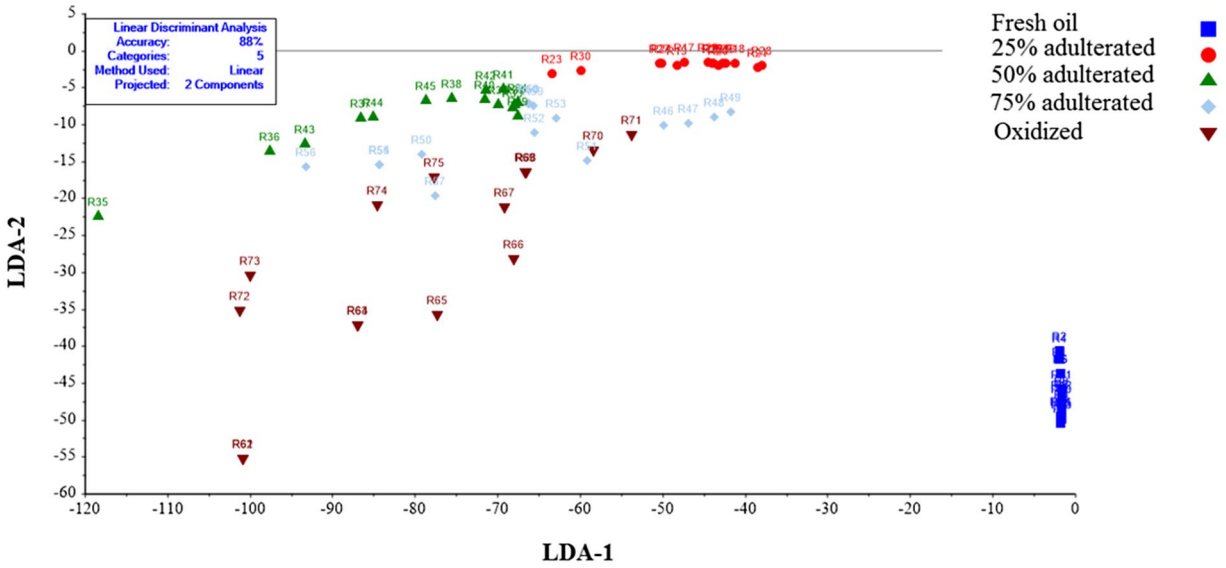

FIGURE 8 LDA results for different levels of adulteration

TABLE 3 Confusion matrix obtained to identify edible oil fresh from adulteration LDA and ANN classifier

Samples	Fresh oil	25% Adulterated	50% Adulterated	75% Adulterated	Oxidized
LDA					
Fresh oil	15	0	0	0	0
25% Adulterated	0	15	0	0	0
50% Adulterated	0	0	13	1	0
75% Adulterated	0	0	2	13	5
Oxidized	0	0	0	1	10
Correct classification rate	88%				
ANN					
Fresh oil	15	0	1	0	0
25% Adulterated	0	15	0	0	0
50% Adulterated	0	0	13	0	0
75% Adulterated	0	0	1	15	0
Oxidized	0	0	0	0	15
Correct classification rate	97.3%				

TABLE 4 Performance parameters for LDA and ANN classifier

Class	Accuracy	Precision	Sensitivity	Specificity	AUC
LDA					
Fresh oil	1	1	1	1	1
25% Adulterated	1	1	1	1	1
50% Adulterated	0.96	0.928571	0.866667	0.983333	0.925
75% Adulterated	0.88	0.65	0.866667	0.883333	0.875
Oxidized	0.92	0.909091	0.666667	0.983333	0.825
Average per class	0.952	0.897532	0.88	0.97	0.925
ANN					
Fresh oil	0.986667	0.9375	1	0.983333	0.991667
25% Adulterated	1	1	1	1	1
50% Adulterated	0.973333	1	0.866667	1	0.933333
75% Adulterated	0.986667	0.9375	1	0.983333	0.991667
Oxidized	1	1	1	1	1
Average per class	0.989333	0.975	0.973333	0.993333	0.983333

TABLE 5 Artificial neural network results for identify edible oil fresh from adulteration

Row	Structure	MSE	*r*	CCR
1	8-5-5	0.0205622	.0925	94.5
2	8-6-5	0.0195811	.0936	96.5
3	**8-7-5**	**0.0027003**	**.0984**	**97.3**
4	8-8-5	0.0186101	.0945	96.2
5	8-9-5	0.0162072	.9485	96.5

Abbreviations: CCR, correct classification rate; MSE, mean square error; *r*, correlation coefficient.

Ayari et al. (2018a) for detecting adulteration between the animal and edible oil. To evaluate the oxidation of Chinese-style sausage fat with determination coefficients (R^2s), more than .914 and .814 were obtained during processing and storage (Gu, Sun, Tu, & Pan, 2017). Similar results have been reported by other researchers (Gonzalez Viejo, Fuentes, Godbole, Widdicombe, & Unnithan, 2020).

