Contents lists available at ScienceDirect

Chemometrics and Intelligent Laboratory Systems

journal homepage: http://ees.elsevier.com

# Comparison of chemometrics and AOCS official methods for predicting the shelf life of edible oil

Hamed Karami[a], Mansour Rasekh *[a], Esmaeil Mirzaee – Ghaleh *[b]

[a] Department of Biosystems Engineering, University of Mohaghegh Ardabili, Ardabil, Iran
[b] Department of Mechanical Engineering of Biosystems, Razi University, Kermanshah, Iran

ARTICLE INFO

*Keywords*
Olfactory machine
Classification
SVM
LDA

ABSTRACT

The present study addressed the determination of the shelf life of edible oil using the non-destructive method of electronic nose (E-Nose) and compared it with the AOCS official method. The studied oils included two samples: newly-produced oils (a) and those produced 6 months before (b). These samples were assessed for 150 days. Data collection was conducted using an electronic nose equipped with 8 metal oxide semiconductor (MOS) sensors. Data analysis was also achieved by various methods including cluster analysis (CA), linear discriminant analysis (LDA) and quadratic discriminant analysis (QDA), support vector machine (SVM), and AOCS official method. According to the results, the classification accuracy of SVM, QDA, and LDA methods was 96.25, 95.8, and 94.4%, respectively. All the methods were in line with the results obtained by AOCS.

## 1. Introduction

Food consumption is rising by the increase of the world's population. In this regard, the consumption rate of edible oil has been rapidly increased. Edible oil quality is highly dependent on its resistance against oxidation. Edible oil oxidation is one of the major concerns in the food industry which could decline the product quality due to causing undesirable taste. Oxidation may also give rise to loss of nutrients and bioactive compounds, the formation of potentially toxic compounds and economic loss [1]. Long-term storage of edible oils under the improper environmental condition such as high temperatures and exposure to light or oxygen makes them prone to oxidation. Hydro-peroxides are the primary products of oxidation; while aldehydes, ketones and other small molecules are among the secondary products [2]. Moreover, these products may cause food poisoning. Therefore, oil oxidation is the major factor in its quality decline and often determined the storage time of the edible oil [3,4].

To monitor the oxidation degree of edible oils, several standard methods have been used to evaluate the oxidation status of the product. Hydro-peroxides and free fatty acids (FFA) are often measured by chemical titration methods which are costly, time-consuming, and difficult requiring high amounts of solvent imposing serious risks to human health and the environment [5].

Conventional non-destructive methods are generally based on analyzing the fatty acid profile (spectroscopic methods). Despite their precision, these methods are complicated, time-consuming, tedious and costly. Moreover, they are sensitive and may not be proper for use under harsh conditions. Furthermore, these methods require highly skilled users. Recently, various spectroscopic methods such as near-IR (NIR) and Fourier transform IR spectroscopy (FTIR) have been widely developed for the evaluation of edible oils. These techniques are fast and environmentally-friendly; however, they require complicated pre-operation [6]. Nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR) methods have been also employed for rapid and effective evaluation of edible oil quality. The mentioned methods are however costly [7]. Therefore, new methods have to be developed to examine oil oxidation. Today, researchers seek non-destructive methods with low cost and high accessibility which are capable of detecting quality indices of edible oil fast and accurately. Furthermore, they have to possess commercialization capability. Nowadays, electronic senses (electronic nose, tongue, and eye) have been widely used for various applications including quality control, process supervision, durability evaluation and authenticity verification [8]. The electronic nose is a tool designed to mimic human olfaction. This device consists of non-selective or semi-selective sensors used for the production of electronic signals in interaction with aromatic compounds [9].

Various studies have employed electronic nose to determine the shelf life of products such as auto-oxidation of canola oil [10], oxidation degree of ultra-virgin olive oil [11,12], vinegar [13], Spiny-head croaker [14], large yellow croaker [15], Wine [16], Chicken [17],

*Corresponding author.
*Corresponding author.
*E-mail addresses:* hamed.wur.nl@gmail.com (H. Karami); ma_rasekh1349@yahoo.com.au (M. Rasekh); e.mirzaee@razi.ac.ir (E. Mirzaee – Ghaleh)

https://doi.org/10.1016/j.chemolab.2020.104165
Received 5 March 2020; Received in revised form 10 August 2020; Accepted 13 September 2020
Available online xxx
0169-7439/

camellia oil authentication [18], edible olive oil characterization and shelf life assessment [19], detection and discrimination of plant oil scents and their mixtures [20], tomato [21,22], apple [23,24], raw milk and meat [25], Valerianella [26,27], locusta, French fries [28] and rice [29]. E-Nose was also applied to determine oil oxidation through sensory data [6]. However, no study has reported the use of E-Noses in the determination of the shelf life of edible oil.

Regarding the application of E-Nose in different fields, the present study is aimed at finding a relationship between the edible oil oxidation and its smell. In this context, this study is intended to determine the shelf life of the edible oils using a combination of olfaction machines, and linear and quadratic discriminant analysis (LDA and QDA) and support vector machine (SVM). The results of this research were confirmed by comparison with the American Official Chemist Society (AOCS). The proposed method can serve as a cost-effective and simple alternative to control the quality of oils and fats during their storage chain.

## 2. Material and methods

In this study, first, mixed edible oils (sunflower, canola, and soy) with new and 6-month production dates were provided from a local market in Kermanshah, Iran. The samples were kept under suitable conditions similar to the kitchen (dry and dark and temperature of 24°C and relative humidity of 34–85%). This condition is identical to the condition in storage places and the selling location of edible oil. 20 mL of each oil sample was poured in a 50-mL glass container. Totally, 40 oil samples (20 with a new production date and 20 with production dates 6 months before) were tested. Therefore, the experiment involved 720 tests (40 samples with 3 replications for 5 months).

The applied E-Node included sensors, electronic parts, pumps, ventilation, and software section for data analysis [30]. Fig. 1 presents a schematic view of the applied E-Nose [52].[].

Data collection involved 3 stages: in the first step, clean air was passed over the sensor chamber for 200 s to clean the sensors until they reached a stable response. In the second stage, head air was injected into the sensor chamber for 150 s. The third stage included the passage of clean air for 200 s to discharge the chamber smell until the response of the sensor reached the baseline and making it ready for the subsequent tests. The sensor array included 8 metal oxide semiconductor (MOS) sensors. MQ3 (alcohol), TGS822 (organic solvents steam), MQ136 (sulfur dioxide), MQ9 (carbon monoxide), TGS813 (methane, propane and butane), MQ135 (ammonia, benzene and sulfide steams), TGS2602 (hydrogen sulfide, ammonia and toluene) and TGS2620 (alcohol and organic solvents steam).

