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INFORMATION PROCESSING IN AGRICULTURE 6 (2019) 20–25

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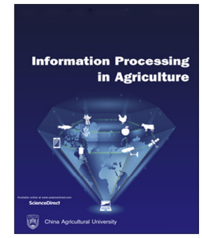

Determination of the oxidative stability of olive oil using an integrated system based on dielectric spectroscopy and computer vision

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ARTICLE INFO

Article history:
Received 16 May 2018
Received in revised form
30 July 2018
Accepted 16 August 2018
Available online 7 December 2018

Keywords:
Computer vision
Dielectric spectroscopy
Olive oil
Oxidative stability index

ABSTRACT

During storage, olive oil may suffer degradation leading to an inferior quality level when purchased and consumed. Oxidative stability is one of the most important parameters for maintaining the quality of olive oil, which affects its acceptability and market value. The current methods of predicting the oxidative stability of edible oils are costly and time-consuming. The aim of the present research is to demonstrate the use of dielectric spectroscopy integrated with computer vision for determining the oxidative stability index (OSI) of olive oil. The most effective features were selected from the extracted dielectric and visual features for each olive oil sample. Three machine learning techniques were employed to process the raw data to develop an oxidative stability prediction algorithm, including artificial neural network (ANN), support vector machine (SVM) and multiple linear regression (MLR). The predictive models showed a great agreement with the results obtained by the Rancimat instrument that was used as a reference method. The best result for modelling the oxidative stability of olive oil was obtained using SVM technique with the R-value of 0.979. It can be concluded that this new approach may be utilized as a perfect replacement for quicker and cheaper assessment of olive oil oxidation.
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1. Introduction

The temperature and concentration of dissolved oxygen in vegetable oils affects the activation energy and the mechanisms of oxidation reactions during oil storage. Degradation of olive oil quality is unavoidable and starts immediately after the olive oil extraction due to lipid oxidation, which may lead to rancidity or to hydrolytic degradations [1,2].

Virgin olive oil (VOO) generally provides greater resistance to oxidation than heat-extracted oil under normal storage conditions (12–18+ months), with resulting changes in sensory qualities [3]. The high resistance of VOO to oxidation is related to both its characteristic fatty acid composition (higher oleic acid concentration) and a considerable natural antioxidant content [4]. Hence, almost all of studies related to the oxidative stability of VOOs have generally been carried out during relatively high-temperature accelerated methods in order to improve the processing and storage conditions.

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Peer review under responsibility of China Agricultural University.
https://doi.org/10.1016/j.inpa.2018.08.008
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The Rancimat method is officially recommended and is most commonly employed for oxidative stability assessments of edible oils and fats [5]. This method can determine the period of time, known as oxidative stability index (OSI), that it takes for the maximum alteration to oxidation of oil or fat. OSI has a close correlation to the stability identified under various conditions for lipid oxidation [6]. Several analytical methods are also used to evaluate oxidative stability of oils, such as ultraviolet spectrophotometry [7], chromatographic methods [8], nuclear magnetic resonance [9], vibrational techniques [10,11], fluorescence spectroscopy [12], spectrofluorimetry [13] and differential scanning calorimetry [5,14]. The main drawback of such methods is that these are time consuming and costly.

The dielectric and colour properties of foods and agricultural products are known as valuable parameters in food engineering and technology [15–17]. Hence, dielectric spectroscopy [18–20] and computer vision technology [21,22] were widely considered in recent years for monitoring qualitative characteristics of olive oil. However, according to our knowledge, to date, no study in the literature on the use of dielectric and computer vision techniques has been reported for determination of the oxidative stability of olive oils.

The main aim of the present work was to evaluate an integrated system based on dielectric spectroscopy and computer vision as a low-cost, simple, rapid, non-destructive method for predicting the oxidative stability of VOO, which had been previously determined by the Rancimat method (reference method). The oxidative stability was predicted and compared by models developed using artificial neural network (ANN), support vector machine (SVM) and multiple linear regression (MLR).

