



Classification of organic olives based on chemometric analysis of elemental data

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ARTICLE INFO

Keywords:

Olive
Multivariate classification
ICP-OES
Chemometrics

ABSTRACT

The aim of this study was to discriminate organic from conventional olive samples based on the levels of macro and trace elements, combined with chemometric techniques. Ten elements (Na, K, Ca, Fe, Mg, Cu, Zn, Se, S and P) were determined in organic ($n = 30$) and conventional ($n = 30$) olive samples by inductively coupled plasma optical emission spectrometry analysis (ICP-OES). The classification of samples was performed by using a well-known chemometric techniques, linear discriminant analysis (LDA), partial least square-discriminant analysis (PLS-DA), support vector machine-discriminant analysis (SVM-DA), k-nearest neighbors (k-NN) and random forest (RF). The k-NN technique showed the best performance in discriminating organic from conventional samples (Accuracy: 94%) using all chemical variables. After variable reduction, an accuracy of 83% was found by using only the elements K and P. The use of a fingerprint based on multielemental levels associated with classification chemometric techniques may be used as a simple method to authenticate organic olive samples.

1. Introduction

There is a growing demand for products obtained in an organic or ecological way, for which this phenomenon creates a new market for products of vegetable origin. Foods are considered organic when they (or their ingredients) are produced according to specific rules, which avoid external substances, such as pesticides, hormones or chemical fertilizers [1, 2].

Certified organic products are generally more expensive than their conventional counterparts. Nevertheless, production costs for organic foods are typically higher because of greater labor inputs per unit. However, customers who recognize organic food are willing to pay their premium price because they are relatively healthier and friendlier to the environment. In the case of organic foods, authenticity is an important issue and a current concern of the food industry. Customers must rely on certificates to confirm the identity of the organic foods, so it is important to have authenticity control systems. The farming system, whether conventional or organic, influences the composition of nutrients in the fruits. Several studies reported authentication models for different organic food by using diverse analytical techniques [3–7].

Inductively coupled plasma optical emission spectrometry analysis (ICP-OES) is a safe technique for simultaneous, precise and rapid determination of chemical elements in complex matrices [8]. In this work, ICP-OES in combination with the microwave-assisted acid digestion was applied to measure ten element concentrations (Na, K, Ca, Fe, Mg, Cu, Zn, Se, S and P) in olives. Nevertheless, to our knowledge, there are no reports of olives classification conducted with samples that were grown in organic and/or conventional production systems from Argentina.

The aim of the current study was to evaluate the multi-elemental information obtained by ICP-OES in combination with chemometrics, to authenticate olive fruit samples according to agricultural system production.

2. Material and methods

2.1. Olive samples

The olive sampling was carried out in four olive farms located in two departments (Tinogasta and Pomán) of Catamarca province

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(Argentina) during 2016–2017. Two establishments in the department of Tinogasta (28°04'00"S 67°34'00"W), and two in the department of Pomán (28°10'26"S 66°12'41"W), that is, one farm of each department produce organic olives. The botanical varieties selected were: *Arbequina* and *Arauco*. Regarding the botanical varieties, all the farms produce both of the studied varieties. A total of 60 samples of olive fruits, organic ($n = 30$) and conventional ($n = 30$), were taken from the internal and external parts of the trees. Once in the laboratory, all fruits were cleaned and washed with deionized water. Olive seeds were removed, and the flesh was cut into small portions with a plastic knife. The edible part of the fruit was homogenized with a domestic mixer, and immediately stored in polyethylene bags and frozen at $-20\text{ }^{\circ}\text{C}$ in a freezer until analysis.

2.2. Sample digestion

Prior to use, all plastic containers were soaked in 10% v/v sub-boiling HNO_3 for at least 24 h, and then rinsed extensively with high-purity deionized water. The digestion procedures were adapted from the Milestone SK-10 High Pressure Rotor application book (Application note HPR-AG-03). An accurately weighed mass (500 mg) of each sample was mixed into a microwave-closed vessel with 6 mL of HNO_3 (65%, v/v) and 2 mL of H_2O_2 (30%, v/v), and placed in the microwave oven. An optimized temperature program with three stages was applied: 25–200 $^{\circ}\text{C}$ for 15 min, then 200 $^{\circ}\text{C}$ for 15 min and 200–110 $^{\circ}\text{C}$ for 15 min, followed by ventilation until the digested solutions reached room temperature. Finally, the digested solutions were brought to 25 mL final volumes with high-purity water. For each sample, this digestion procedure was carried out in triplicate. A blank solution was prepared in the same way.