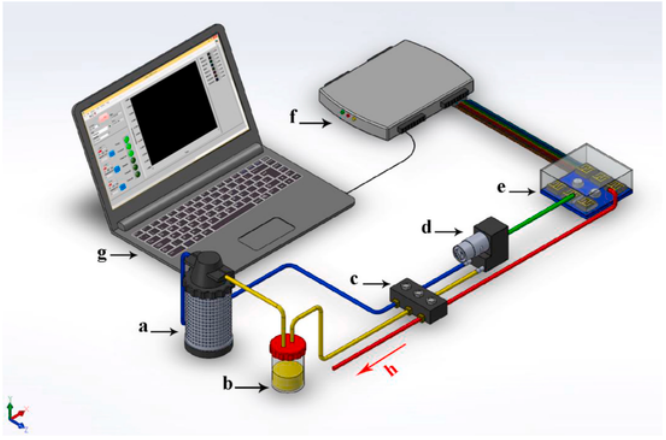


**Fig. 1.** Schematic of olfactory system used a) Carbone active filter, b) sample, c) valve, d) pump, e) sensor array, f) date acquisition card, g) PC and h), air outlet.

Throughout the mentioned steps, the output voltage of the sensors changed due to exposure to different aromas. Their smell response was collected by the data collection cards, sensors signals were recorded in the USB gate of the PC in 1-s intervals and then saved. The sensor response was expressed in Ohm (the unit of electrical resistance). In this study, the baseline correction was conducted by a fractional method in which the noise or possible deviations were eliminated and the responses of the sensors became dimensionless in addition to being normalized [32]:

$$Y_s(t) = \frac{X_s(t) - X_s(0)}{X_s(0)} \quad (1)$$

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

To analyze the pre-processed data, cluster analysis (CA), linear discriminant analysis (LDA) and support vector machine were employed.

CA is a technique trying to divide the data into specific groups based on the observations similarity or distance [33]. The results of hierarchical cluster analysis are often displayed as a dendrogram [34]. In this study, Ward's method was employed using square Euclidian distance to determine the membership cluster based on the nearest central ordering method.

Linear discriminant analysis is a statistical method employed for machine learning and pattern recognition to find a linear combination of the features capable of presenting the difference between two or more objects in the best possible manner. LDA is similar to the variance analysis and regression as all of them model the dependent variable as a linear combination of the other independent variables [35]. To optimize the inter-group discrimination, the LDA method maximizes the intra-group variance while minimizing the inter-group variance [36].

SVM can be also used to classify the linear and nonlinear data. This method is a supervised learning method to classify the data based on the statistical learning theory. In the SVM method, two approaches can be adapted for data classification: C-SVM and Nu-SVM. Their difference lies in their problem description in the form of an optimization problem as well as the selection of Nu, C and v parameters to minimize the error function. SVM classifier operates based on the linear classification of the data. In linear data classification, it is tried to select the line with a higher confidence margin [36].

In the present study, 70% of the data were considered to train the model and the remaining 33% were applied for test and evaluation. The model inputs included the data obtained from 8 sensors and the output was the oxidation degree. The confusion matrix was also used as one of the indices for selecting the best model. Confusion matrix analysis resulted in 4 true positive states for edible oil classification (TP, cells which were correctly allocated to their corresponding class), true negative (TN, cells which were not correctly allocated to the intended class) false positive (FP, incorrect cells which were allocated to their class) and false negative (FN, cells which were not correctly allocated to their intended class) [33]. Sensitivity, accuracy and validity were employed to analyze the system performance [34]:

$$\text{Sensitivity} = \frac{TP}{TP + FN} \quad (2)$$

$$\text{Specificity} = \frac{TN}{TN + FP} \quad (3)$$

$$\text{Precision} = \frac{TP}{TP + FP} \quad (4)$$

$$\text{Accuracy} = \frac{TP + TN}{TP + TN + FN + FP} \quad (5)$$

$$\text{AUC} = \frac{\text{Sensitivity} + \text{Precision}}{2} \quad (6)$$

It must be noted that in this study, the weight and significance of the criteria were considered the same and Unscrambler X 10.4 software was employed for data analysis.

A complicated chain of reaction is involved in oil oxidation. Hydroperoxides are the major products of oil oxidation. These compounds are unstable and can be easily decomposed in a complex of secondary products such as aldehydes, ketones, acids, alcohols, esters and other small molecules [37]. Chemical parameters measurements were conducted using the AOCS official method [38].

Acidity Value (AV) was measured using AOCS official method Ca 5a-40, and using the following equation, the percentage of oil acidity was determined [39,40]:

$$Acidvalue = \frac{mLNaOH \times N \times 28.2 \times 1.99}{gofsample} \quad (7)$$

N, is the normality of sodium hydroxide, and here the acid value was calculated in terms of the molecular weight of oleic acid. AV (acidity value or the free fatty acid content) indicates the level of the free fatty acids in the oil expressed as the percentage of oleic acid. Free fatty acids are present in the raw oils which will be eliminated during the refinery process. In comparison with the esterified fatty acids, free fatty acids are more prone to autoxidation. Therefore, FFAs act as pro-oxidants in the edible oil [2].

Peroxide value (PV) was measured using AOCS official method Cd 8b-90. The peroxide value was measured using the following equation [39,40]:

$$PV = \frac{(S-B) \times N \times 1000}{g\ of\ sample} \quad (8)$$

PV is expressed as mili-equivalent of oxygen per kg of oil, B ml of sodium sulfate used for the blank sample, S ml of sodium thiosulfate used for oil samples, and N is the normality of sodium thiosulfate solution. PV is usually used as a quality parameter for the primary oxidation of the lipids. In other words, it measures the extent of primary oxidation reactions. This index is a measure of hydro-peroxides based on the amount of active oxygen of the fat. Hydro-peroxides are the primary products of oxidation. They have no taste or smell, but they will be rapidly decomposed to aldehydes with undesirable smell and taste. During fats and oils oxidation, the primary rate of hydro-peroxide formation is higher than their decomposition; which will be reversed in the subsequent stages [41].

Anisidine value (AnV) was measured using AOCS official method Cd 18–90, and its value was determined using the following equation [39,40]:

$$PAV = \frac{25 \times (1.2As - Ab)}{m} \quad (9)$$

As, adsorption of oil solution after reaction with *para*-anisidine reagent, Ab, adsorption of the oil solution before adding the *p*-anisidine reagent, and m is the weight of the oil in terms of grams.

Totox index was also calculated by the following equation [42]:

$$Totox = 2 \times (PV) + AnV \quad (10)$$

The oils with PV 10 meq/kg and AV > 0.6 mg/g are considered as the oxidized, and oils with PV ≤ 10 meq/kg and AV ≤ 0.6 mg/g are defined as the non-oxidized [6]. 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 analysis were conducted using a completely randomized factorial test.

## 3. Results and discussions

### 3.1. Variation in the quality indices of oil during the storage period

The main components of the oil samples were first assessed by E-Nose and then measured by the AOCS method. The other important parameter used in the evaluation of the edible oil quality was peroxide value (PV) which indicates the oxidation level of lipids. Peroxide index is a measure to detect the primary stages of oxidation. The mean PV was about 3 for the samples on the first day which ascended during the storage period (150 days) and reached 6.5. However, as this index is not a reliable indicator of oil oxidation, the oil oxidation was further assessed through the calculation of Totox index using Eq. (10) [43]. Table 1 lists the mean primary values of the two groups of samples (newly-produced oils (a) and those produced 6 months before (b)).