2. Materials and methods

2.1. Sample preparation

The VOO was supplied by Etka oil company (Rudbar, Iran). The oils were stored at the temperature of 8 °C until the test time. In order to do the measurements under the accelerated storage condition, VOO was poured into glass bottles and kept open in the oven at 60 ± 1 °C. For 24 days, samples were taken out of the oven at 3-day intervals. Therefore, 9 steps of the oxidative stability measurement were carried out by the Rancimat test of samples. These 9 steps constituted different degrees of VOO oxidized in this study. The measurements were done with five replications of different samples for each day. All of the experiments in the laboratory were conducted at the temperature of 22 °C and the temperature was maintained constant with an accuracy of ±1 °C. Then, the ability of the integrated system was evaluated in predicting the oxidative stability.

2.2. Reference method: oxidative stability determination

The oxidative stability was measured by a Metrohm Rancimat model 743 (Herisau/Switzerland) as the reference analysis for all olive oil samples. Increasing the electric conductivity of the water was continually monitored while air (25 L/h) was bubbled into each oil (5 g) heated to 110 °C and their volatile oxidation products were collected in water. The OSI was expressed in hours, which is needed to reach the maximum change of conductivity, which is commonly named the induction period.

2.3. System structure

An integrated system based on dielectric spectroscopy and computer vision for quality evaluation of olive oil has been already developed by our research group and is shown in Fig. 1 [18]. The main components of this integrated system were composed of an AVR microcontroller (ATmega 16), parallel-plate capacitive sensor, signal generator unit, signal conditioning circuit (CE 8302), serial transmitter and the receiver port, digital camera (Canon, PowerShot SX220 HS), LCD display and a personal computer. The sensor was made in the form of a rectangular cube with two walls from an aluminium sheet and the other two walls were made of glass to let the light from the bulb to pass through the oil inside the sensor and reach the camera on the other side of the sensor.

The signal generator unit was used for generating 192 sine waves with different frequencies in the range of 40 kHz to 20 MHz. The output voltage of the sensor was sent to the AD8302 chip and compared with the input signal. The chip was used for measuring the gain ratio (dB) and the phase difference between two signals.

The dielectric properties (permittivity) of a material characterize the interaction of that material with electric fields. The relative complex permittivity (ε) describes permittivity related to free space as $\varepsilon = \varepsilon' - j\varepsilon'' = |\varepsilon|e^{-j\delta}$ where δ is the loss angle of the dielectric. The real part (ε') describes the capability of a material to store energy when it is subjected to an electric field and the imaginary part (ε'') is associated with the ability to dissipate energy in response to an applied electric field or various polarization mechanisms, which commonly results in conversion of electric energy to heat energy in the material. The amount of thermal energy converted in the food corresponds with the loss factor value [23]. It is worth mentioning that the phase shift and gain are related to the real and imaginary (loss factor) part of the complex permittivity of dielectric material in the sensor [24]. So, instead of measuring the complex permittivity of oil samples, the voltages corresponding to these parameters were used in this study to predict the oxidative stability of VOO. To analyze the obtained data, the measured voltages in different frequencies were transferred to a computer via USB.

For taking pictures of the oil samples, a box made of wood was used which was divided into two dark and bright parts. The two parts were separated by a plate with a square-shaped orifice in the middle. In the dark part, the camera lens was embedded and in the bright part, the halogen lamp was placed in order to illuminate. One of the glass sides of the sensor was stuck to the orifice so that the light passing through the oil could reach the camera placed in the dark side of the box. In order to have a more homogenous lighting on the sample, we used diffused lightning by putting a thick