2.3. Reagents

High-purity deionized water with a resistivity of $18.2\text{ M}\Omega\text{ cm}^{-1}$ was obtained from a Milli-Q Pluswater purification system Millipore (Molsheim, France). Analytical reagent grade HNO_3 65% and ultra-pure grade 30% (m/m) H_2O_2 were acquired from Sigma (St. Louis, MO, USA). Nitric acid was additionally cleaned by sub-boiling distillation. Working standard solutions were prepared by dilution of a multi-element standard solution III for ICP (in 5% HNO_3) and a multi-element standard solution IV for ICP (in 10% HNO_3) TraceCERT (Sigma-Aldrich, St. Louis, MO, USA).

2.4. Instruments

The samples were digested by microwave-assisted digestion using an Ethos One microwave system (Milestone, Chicago, USA), equipped with programmable power control (maximum power 1600 W) and segmented rotor HPR 1000/10s (operating pressure up to 35 bar maximum; operating temperature 260 $^{\circ}\text{C}$ maximum) with 10 reaction vessels. The ICP-OES measurements were performed with a simultaneous ICP spectrometer (VISTA PRO, Varian, Mulgrave, Australia), which was equipped with a solid-state detector. Nebulization of samples was performed with an ultrasonic nebulizer with a desolvation system (U-5000 AT, CETAC Technologies, Omaha, NE). The operating conditions are summarized in Table 1. The lines that exhibited low interference, high analytical signal and background ratios were selected. These wavelengths were as follow: Ca 373.690 nm, Cu 324.754 nm, Fe 238.204 nm, K 769.897 nm, Mg 285.213 nm, Na 589.592 nm, P 213.618 nm, S 182.562 nm, Se 196.022 nm, and Zn 213.856 nm.

2.5. Analytical quality control

The accuracy of the method was evaluated by spike recovery studies for all analytes in randomly selected samples. Calibration curves were

Table 1

The operating conditions for ICP-OES analysis.

| | |
|-------------------------|------------|
| RF generator | 40.68 MHz |
| Forward power | 1.0 kW |
| Nebulizer | Ultrasonic |
| Plasma gas flow rate | 8.5 L/min |
| Auxiliary gas flow rate | 1.0 L/min |
| Sample gas flow rate | 0.5 L/min |
| Sample uptake rate | 1.5 mL/min |
| Observation height | 15 mm |
| Sample uptake delay | 30 s |

obtained at five different concentration levels in triplicate. Calibration ranges were modified according to the expected mineral concentration ranges. The detection limit (DL) for each analyte was calculated as three times the standard deviation, and the quantification limit (LQ) was calculated as ten times the standard deviation from the standard deviation of seven replicates of diluent blank. The precision of the proposed procedure was also evaluated by measuring the repeatability and reproducibility. In the repeatability test (within-day precision), a digested sample was analyzed three times within one day; and in the reproducibility test (day to-day precision), sample digestion and ICP OES analysis were studied by triplicate analyses of three samples on three days for a period of three weeks.

2.6. Data analysis

Based on the chemical analysis of the olive samples, a data matrix was constructed, in which the rows corresponded to the 60 samples from organic and conventional products and the columns to the ten mineral variables measured by ICP-OES. An autoscaling procedure was performed to overcome any influence of the different size of variable in the chemometric study.

Once the resulting matrix was obtained, the chemometric analysis was performed in two successive steps. First, to obtain a first approximation regarding the possibility of differentiating the different types of samples and visualizing their correlation with variables, principal component analysis (PCA) was carried out. Second, different chemometric pattern recognition techniques were used to develop mathematical models to predict the category of olive fruits (organic or conventional), according to multielemental information. In this work, the most frequently used techniques were tested: linear discriminant analysis (LDA), partial least square-discriminant analysis (PLS-DA), support vector machine-discriminant analysis (SVM-DA), random forest (RF) and k-nearest neighbors (k-NN). All calculations were made using Orange data mining toolbox in Python [9], and R-software version 3.2.0 [10] with caret package [11].