A factorial test was conducted including two factors: oil type and storage time. The considered levels encompassed two types of oil (newly produced oils and those produced 6 months before) and storage time (5 months) which were assessed in one-month intervals. The results of the variance analysis of the samples are listed in Table 2 for acidity, peroxide, anisidine, and totox indices. Accordingly, the impact of oil type (A) and time (B), as well as the interactive impact of oil

**Table 1**
Mean primary values of edible oil.

| | Acetic Acid | *p*-Anisidine | Proxide | Totox |
|---|---|---|---|---|
| A | 0.5 | 6.36 | 3.36 | 13.09 |
| B | 0.45 | 8.86 | 3 | 14.86 |

**Table 2**
Analysis of variance for the chemical parameters of edible oil.

| | Sources | Degress of freedom | Mean of squares |
|---|---|---|---|
| *p*-Anisidine Value | Factor A | 1 | 88.988** |
| | Factor B | 5 | 0.571** |
| | AB | 5 | 0.368** |
| | Error | 24 | 0.071 |
| | Total | 35 | |
| Proxide Value | Factor A | 1 | 0.034 |
| | Factor B | 5 | 9.682** |
| | AB | 5 | 0.052 ns |
| | Error | 24 | 0.020 |
| | Total | 35 | |
| Acetic Acid Value | Factor A | 1 | 0.314** |
| | Factor B | 5 | 0.120** |
| | AB | 5 | 0.122** |
| | Error | 24 | 0.000 |
| | Total | 35 | |
| Totox Value | Factor A | 1 | 82.204** |
| | Factor B | 5 | 34.534** |
| | AB | 5 | 0.697** |
| | Error | 24 | 0.104 |
| | Total | 35 | |

** significant at p ≤ 0.01.

type-time (AB), was significant (at the p-value of 1%) for anisidine, acidity and Totox indices; while the oil type was not significant for the PV index. Fig. 2 presents a comparison of the mean values using Duncan's multi-range mean comparison test at the p-value of 1%.

Results indicate that FFA (%) increased in both types of oil during the storage period. This increase can be attributed to the endemic species of microorganisms entered the oil during various processing and transportation stages from the plant [44]. As suggested by Fig. 2, the highest acidity was observed in two time periods (120 and 150 days) for the second type of oil (0.6) while the lowest value was recorded in 90-day storage of the first type of oil (0.4). The changes in the obtained values during the storage period were in line with the results obtained by Ndando et al., 2011 [38]. This does not necessarily indicate a real decline as unsaturated FFA may be influenced by the subsequent chemical reactions such as peroxidation and give rise to secondary products that are unidentified by the acidity assessment methods. Regarding the quality of oils produced in Iran and strict standards, acidity over 0.6 and PV over 5 are recognized as the spoiled oil.

On the first day, PV was 3.36 and 3 for the first and second types of oil, respectively. According to the conducted tests, the influence of oil type was not significant at 1%. In other words, it can be said that this index is a function of oxidation time and will increase upon opening the oil and initiation of the oxidation reactions. As the results indicate, this index exhibited an ascending trend and reached to its maximum (6.6 $meqO_2/kg$) at the end of the 5th month. As shown in Fig. 2, the highest PV was observed in the first type of oil and on the 150th day (6.6) while the lowest value was for the second type of oil and on the first day (3). These two values have a significant difference at 1%. On the other hand, as the applied oil was refined, some of its natural compounds such as tocopherols were lost which may accelerate the oxidation process. This index is a measure of hydro-peroxides based on the fat active oxygen level. Hydro-peroxides have no taste and smell, but they can be rapidly decomposed to aldehydes with highly undesirable taste and smell. Hydro-peroxides are recognized as the primary products of the oxidation reaction which may decompose to volatile and non-volatile secondary products [45].

In contrary to peroxides, Anisidine index indicates the secondary products of oxidation produced from the destruction of the hydro-peroxides [46]. Based on Fig. 2, AnV of the second oil was higher than the first one. Increased AnV indicates the development of spontaneous oxidation and enhanced secondary products due to the decomposition of hydro-peroxides and carbonyl compounds. Generally, this index exhibited an increasing trend followed by a slight decrease which might be assigned to the complete destruction of the hydro-peroxides.

Totox index is a measure of total oxidation including both the primary and secondary products [45]. As depicted in Fig. 2, the highest Totox value was observed in the second oil after 150 days (22.3) while the lowest Totox value was recorded on the first day for the first oil (12.63). Totox index increased by time for both types of oils; this is completely in line with the results obtained by the E-nose (Fig. 3). As suggested by Fig. 3, the normalized response of the 8 sensors to the oil smell showed an ascending trend in 5 months which was highest for MQ9 and TGS2620 sensors.

### 3.2. CA analaysis

For cluster analysis to classify 240 edible oil samples with 3 replications based on the response of 8 sensors, square Euclidian distance was employed as a measure of similarity while the clustering method of Ward served as the amalgamation law. The results are shown in (Fig. 4) in the form of a dendrogram. Clustering results revealed that all the oils can be classified into two major classes (non-oxidized and oxidized). Each class included three clusters. The oils of the month 0, 1, and 2 belonged to the first class of the non-oxidized oils while those of the moth 3, 4, and 5 belonged to the second class of the oxidized oils. Xu, Yu, Liu and Zhang [6] divided the edible oils into two groups of oxidized and non-oxidized with the inter-group distance of 5.01.

### 3.3. LDA and QDA results

To classify the shelf life of edible oil every month, LDA and QDA were employed. The models' input included the data obtained from 8 sensors. All the data had a weight of 1. The results indicated that using the LDA method, only 13 data were not correctly classified and the total detection of the model amounted up to 94.58% (Fig. 5). As can be seen, according to the chemical properties of the oils, the non-oxidized