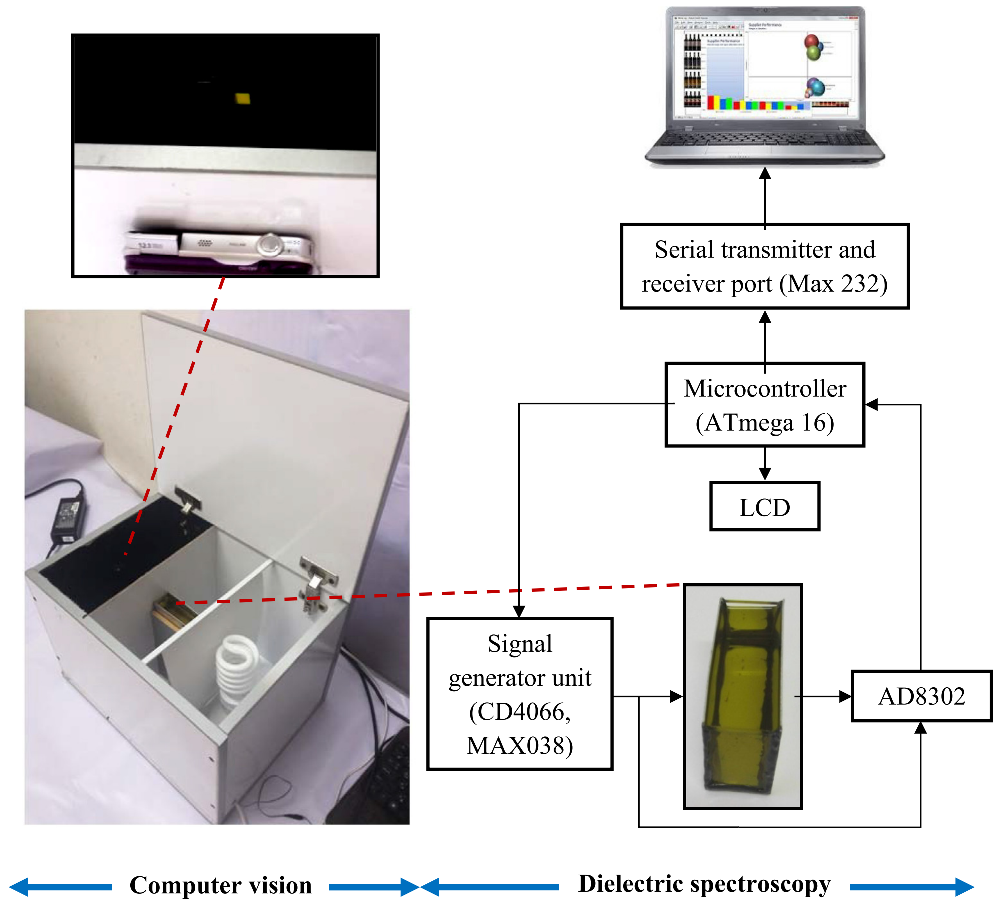

Fig. 1 – Schematic diagram of the set-up developed for quality evaluation of olive oil.

paper in front of the bulb. So the scene was being illuminated just by diffused lights reflecting from the side walls of the chamber. The oils images were acquired in the RGB colour space and, after that, they were converted to different colour spaces such as HSV and $L^*a^*b^*$ in order to get more information only appreciated in these spaces. The values describing the red, green, blue, hue, saturation, intensity, lightness, and also a^* and b^* chromatic components were determined on the surface of olive oils. The average value of each feature was used for further analysis. The extracted values were then averaged and saved for further analysis.

2.4. *Data analysis*

The 192 waves were produced in the range of radio frequency (40 kHz–20 MHz) and total 384 voltage values related to the real and imaginary part of complex dielectric permittivity were extracted as dielectric features of each sample. In addition, the 9 colour components were extracted in three different spaces as colour features of each sample. So, a total of 393 data were used as input features of each sample and the most effective features were selected by correlation-based feature selection (CFS) method. CFS algorithm selects discriminative features and eliminates irrelevant data and it can be effective in improving the robustness and rapidity of the system for monitoring quality characteristics of olive oil. CFS relies on a heuristic to evaluate the worth or merit of a subset of features. This heuristic considers the effectiveness of individual features for predicting the class label and also the level of intercorrelation among them. The hypothesis in this algorithm is: "Good feature subsets contain features highly correlated with the class, yet uncorrelated with each other" [25].