3. Results and discussion

3.1. Method validation

The proposed method was evaluated by using a series of validation experiments, which included tests for linearity, selectivity, accuracy, precision, detection limit and quantification limit. The LQs of most elements are below 2 mg/kg, which demonstrates that the method is suitable for elements determination in fruit samples. For K and Ca, which are macroelements in vegetables, the method met the determination requirements and the LQ were 6 mg/kg and 3.9 mg/kg, respectively. The measurements reliability was assessed by recovery of known added amounts of analytes in the matrix. The trueness of the method was investigated by means of average recoveries for three replicates of samples by adding a standard of a specific concentration. According to the different contents of elements in the flesh sample, the spiking concentrations of the various elements were different. The addition amount was 5 mg/kg for Ca, K, Mg, Na, P and S; and 0.5 mg/kg Cu, Fe,

Table 2

Detection limits (DL) and quantification limits (LQ) of elements achieved with ICP-OES, average precision for repeatability of solutions (RSD) and recoveries for spiked olive samples ($n = 3$).

| Element | DL (mg/kg) | LQ (mg/kg) | RSD (%) | Recovery (%) |
|---------|------------|------------|---------|--------------|
| Ca | 1.6 | 3.9 | 3.4 | 98.2 |
| Cu | 0.02 | 0.06 | 1.1 | 99.0 |
| Fe | 0.4 | 1.7 | 4.9 | 92.7 |
| K | 3 | 6 | 2.1 | 100.2 |
| Mg | 0.8 | 1.5 | 0.8 | 97.1 |
| Na | 0.2 | 0.7 | 1.5 | 102.2 |
| P | 0.055 | 0.185 | 0.9 | 98.5 |
| S | 0.009 | 0.030 | 2.7 | 96.0 |
| Se | 0.006 | 0.019 | 4.2 | 107.8 |
| Zn | 0.05 | 0.12 | 1.1 | 101.1 |

Se and Zn. The obtained recoveries ranged from 92.7% to 107.8% (Table 2), which confirmed that no significant elemental losses occurred during the digestion process. Repeatability and reproducibility precision were estimated using the described procedure, the relative standard deviations (RSD) were lower than 10.8 and 7.3% for all the elements for inter- and intra-day, respectively.

3.2. Olive fruits mineral contents

A total of sixty (60) olive samples were investigated in this study. Thirty (30) of them consisted of conventional olives and the remaining thirty (30) were organic olive samples. Each sample was independently microwave digested and analyzed in triplicate. Table 3 shows the range of concentrations of each element in the analyzed samples, according to their system of production. There were significant differences ($p < 0.05$) for all element concentrations between organic and conventional olives samples, except for Se. The decreasing sequence of the mean elemental level was: $K > Ca > P > Mg > S > Na > Fe > Se > Zn > Cu$. The levels of K, Fe and Cu were statistically higher in organic olive samples compared with conventional samples. Potassium is the most abundant element in the olive fruit, followed by calcium. The variations of element concentrations are related to olive varieties or the distribution of metals in the soil, as well as environmental and weather conditions during the ripening period [12].

Table olives and oil are two important products obtained from olive fruits. In this study, the concentrations of elements found in olive samples were lower than those found in black and green table olives from Turkey [13], except for Mg levels. However, the levels found in our samples were higher than those found in olive oil from Spain, except for Cu and Zn levels [14]. The organic farming system uses biological waste material as fertilizers instead of agrochemicals used in conventional production. The inorganic fertilizers traditionally used are based on phosphates that can increase the contribution of heavy metals to the crop [6]. Thus, organic olive samples have lower P concentrations than conventional olives. The t -test, assuming different variances, has shown that P concentration in conventional samples is higher than

Table 3

Element concentrations in olive samples determined by ICP-OES. Results expressed as median \pm standard deviation, (min-max). Concentration in mg/kg.