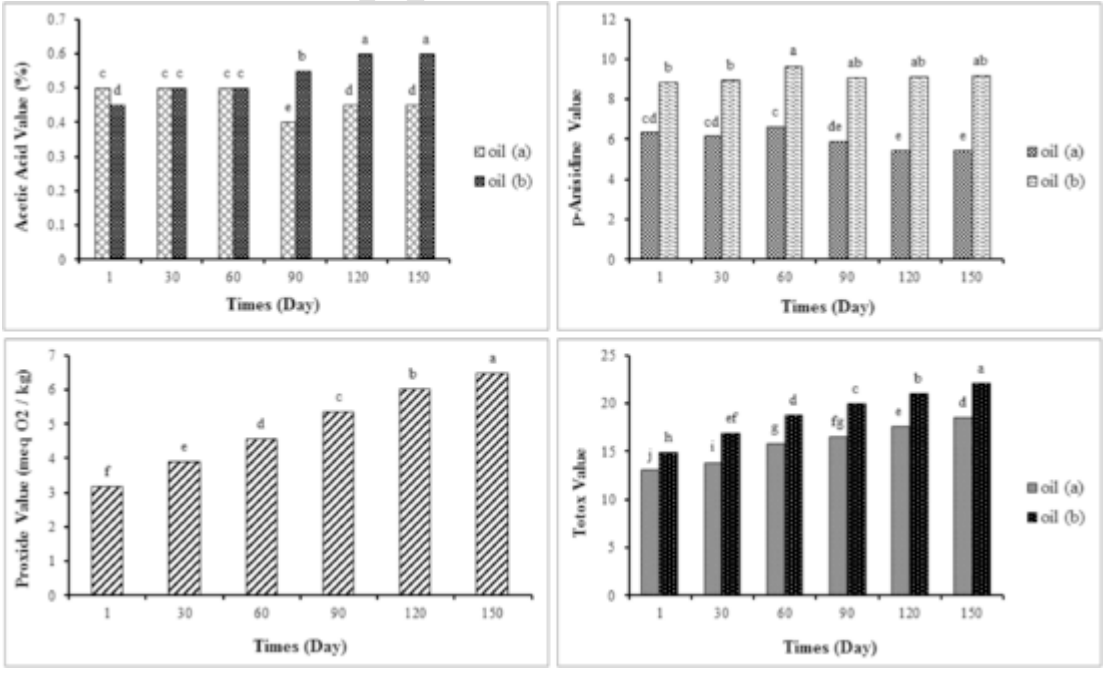


**Fig. 2.** Result of Duncan mean comparison test.

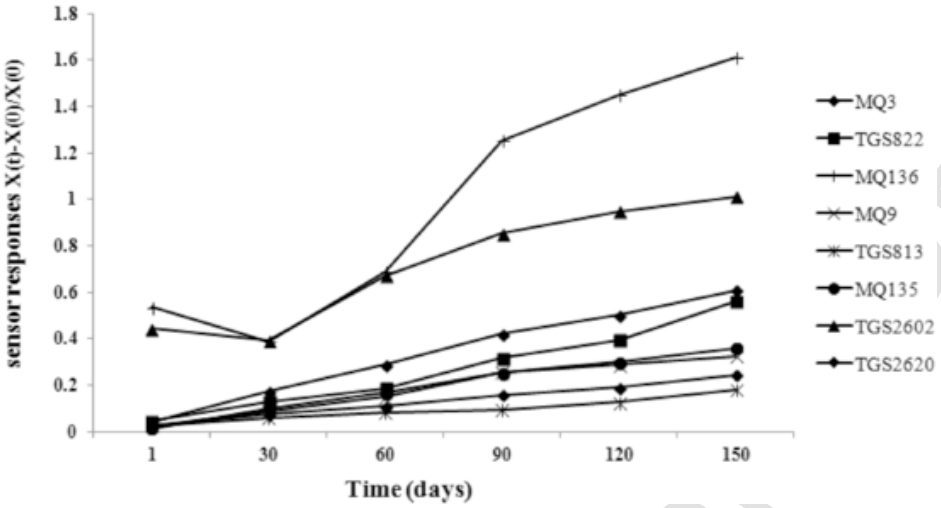


**Fig. 3.** Sensor responses of the electronic nose system to shelf life of the edible oils.

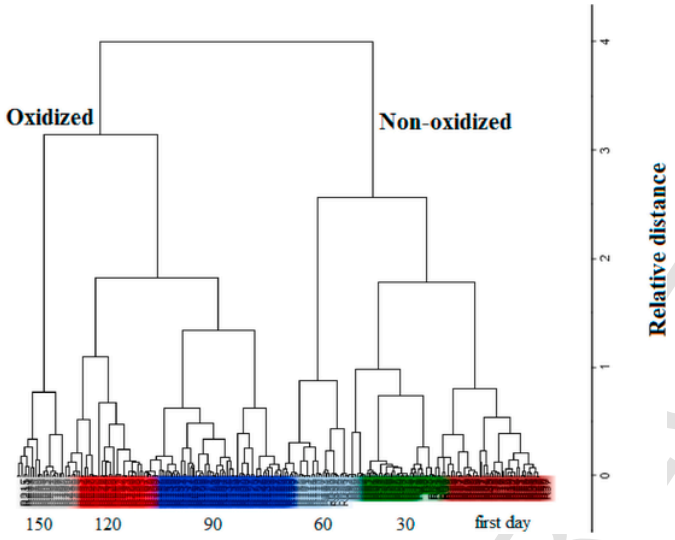


**Fig. 4.** CA dendrogram responds to Oxidized and Non-oxidized oil samples.

data were completely classified; the oxidized oils, however, showed some overlap which could be assigned to their pungent smell. Table 3 presents the confusion matrix of the shelf life of edible oils obtained by LDA and QDA methods. Regarding Eqs. (2)–(6), performance parameters of LDA and QDA methods for classification of the shelf life of edible oils can be summarized in Table 3. The confusion matrix was employed to calculate the performance parameters of the detection models. For each class, the main diagonal data are TP, the sum of the other main diagonal data is TN; while the sum of the data in the relevant column is related to FP and the sum of data in the relevant row can be assigned to FN. According to Table 4, the classification accuracy of the LDA and QDA method was 94.4% and 95.8%, respectively.

In a study on pure diesel and biodiesel fuels, the classification accuracies of the data were 94.4% and 87.1% for QDA and LDA, respectively [33]. In another research LDA and QDA methods were exploited to classify apples based on their storage time using frequency response; the accuracies of LDA and QDA methods were 80.56% and 83.33%, respectively [47].

Intra-group classifications of the oils into 12 groups (the oils of each 6 groups were divided into two subgroups: newly produced (a) and those produced 6 months before (b)) were also conducted using LDA and QDA methods. The results indicated that LDA and QDA methods had a total detection of 87.08% and 93.75%, respectively (Fig. 6). Intra-group classification confusion matrix of the edible oils through LDA and QDA methods is listed in Table 5. Table 6 also presents the performance parameters of LDA and QDA methods for intra-group classification of edible oils. According to Table 5, the data classification accuracy of LDA and QDA methods was 88.1%, and 94.1%, respectively. The confusion matrix also revealed that out of 240 data of edible oil, 209 and 225 data were correctly allocated to their corresponding classes using LDA and QDA methods, respectively. In other words, as the experiments were conducted in 6 periods and all the oxidation stages of the oil were classified into 6 groups, it is important to differentiate the newly-produced oils from those produced earlier. Therefore, LDA and QDA managed in the intra-group classification of data with high precision in line with the results of the AOCS method. Based on Tables 5 and 6, the QDA method offered higher inter-group classification accuracy in comparison with the LDA method. In a study aimed at detecting adulteration in virgin olive oil, MOS sensor E-Nose was employed and the data were analyzed by LDA, QDA and ANN methods which resulted in prediction accuracy over 95% [48]. Karami et al., 2020, classified fresh and oxidized oil, with an accuracy of 100% . Nouri et al., 2019, to classify different percentages of cocoa in chocolate, they obtained a 100% detection accuracy [49]. Also Karami et al., 2020, for detection of oil adulteration with the LDA method indicated an accuracy of 85% [32].