In the present study, the samples number for each degree of oxidation was 30 and a total of 270 samples consisted of 9 steps during 24 days storage. 50% of data set was randomly selected as the training set (135 samples), 20% for cross-validation (54 samples) and the remaining 30% of data set was used as the testing set (81 samples). The collected data was analyzed using an artificial neural network (ANN), support vector machine (SVM) and multiple linear regression (MLR) techniques. Detailed descriptions of these algorithms can be found in [15,18].

The obtained results were compared to find the best predictor for the oxidative stability index. The performances of the mentioned techniques were expressed in terms of the root mean square error (RMSE), mean absolute error (MAE) and correlation coefficient (R). These statistical criterions can be calculated as follows:

$$\mathrm{RMSE} = \sqrt{\frac{\sum_{i=1}^{n}(a_i - p_i)^2}{n}} \qquad (1)$$

$$\mathrm{MAE} = \frac{1}{n}\sum_{i=1}^{n}|a_i - p_i| \quad (2)$$

$$R = \frac{\sum_{i=1}^{n}(a_i - \bar{a})(p_i - \bar{p})}{\sqrt{\sum_{i=1}^{n}(a_i - \bar{a})^2 \sum_{i=1}^{n}(p_i - \bar{p})^2}} \quad (3)$$

where p_i is the predicted value, a_i is the actual value and n is the number of observations. All the evaluations have been performed in WEKA software.

3. Results and discussion

3.1. *VOO stability during storage*

The initial amount of the chemical parameters of the VOO samples related to oxidative status are presented in Table 1. All of these values are below the limits set by the European Commission Regulation (EEC) No. 2568/91 for VOO [26]. The changes in the OSI of VOO samples, regularly evaluated by the Rancimat test, are shown during 24 days storage at 60 °C in Fig. 2. A substantial decrease in the OSI of the oils observed during the entire period of storage and decreased from 27.2 to 16.63 h. Extrinsic factors such as storage temperature, diluted oxygen amount, and light, greatly influence the oxidative stability of olive oils [11]. Losing their oxidative stability during the oxidation can be anticipated that natural antioxidants like tocopherol and carotenoids are being slowly depleted.

3.2. *Oxidative stability prediction*

At first, the dimensions of the features of each VOO sample (393 dielectric and colour features) should be reduced. Using CFS algorithm, the size of the feature vector showed a reduction from 393 features to 65 features, including 62 dielectric voltages and 3 chromatic components (hue, saturation and b^*). In order to predict based on a fusion of dielectric spectroscopy and computer vision, several machine learning techniques were developed including ANN, SVM and MLR and the selected features were the input of these techniques. To choose the most effective technique, RMSE and R values for the test dataset (81 samples) were computed for each model.

The structure of ANNs has a significant influence on the learning rate and performance of a network. The numbers of neurons in the input (65 extracted features) and output (OSI) layers were fixed. In order to determine the best ANN structure, the different number of neurons (1–30) in the hidden layer was investigated. Fig. 3 shows the RMSE of ANNs with the different structure using the test data. Results showed the hidden layer with 25 neurons (i.e., 65-25-1 topology) achieved the lowest RMSE (0.778) and the highest R (0.978), compared to the other structures and its results had a perfect capability for OSI prediction.

Increasing the dimensionality of the feature vector provides the possibility to recognize the pattern while in the case of complex patterns it calls for a deep neural network or advanced machine learning techniques. In this study, 384 features were extracted from the dielectric measurements at numerous frequencies which significantly increased the dimensionality of the feature vector. It should be also noted that without the inclusion of these frequencies, predicting the oxidative stability was completely impossible because no significant difference was evident at most of the frequencies.