| Element | Conventional olive ($n = 30$) | Organic olive ($n = 30$) | Element | Conventional olive ($n = 30$) | Organic olive ($n = 30$) |
|---------|--------------------------------------|---------------------------------------|---------|-----------------------------------|-----------------------------------|
| Ca | 62.66 \pm 1.01 (60.03–64.77) | 60.54 \pm 0.75 (59.96–62.90) | Na | 10.35 \pm 0.94 (8.58–11.24) | 8.5 \pm 0.39 (8.25–9.38) |
| Cu | 0.42 \pm 0.03 (0.38–0.48) | 0.44 \pm 0.03 (0.32–0.42) | P | 54.93 \pm 4.81 (43.32–60.09) | 43.94 \pm 3.08 (41.56–51.84) |
| Fe | 2.42 \pm 0.11 (2.29–2.66) | 2.66 \pm 0.13 (2.40–2.79) | S | 23.84 \pm 5.25 (13.03–29.07) | 14.47 \pm 3.07 (12.73–22.89) |
| K | 216.05 \pm 8.98 (205.66–238.89) | 246.48 \pm 10.17 (222.60–253.51) | Se | 0.89 \pm 0.04 (0.81–0.97) | 0.90 \pm 0.06 (0.81–1.06) |
| Mg | 38.22 \pm 5.77 (24.24–42.51) | 25.61 \pm 5.31 (22.09–38.98) | Zn | 0.64 \pm 0.04 (0.54–0.70) | 0.62 \pm 0.05 (0.53–0.70) |

in organic samples.

3.3. Multivariate data analysis

3.3.1. Principal component analysis (PCA)

As preliminary stage, prior to the classification modelling, PCA was carried out for exploratory analysis. This technique was used to visualize the distribution of samples in a reduced-dimensional space to explore the presence of natural groups, outliers or trends in the data. The results for elemental concentrations in the 60 samples were arranged as a data matrix (60×10) using the element concentration as column and the samples as rows. Prior to the multivariate processing, the original variables were auto-scaled by subtracting the mean value of the variable and dividing it by the standard deviation, since the element concentrations were at different orders of magnitude.

In the PCA performance, the scores corresponding to the studied samples tended to group according to the production system used; this tendency was not observed when the geographic origin or botanical variety was considered. Possibly, the low grouping according to the geographical origin could be due to that both studied departments are in the same phytogeographic region of the Province of Catamarca (Phytogeographic Region of 'Monte'). In the biplot of the two first PCs (Fig. 1), representing 76.3% of the total variance, a natural separation between conventional and organic scores was detected; both groups are in separated regions of the space defined by PC1 vs PC2. The ORG samples showed positive scores on PC1 strongly associated with the higher concentrations of Fe and K; on the other hand, CNV samples showed negative scores on PC1, indicating higher levels of Ca, Mg, Na, S and P. Despite the natural separation between classes by PC1, a small overlap between the two categories can be observed when PC2 is also taking account. In summary, in this first step of the chemometric analysis, PCA showed that both classes (organic and conventional) can be discriminated with a certain degree of certainty, considering only the first PC. In addition, the relationship between the variables with the distribution of samples in both sets is clearly different. However, it is necessary to refine the proposed models for predictive purposes in future samples.

3.3.2. Classification of olive fruits

The goal of the supervised pattern recognition techniques is to create classification rules. Training set with known class memberships is used to calculate a classifier. A test set, containing objects not included in the training and also with known class memberships, serves to support the model built. In this work, we randomly selected a training data set (70% of the objects of the whole data matrix), and used the derived classification rule to predict the group membership of the remaining data. The random sampling was done according to the system of production (organic and conventional) of samples, to balance the class distributions within the splits (stratified sampling). Since the results gained in each split of the whole matrix depend on the choice of the test data, the procedure was repeated 100 times. This procedure