### *3.4. SVM results*

SVM is one of the most important data mining models in recent years. This model relies on statistical learning and mathematical optimization using the principle of minimizing the structural error leading to an overall optimized solution. Samples were classified by two methods of C-SVM and Nu-SVM. Nu, C and γ parameters were verified by trial and error through minimization. 70% of the data were used for training while 30% of them were employed for testing. The weight of all inputs was equal to 1. Four types of kernel functions including polynomial, linear, sigmoid and radial were also used.

The SVM method results are summarized in Table 7. As for the validation set, the classification accuracies for the 6 oil groups based C-SVM models were 95%, 75.83%, 92.5%, and 95% for linear, Polynomial, Radial basis function, and sigmoid, respectively. Also for the validation set, based Nu-SVM models were 95.14%, 87.92%, 95.83%, and 90.14% for linear, Polynomial, Radial basis function, and sigmoid, respectively. FAor 6 oil groups in C-SVM and Nu-SVM methods, the highest accuracy was for linear function and sigmoid (95 for training and

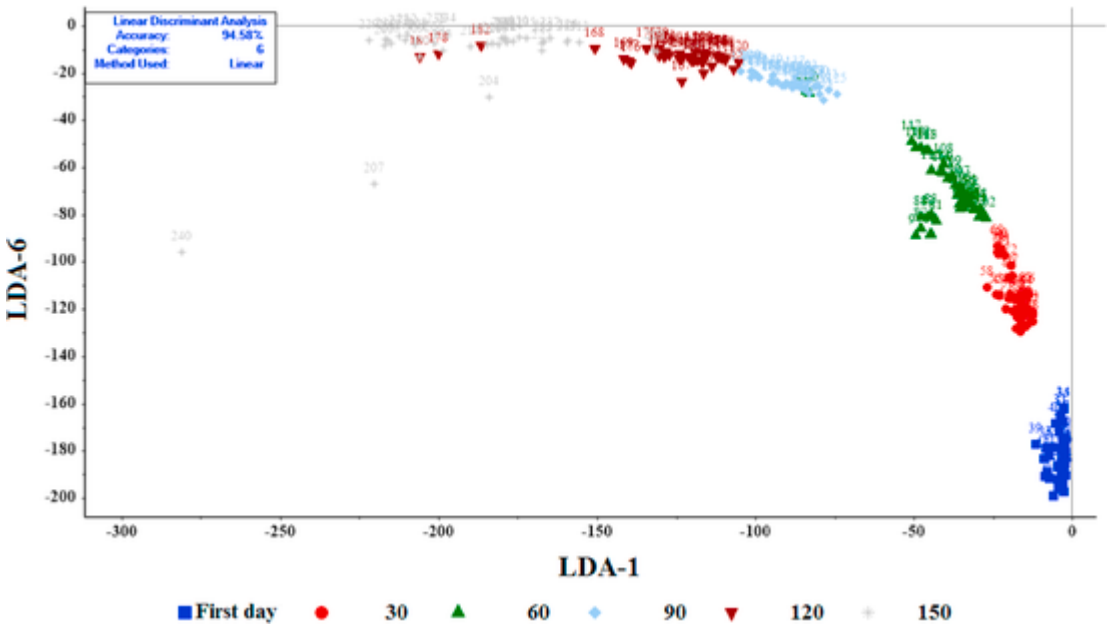


**Fig. 5.** Classification of the edible oils shelf life per month using LDA method.

**Table 3**
Confusion matrix of the edible oils shelf life per month classification using LDA and QDA methods.

| Model | Months of storage | 0 | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|---|
| **LDA** | **0** | 40 | 0 | 0 | 0 | 0 | 0 |
| | **1** | 0 | 40 | 0 | 0 | 0 | 0 |
| | **2** | 0 | 0 | 38 | 0 | 0 | 0 |
| | **3** | 0 | 0 | 2 | 39 | 3 | 0 |
| | **4** | 0 | 0 | 0 | 1 | 36 | 6 |
| | **5** | 0 | 0 | 0 | 0 | 1 | 34 |
| **QDA** | **0** | 40 | 0 | 0 | 0 | 0 | 0 |
| | **1** | 0 | 40 | 0 | 0 | 0 | 0 |
| | **2** | 0 | 0 | 38 | 0 | 0 | 0 |
| | **3** | 0 | 0 | 2 | 39 | 1 | 0 |
| | **4** | 0 | 0 | 0 | 1 | 38 | 5 |
| | **5** | 0 | 0 | 0 | 0 | 1 | 35 |

**Table 4**
Performance parameters of LDA and QDA models for classification of the edible oils shelf life.

| Model | Months of storage | Accuracy | Precision | Sensitivity | Specificity | AUC |
|---|---|---|---|---|---|---|
| **LDA** | **0** | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| | **1** | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| | **2** | 0.991 | 1.000 | 0.951 | 1.000 | 0.975 |
| | **3** | 0.973 | 0.886 | 0.975 | 0.973 | 0.974 |
| | **4** | 0.951 | 0.837 | 0.911 | 0.962 | 0.931 |
| | **5** | 0.969 | 0.971 | 0.851 | 0.994 | 0.922 |
| **Average per class** | | **0.981** | **0.944** | **0.965** | **0.988** | **0.976** |
| **QDA** | | | | | | |
| | **0** | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| | **1** | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| | **2** | 0.991 | 1.000 | 0.951 | 1.000 | 0.975 |
| | **3** | 0.982 | 0.928 | 0.975 | 0.984 | 0.979 |
| | **4** | 0.965 | 0.863 | 0.951 | 0.968 | 0.959 |
| | **5** | 0.973 | 0.972 | 0.875 | 0.994 | 0.934 |
| **Average per class** | | **0.985** | **0.958** | **0.975** | **0.991** | **0.982** |

96.27% for validation), and Radial basis function (95.83 for training and 96.27% for validation), respectively. Also for the validation set, the classification accuracies for the 12 oil groups based C-SVM models were 90.416%, 67%, 89.58%, and 89.583% for linear, Polynomial, Radial basis function, and sigmoid, respectively. Finally for the validation set, based Nu-SVM models were 90.416%, 80%, 89.17%, and 89.583% for linear, Polynomial, Radial basis function, and sigmoid, respectively. Moreover, for 12 oil groups in C-SVM and Nu-SVM methods, the highest accuracy was for linear function (91.67 for training and 90.42% for validation).

In a study on the classification of Damask rose essential oil by an E-Nose, the classification accuracies of LDA and SVM methods were 95% and 99%, respectively [50]. In another study aimed at describing the freshness of strawberries packed in polymeric packages by response surface method (RSM), the accuracy of samples classification by SVM method through C-SVM and polynomial function was 86.4% and 50.6% for training and validation, respectively. In the case of Nu-SVM, the training and validation accuracies were 85.2% and 55.6% through the use of a radial function [51]. Also for edible oil oxidation using an oil-factory machine, the results for the linear vector kernel support machine, training accuracy and validation for C-SVM and Nu-SVM were 98, 97, 97 and 95%, respectively [].