Several SVMs with different kernel functions were developed and tested for OSI prediction of VOO samples. In this study, four common types of kernel functions were used including polynomial, normalized polynomial, radial basis function (RBF) and Pearson VII universal kernel (PUK). Results showed that the normalized polynomial kernel function had the lowest value of RMSE (0.765) and the highest correlation coefficient (0.979) compared to the other kernels for modelling OSI of VOO samples (Table 2). The optimal cost value of SVM and the kernel parameters were selected by reducing the error in cross-validation. Fig. 4 shows the RMSE when the normalized polynomial kernel function was employed. For this kernel, the minimum error value was obtained when C value was equal to 100 and the kernel parameter was equal to 2.26.

The best results obtained from ANN and SVM techniques for prediction of oxidative stability index are compared with MLR technique in Table 2. As shown, all of the machine learning techniques used in this research showed acceptable performance in OSI prediction. Among predictive models, the SVM had the highest performance with R of 0.979, RMSE of 0.765 and MAE of 0.575, which indicated the efficiency of the model to perform the predictions. Therefore, the SVM model was proved useful to predict changes in the oxidative stability of VOO samples based on the fusion of dielectric

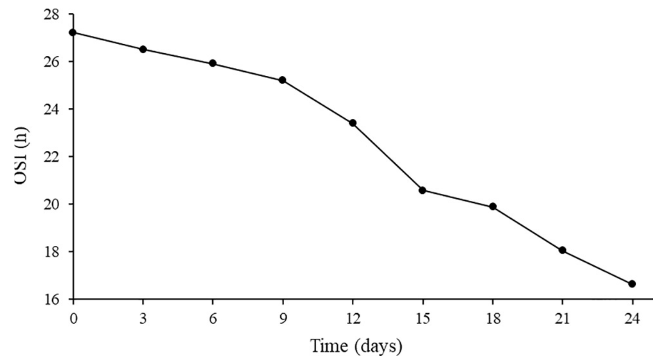

Fig. 2 – Changes in oxidative stability index (measured at 110 °C) of VOO samples subjected to accelerated storage conditions at 60 °C.

Table 1 – Initial quality indices of the virgin olive oil studied.

Parameters	Amount
Free acidity (FA) (oleic acid %)	0.89 ± 0.050
UV absorbance at 232 nm (K_{232})	1.898 ± 0.040
UV absorbance at 268 nm (K_{268}),	0.170 ± 0.008
Peroxide value (PV) (meq O_2/kg)	7.385 ± 0.521
P-Anisidine value (AV) (mg/kg)	3.371 ± 0.171
Total oxidation value (TOTOX)	18.141 ± 0.936
Chlorophyll (ppm)	8.763 ± 0.081
Carotenoid (ppm)	5.973 ± 0.151

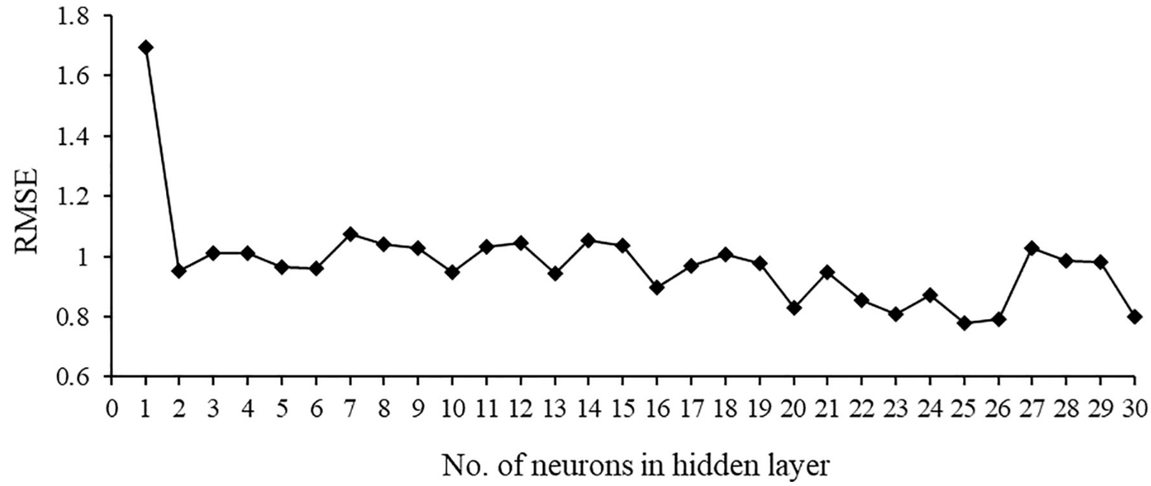

Fig. 3 – Variation of root mean square error criterion with the different neurons in the hidden layer.