Confusion matrix of this network is also presented in Table 3; while Table 4 lists the classification efficiency parameters according to the confusion matrix. The mean classification accuracy of each class was obtained as 97.3%. Table 4 gives the performance parameters of the classifier according to the aforementioned confusion matrix including precision, accuracy, specificity, sensitivity, and area under the curve for (1) fresh oil, (2) 25%, (3) 50%, (4) 75%, and (5) oxidized adulteration. The average per class for precision, accuracy, specificity, sensitivity, and area under the curve were 99.3, 98.3, 97.5, 97.3, and 98.9, respectively.

3.6 | Chemical analysis of the oil

The major components of the oil samples were analyzed according to official AOCS methods after E-nose analysis and the mean values are listed in Table 6.

TABLE 6 Analysis of variance for the chemical parameters of edible oil

	Sources	Mean square
p-Anisidine value	Treatments	6.691**
	Error	0.005
Peroxide value	Treatments	30.61**
	Error	0.005
Acetic acid value	Treatments	0.00002**
	Error	0.0001
Totox value	Treatments	72.458**
	Error	0.033

**Significant at $p \leq .01$.

Free fatty acids are the consequence of enzymic hydrolysis of triglycerides in which heat and humidity play the role of catalysts. These compounds contribute in auto-oxidation and give rise to products, which are the main cause of unpleasant taste and smell in the oil products (Brain & Yada, 2009). Peroxide index is a criterion to measure the hydro-peroxides. Hydro-peroxides are the primary product of the oxidation in oils and fats, which can be degraded to volatile and nonvolatile secondary products. Peroxide index can be a proper indicator of initial stages of oxidation (Shahidi & Zhong, 2005). Anisidine index indicates the secondary products of oxidation produced as the result of peroxides destruction (Bonilla, Atares, Vargas, & Chiralt, 2012). According to the strict standard regulation in Iran, the oils with acidity index above 0.6 and peroxide levels more than 5 are considered as the spoiled oil (Karami, Rasekh, & Mirzaee-Ghaleh, 2020).

Variance analysis on the impact of samples on the acidity, peroxide, anisidine, and Totox is summarized in Table 6. It can be seen that the effect of each components became significant at the probability level of 1%. The mean comparison of 5 testing methods were compared by multi-range Duncan mean comparison test at probability

TABLE 7 Mean comparison of five testing methods by multi-range Duncan mean comparison test

	Acetic acid value	Peroxide value	*p*-Anisidine value	Totox value
Fresh oil	0.055^{E}	1.693^{E}	11.84^{A}	15.23^{E}
25% Adulterated	0.060^{D}	3.633^{D}	11.05^{B}	18.32^{D}
50% Adulterated	0.065^{C}	5.90^{C}	10.10^{C}	21.90^{C}
75% Adulterated	0.070^{B}	8.40^{B}	8.467^{D}	25.27^{B}
Oxidized	0.075^{A}	9.333^{A}	8.563^{D}	27.23^{A}

The upper case letters A are for the highest value and D is for the lowest value.

level of 1% as listed in Table 7. Totox index is a criterion of total oxidation including initial and secondary products of oxidation (Shahidi & Zhong, 2005). The results of this index were similar to those of peroxide. As peroxide index is not a reliable index for the oils oxidation and it can be broken during the heat procedures, Totox index was used to calculate the oil oxidation (Billek, 1978).

According to Table 7, as expected, spoiled oils had higher Totox index compared to the fresh samples. The most important point was, however, the fact that the fresh and 25% adulterated samples were considered as the healthy oils and those with 50%, 75%, and 100% adulteration were determined as the spoiled or oxidized samples. This means that the chemical tests could not detect adulteration in the sample containing 25% oxidized oil. Therefore, it is possible that the producers mix their fresh oils with oxidized one at the mentioned level to reach to higher profit. This could be highly dangerous for human health.

4 | CONCLUSIONS

In this study, a portable eight-sensor E-nose was employed to investigate the oxidation degree of the edible oils. These results indicated that application of E-nose in combination with CA, PCA, PCR, LDA, and ANN methods could be a promising approach in successful detection of adulteration in the edible oils.

Eight sensors of the electronic nose exhibited different response signals to the oxidized oils which were different from the nonoxidized one. Based on the findings of this study, it is suggested to use E-nose along with CA, PCA, PCR, LDA, and ANN methods to determine adulteration in the oil. The results of this research were mainly in line with the results of the official AOCS method except for the sample with 25% adulteration. Therefore, the E-nose, which is similar to the human olfaction system, requires no specific design to detect the volatile compounds. This technique is superior over the conventional official method for detection of oxidation degree in the edible oils as it is a nondestructive and timesaving method which reduced the use of toxic organic solvents. The results of this study showed that application of the proposed E-nose could decrease the dependence to the olfaction evaluator individuals or time-consuming data analysis to differentiate the oxidized oils from the nonoxidized ones.

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CONFLICT OF INTEREST

The authors have declared no conflicts of interest for this article.

ETHICAL STATEMENT

Ethics approval was not required for this research.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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