## 4. Conclusion

In this study, the edible oil samples were purchased from a local market in Kermanshah and stored for 5 months under normal conditions to determine their shelf life. The oil data were collected by an E-Nose equipped with 8 MOS sensor and then analyzed by different methods. Based on the CA results, all the samples were classified into two groups of oxidized and non-oxidized oils which are in line with the AOCS method. Furthermore, the SVM method possessed higher accuracy in the determination of the shelf life of the edible oils as compared with QDA and LDA methods. The classification precision of SVM, QDA, and LDA was 96.25%, 95.8%, and 94.4%, respectively.

## CRediT authorship contribution statement

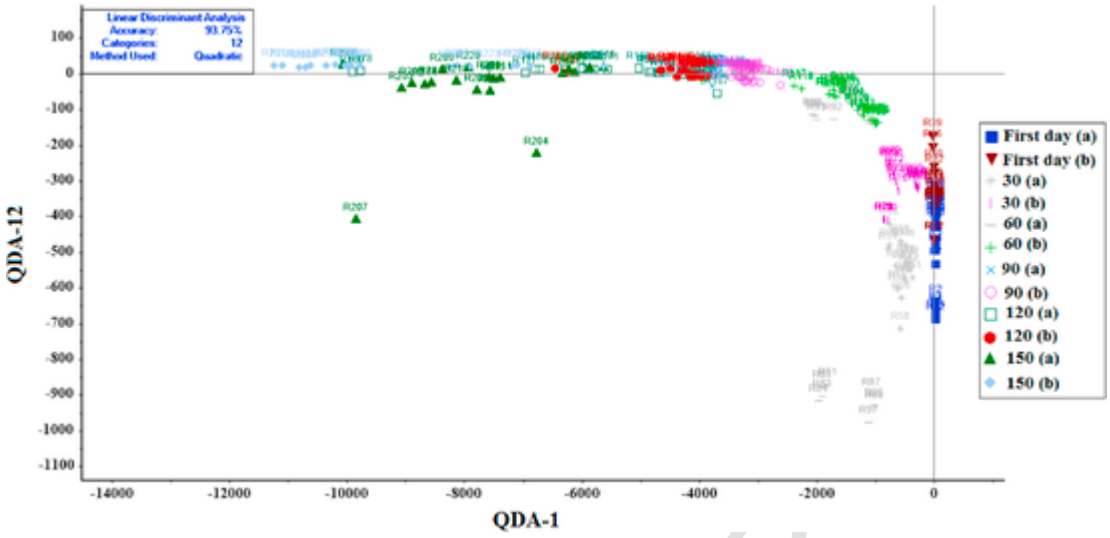


**Fig. 6.** Classification Intergroup of the edible oils shelf life using QDA method.

**Table 5**
Confusion matrix of the edible oils shelf life per month classification using LDA and QDA methods.

| Model | Months of storage | 0(a) | 0(b) | 1(a) | 1(b) | 2(a) | 2(b) | 3(a) | 3(b) | 4(a) | 4(b) | 5(a) | 5(b) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| LDA | **0(a)** | 17 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | **0(b)** | 3 | 19 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | **1(a)** | 0 | 0 | 20 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | **1(b)** | 0 | 0 | 0 | 20 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | **2(a)** | 0 | 0 | 0 | 0 | 12 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | **2(b)** | 0 | 0 | 0 | 0 | 8 | 18 | 0 | 0 | 0 | 0 | 0 | 0 |
| | **3(a)** | 0 | 0 | 0 | 0 | 0 | 2 | 18 | 0 | 0 | 0 | 0 | 0 |
| | **3(b)** | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 20 | 1 | 0 | 0 | 0 |
| | **4(a)** | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 13 | 1 | 2 | 2 |
| | **5(b)** | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 4 | 18 | 0 | 0 |
| | **5(a)** | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 16 | 0 |
| | **5(b)** | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2 | 0 | 2 | 18 |
| QDA | | | | | | | | | | | | | |
| | **0(a)** | 19 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | **0(b)** | 1 | 20 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | **1(a)** | 0 | 0 | 20 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | **1(b)** | 0 | 0 | 0 | 20 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | **2(a)** | 0 | 0 | 0 | 0 | 15 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | **2(b)** | 0 | 0 | 0 | 0 | 5 | 19 | 1 | 0 | 0 | 0 | 0 | 0 |
| | **3(a)** | 0 | 0 | 0 | 0 | 0 | 1 | 19 | 0 | 0 | 0 | 0 | 0 |
| | **3(b)** | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 20 | 0 | 0 | 0 | 0 |
| | **4(a)** | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 18 | 1 | 0 | 0 |
| | **5(b)** | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 2 | 19 | 1 | 1 |
| | **5(a)** | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 18 | 1 |
| | **5(b)** | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 18 |

**Hamed Karami:** Investigation, Conceptualization, Methodology, Formal analysis, Software, Writing - original draft, Data curation, Review & editing. **Mansour Rasekh:** Project administration, Formal analysis, Funding acquisition, Review & editing. **Esmaeil Mirzaee – Ghaleh:** Supervision, Investigation, Conceptualization, Methodology, Review & editing, Resources.

## 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.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemolab.2020.104165.

**Table 6**
Performance parameters of LDA and QDA models for classification Intergroup of the edible oils shelf life.

| Model | Months of storage | Accuracy | Precision | Sensitivity | Specificity | AUC |
|---|---|---|---|---|---|---|
| **LDA** | **0(a)** | 0.981 | 0.944 | 0.850 | 0.995 | 0.922 |
| | **0(b)** | 0.986 | 0.864 | 1.000 | 0.984 | 0.992 |
| | **1(a)** | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| | **1(b)** | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| | **2(a)** | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| | **2(b)** | 0.962 | 0.692 | 1.000 | 0.958 | 0.979 |
| | **3(a)** | 0.990 | 0.900 | 1.000 | 0.990 | 0.995 |
| | **3(b)** | 0.990 | 0.909 | 1.000 | 0.989 | 0.995 |
| | **4(a)** | 0.976 | 0.722 | 1.000 | 0.974 | 0.987 |
| | **5(b)** | 0.976 | 0.783 | 1.000 | 0.974 | 0.987 |
| | **5(a)** | 0.995 | 0.941 | 1.000 | 0.995 | 0.997 |
| | **5(b)** | 0.981 | 0.818 | 1.000 | 0.979 | 0.990 |
| **Average per class** | | **0.986** | **0.881** | **0.988** | **0.987** | **0.987** |
| **QDA** | **0(a)** | 0.995 | 1.000 | 0.950 | 1.000 | 0.975 |
| | **0(b)** | 0.995 | 0.952 | 1.000 | 0.995 | 0.997 |
| | **1(a)** | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| | **1(b)** | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| | **2(a)** | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| | **2(b)** | 0.971 | 0.760 | 1.000 | 0.968 | 0.984 |
| | **3(a)** | 0.995 | 0.950 | 1.000 | 0.995 | 0.997 |
| | **3(b)** | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| | **4(a)** | 0.995 | 0.947 | 1.000 | 0.995 | 0.997 |
| | **5(b)** | 0.976 | 0.792 | 1.000 | 0.974 | 0.987 |
| | **5(a)** | 0.995 | 0.947 | 1.000 | 0.995 | 0.997 |
| | **5(b)** | 0.995 | 0.947 | 1.000 | 0.995 | 0.997 |
| **Average per class** | | **0.993** | **0.941** | **0.996** | **0.993** | **0.994** |