Table 2 – Performance comparison of predictors for prediction of oxidative stability index based on statistical criteria.

	ANN	SVM				MLR
		Polynomial	Normalized polynomial	RBF	PUK	
R	0.978	0.975	0.979	0.978	0.966	0.974
RMSE	0.778	0.846	0.765	0.769	1.180	0.847
MAE	0.596	0.637	0.575	0.580	0.865	0.630

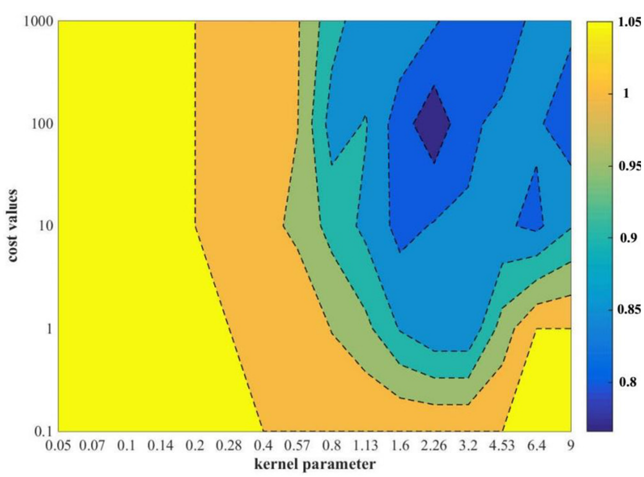

Fig. 4 – Variation of root mean square error criterion with C values ranging from 0.1 to 1000, using the normalized polynomial kernel function.

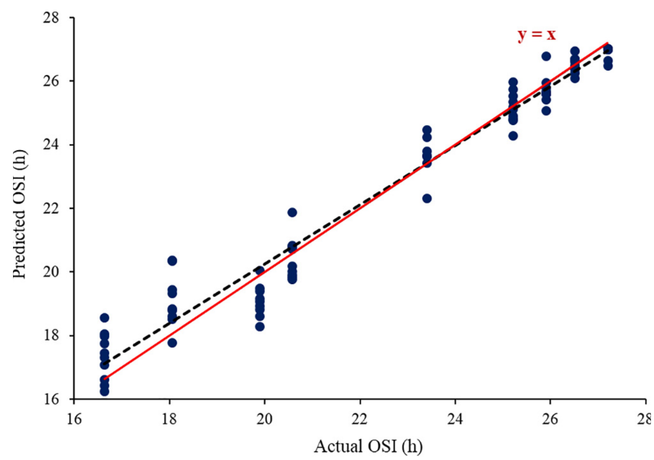

Fig. 5 – Correlation between the observed and predicted oxidative stability index of VOO samples by SVM model with the normalized polynomial kernel.

spectroscopy and computer vision. Fig. 5 presents the graphic of the reference versus the predicted oxidative stability values obtained using the testing set for the best model.

4. Conclusions

In this paper, an integrated system based on dielectric spectroscopy and computer vision was proven perfectly suitable as an analytical method to predict the oxidative stability of the olive oil. The prediction of the oxidative stability showed great agreement with the obtained results by the Rancimat instrument that was used as a reference method. Performance evaluation of the predictors indicated that the SVM technique with normalized polynomial kernel function was the best model with R of 0.979. The obtained results demonstrate that this fusion system can be an advantageous alternative approach for the evaluation of the oxidative stability of olive oils.

Conflict of interest

The authors declare that there is no conflicts of interest.

Acknowledgment

The authors express acknowledgement to Iran National Science Foundation (INSF) for their financial support under grant no. 95831975.

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