**Table 7**
Results and comparison of Nu-SVM and C-SVM models subjected to the kernel functions.

| Kernel function | C-SVM | | | | Nu-SVM | | | |
|---|---|---|---|---|---|---|---|---|
| | C | γ | Train | Validation | Nu | γ | Train | Validation |
| **Categories 6** | | | | | | | | |
| linear | 10 | 1 | 96.25 | 95 | 0.225 | 1 | 96.25 | 95.14 |
| Polynomial | 100 | 100 | 75.83 | 75.83 | 0.255 | 100 | 82.08 | 87.92 |
| Radial basis function | 10 | 1 | 95.42 | 92.5 | 0.255 | 10 | 96.25 | 95.83 |
| sigmoid | 100 | 0.01 | 96.25 | 95 | 0.05 | 0.01 | 95 | 90.14 |
| **Categories 12** | | | | | | | | |
| linear | 10 | 1 | 91.67 | 90.416 | 0.5 | 1 | 91.67 | 90.416 |
| Polynomial | 100 | 100 | 74 | 67 | 0.255 | 1 | 87.5 | 80 |
| Radial basis function | 100 | 10 | 90 | 89.58 | 0.255 | 10 | 92.92 | 89.17 |
| sigmoid | 100 | 0.1 | 91.67 | 89.583 | 0.05 | 0.01 | 91.67 | 89.583 |

## References


[1] V.N. Castelo-Branco, I. Santana, V.O. Di-Sarli, S.P. Freitas, A.G. Torres, Antioxidant capacity is a surrogate measure of the quality and stability of vegetable oils, Eur. J. Lipid Sci. Technol. 118 (2016) 224–235.

[2] E. Choe, D.B. Min, Mechanisms and factors for edible oil oxidation, Compr. Rev. Food Sci. Food Saf. 5 (2006) 169–186.

[3] Y. Yang, Q. Li, X. Yu, X. Chen, Y. Wang, A novel method for determining peroxide value of edible oils using electrical conductivity,, Food Contr. 39 (2014) 198–203.

[4] M. Wang, Z. Huyan, B. Jing, X. Mao, X. Yu, Analysis of edible oil oxidation based on changes in the electrical conductivity of the extracted aqueous phase, Eur. J. Lipid Sci. Technol. 121 (2019) 1800441.

[5] L. Xu, X. Yu, l. Liu, R. Zhang, A novel method for qualitative analysis of edible oil oxidation using an electronic nose,, Food Chem. 202 (2016) 229–235.

[6] L. Xu, X. Yu, L. Liu, R. Zhang, A novel method for qualitative analysis of edible oil oxidation using an electronic nose,, Food Chem. 202 (2016) 229–235.

[7] J. Li, W. Cai, D. Sun, Y. Liu, A quick method for determining total polar compounds of frying oils using electric conductivity,, Food Anal. Methods 9 (2016) 1444–1450.

[8] M. Śliwińska, P. Wiśniewska, T. Dymerski, J. Namieśnik, W. Wardencki, Food analysis using artificial senses, J. Agric. Food Chem. 62 (2014) 1423–1448.

[9] E.A. Baldwin, J. Bai, A. Plotto, S. Dea, Electronic noses and tongues: applications for the food and pharmaceutical industries, Sensors 11 (2011) 4744–4766.

[10] S. Mildner-Szkudlarz, H.H. Jeleń, R. Zawirska-Wojtasiak, The use of electronic and human nose for monitoring rapeseed oil autoxidation,, Eur. J. Lipid Sci. Technol. 110 (2008) 61–72.

[11] M.S. Cosio, D. Ballabio, S. Benedetti, C. Gigliotti, Evaluation of different storage conditions of extra virgin olive oils with an innovative recognition tool built by means of electronic nose and electronic tongue, Food Chem. 101 (2007) 485–491.

[12] M.J. Lerma-García, E.F. Simó-Alfonso, A. Bendini, L. Cerretani, Metal oxide semiconductor sensors for monitoring of oxidative status evolution and sensory analysis of virgin olive oils with different phenolic content, Food Chem. 117 (2009) 608–614.

[13] Y. Yin, Y. Zhao, A feature selection strategy of E-nose data based on PCA coupled with Wilks Λ-statistic for discrimination of vinegar samples,, J. Food Measure. Char. 13 (2019) 2406–2416.

[14] H. Zheng, S. Wang, X. Ping, C. Shao, H. Zhou, B. Xiang, J. Li, X. Lou, X. Yi, H. Guohua, Study of Spinyhead croaker (collichthys lucidus) fat content forecasting model based on electronic nose and non-linear data resolution model, Food Anal. Methods 12 (2019) 1927–1937.

[15] H. Zhiyi, H. Chenchao, Z. Jiajia, L. Jian, H. Guohua, Electronic nose system fabrication and application in large yellow croaker (Pseudosciaena crocea) fressness prediction, J. Food Measure. Char. 11 (2017) 33–40.

[16] H. Liu, Q. Li, B. Yan, L. Zhang, Y. Gu, Bionic electronic nose based on MOS sensors array and machine learning algorithms used for wine properties detection, Sensors 19 (2019) 45.

[17] E. Mirzaee-Ghaleh, A. Taheri-Garavand, F. Ayari, J. Lozano, Identification of fresh-chilled and frozen-thawed chicken meat and estimation of their shelf life using an E-nose machine coupled fuzzy KNN, Food Anal. Methods 13 (2020) 678–689.

[18] T. Shi, G. Wu, Q. Jin, X. Wang, Camellia oil authentication: a comparative analysis and recent analytical techniques developed for its assessment. A review,, Trends Food Sci. Technol. 97 (2020) 88–99.

[19] S. Buratti, C. Malegori, S. Benedetti, P. Oliveri, G. Giovanelli, E-nose, e-tongue and e-eye for edible olive oil characterization and shelf life assessment: a powerful data fusion approach,, Talanta 182 (2018) 131–141.

[20] S. Okur, Z. Zhang, M. Sarheed, P. Nick, U. Lemmer, L. Heinke, Towards a MOF e-Nose: a SURMOF sensor array for detection and discrimination of plant oil scents and their mixtures, Sensors and Actuators B:, Chemicals 306 (2020) 127502.

[21] A.H. Gómez, J. Wang, G. Hu, A.G. Pereira, Monitoring storage shelf life of tomato using electronic nose technique, J. Food Eng. 85 (2008) 625–631.

[22] A.Z. Berna, J. Lammertyn, S. Saevels, C.D. Natale, B.M. Nicolaı¨, Electronic Nose Systems to Study Shelf Life and Cultivar Effect on Tomato Aroma Profile, Sensors and Actuators B: Chemical, 97, 2004, pp. 324–333.

[23] J. Brezmes, E. Llobet, X. Vilanova, J. Orts, G. Saiz, X. Correig, Correlation between Electronic Nose Signals and Fruit Quality Indicators on Shelf-Life Measurements with Pinklady Apples, Sensors and Actuators B: Chemical, 80, 2001, pp. 41–50.

[24] S. Saevels, J. Lammertyn, A.Z. Berna, E.A. Veraverbeke, C. Di Natale, B.M. Nicolaı¨, An electronic nose and a mass spectrometry-based electronic nose for assessing apple quality during shelf life, Postharvest Biol. Technol. 31 (2004) 9–19.

[25] A. Amari, N.E. Barbri, N.E. Bari, E. Llobet, X. Correig, B. Bouchikhi, Potential application of the electronic nose for shelf-life determination of raw milk and red meat, AIP Confer. Proc. 1137 (2009) 457–460.

[26] G. Cortellino, S. Gobbi, A. Rizzolo, Shelf life of fresh-cut lamb's lettuce (Valerianella locusta L.) monitored by electronic nose and relationship with chlorophyll a fluorescence and mechanical-acoustic test, Postharvest Biol. Technol. 136 (2018) 178–186.

[27] V. Giovenzana, R. Beghi, S. Buratti, R. Civelli, R. Guidetti, Monitoring of fresh-cut Valerianella locusta Laterr. shelf life by electronic nose and VIS–NIR spectroscopy, Talanta 120 (2014) 368–375.

[28] D. Chatterjee, P. Bhattacharjee, N. Bhattacharyya, Development of methodology for assessment of shelf-life of fried potato wedges using electronic noses: sensor screening by fuzzy logic analysis, J. Food Eng. 133 (2014) 23–29.

[29] C. Malegori, S. Buratti, S. Benedetti, P. Oliveri, S. Ratti, C. Cappa, M. Lucisano, A modified mid-level data fusion approach on electronic nose and FT-NIR data for evaluating the effect of different storage conditions on rice germ shelf life,, Talanta 206 (2020) 120208.

[30] F. Ayari, E. Mirzaee- Ghaleh, H. Rabbani, K. Heidarbeigi, Using an E-nose machine for detection the adulteration of margarine in cow ghee, J. Food Process. Eng. 41 (2018) e12806.

[32] H. Karami, M. Rasekh, E. Mirzaee-Ghaleh, Application of the E-nose machine system to detect adulterations in mixed edible oils using chemometrics methods, Journal of Food Processing and Preservation. 44 (9) (2020) e14696, doi:10.1111/jfpp.14696.

[33] K. Mahmodi, M. Mostafaei, E. Mirzaee-Ghaleh, Detection and classification of diesel-biodiesel blends by LDA, QDA and SVM approaches using an electronic nose, Fuel 258 (2019) 116114.

[34] K.N. Basri, M.N. Hussain, J. Bakar, Z. Sharif, M.F.A. Khir, A.S. Zoolfakar, Classification and Quantification of Palm Oil Adulteration via Portable NIR Spectroscopy, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 173, 2017, pp. 335–342.

[35] J. Läuter, McLachlan, J. Geoffrey, Discriminant Analysis and Statistical Pattern Recognition, John Wiley & Sons, Inc, New York, Chichester, Brisbane, Toronto, Singapore, 0-471-61531-5, 1992, p. 526 £ 92.00, Biometrical Journal, 35 (1993) 784–784.

[36] A. Sanaeifar, S.S. Mohtasebi, M. Ghasemi-Varnamkhasti, H. Ahmadi, Application of MOS based electronic nose for the prediction of banana quality properties, Measurement 82 (2016) 105–114.

[37] E. Goicoechea, M.D. Guillén, Volatile compounds generated in corn oil stored at room temperature. Presence of toxic compounds, Eur. J. Lipid Sci. Technol. 116 (2014) 395–406.

[38] G. Ngando, M.E.A. Mpondo, E.E.L. Dikotto, P. Koona, Assessment of the quality of crude palm oil from smallholders in Cameroon, J. Stored Prod. Postharvest Res. 2 (2011) 52–58.

[39] A.O.C. Society, AOCS Official Method Cd 3a-63 Acid Value Method, Official Methods and Recommended Practices of the AOCSChampaign, IL, 2003.

[40] A.O.C. Society, AOCS Official Method Cd 8b-90 Peroxide Value Acetic Acid-Isooctane Method, Official Methods and Recommended Practices of the AOCSChampaign, IL, 2003.

[41] R.D. O'Brien, Fats and Oils: Formulating and Processing for Applications, third ed., CRC Press, 2008.

[42] F. Shahidi, J. Wang, U. Wanasundara, 19 Methods for Measuring Oxidative Rancidity in Fats and Oils: Chemistry, Nutrition, and Biotechnology, fourth ed., 2017, pp. 519–542.

[43] G. Billek, G. Guhr, J. Waibel, Quality assessment of used frying fats: a comparison of four methods,, JAOCS (J. Am. Oil Chem. Soc.) 55 (1978) 728–733.

[44] N.N. Nkpa, F.C. Osanu, T.A. Arowolo, Effect of packaging materials on storage stability of crude palm oil, JAOCS (J. Am. Oil Chem. Soc.) 67 (1990) 259–263.

[45] F. Shahidi, Y. Zhong, Lipid Oxidation: Measurement Methods, 2005.

[46] J. Bonilla, L. Atarés, M. Vargas, A. Chiralt (Eds.), Edible films and coatings to prevent the detrimental effect of oxygen on food quality: possibilities and limitations, J. Food Eng. 110 (2012) 208–213.

[47] M. Lashgari, R. MohammadiGol, Discrimination of Golab apple storage time using acoustic impulse response and LDA and QDA discriminant analysis techniques, Iran Agric. Res. 35 (2016) 65–70.

[48] M.C. Cerrato Oliveros, J.L. Pérez Pavón, C. García Pinto, M.E. Fernández Laespada, B. Moreno Cordero, M. Forina, Electronic nose based on metal oxide semiconductor sensors as a fast alternative for the detection of adulteration of virgin olive oils, Anal. Chim. Acta 459 (2002) 219–228.

[49] B. Nouri, S.S. Mohtasebi, A. Jahanbakhshi, Application of an olfactory system to detect and distinguish bitter chocolates with different percentages of cocoa, J. Food Process. Eng. 42 (2019) e13248.

[50] A. Gorji-Chakespari, A.M. Nikbakht, F. Sefidkon, M. Ghasemi-Varnamkhasti, E.L. Valero, Classification of essential oil composition in Rosa damascena Mill. genotypes using an electronic nose, J. Applied Res. Med. Aromatic Plants 4 (2017) 27–34.

[51] M. Ghasemi-Varnamkhasti, A. Mohammad-Razdari, S.H. Yoosefian, Z. Izadi, G. Rabiei, Selection of an optimized metal oxide semiconductor sensor (MOS) array for freshness characterization of strawberry in polymer packages using response surface method (RSM), Postharvest Biol. Technol. 151 (2019) 53–60.

[52] H Karami, M Rasekh, E Mirzaee-Ghaleh, Qualitative analysis of edible oil oxidation using an olfactory machine, Journal of Food Measurement and Characterization 14 (5) (2020) 2600–2610, doi:10.1007/s11694-020-00506-0.