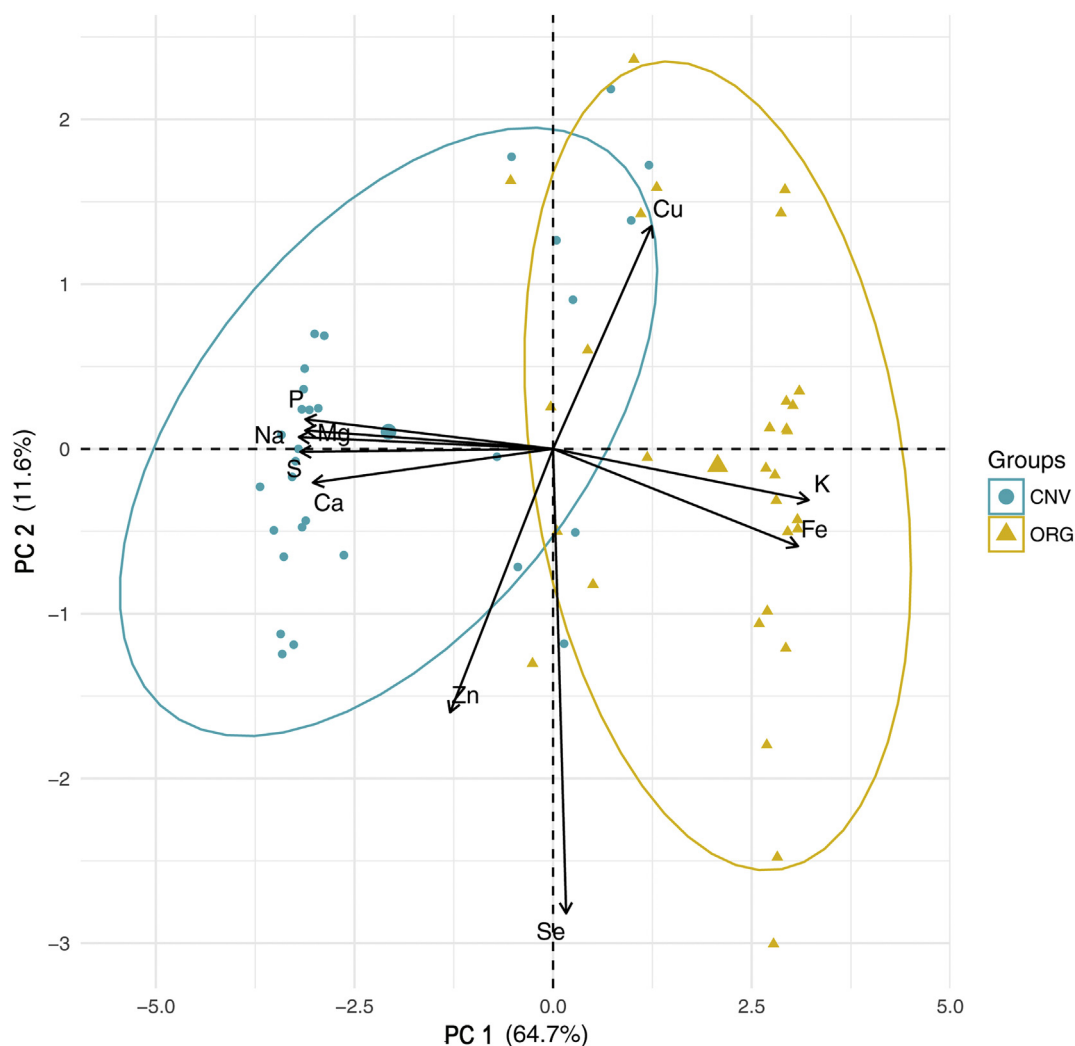


Fig. 1. Biplot of the first principal component (PC1) versus the second principal component (PC2).

gave a distribution for the misclassification rate, allowing comparison between the different discriminatory methods tested. The function “createdatapartition” (caret package) was used to create divisions of balanced data, allowing one to perform the random sampling within each class and preserve the distribution of classes in the subgroups. Regarding the reproducibility, the function “set.seed (seed)” was used, which is a random number generator in r-project software that allows reproduction of random objects as long as the same seed value is used.

PLS-DA, kNN and SVM need to optimize several features in such a way that a suitable number of parameters are selected to build the model. In this work, the choices of number of latent variables (LVs) for PLS-DA; number of neighbors (k) for kNN; penalty factor C , e of the ϵ -insensitive loss function, and kernel type for SVM, were calculated by using the ten-fold cross-validation technique by which maximum accuracy is selected. In addition, we ran the SVM with four types of kernel functions: linear, radial basis, polynomial and sigmoid. The best results were obtained when the radial kernel function was used for SVM. Once selected the optimal values for each model, the sensitivity (samples belonging to the class and classified correctly in this class), specificity (samples not belonging to the modeled class and correctly classified as not belonging), and the mean accuracy rate, were considered for the evaluation of the classification achieved with the multivariate methods [15]. Table 4 summarizes the results obtained after applying the different classification models. From the above analysis, we can see that the five models displayed different degrees of success. The best performance was achieved by using the k-NN technique, with a success

Table 4
Accuracy, specificity and sensitivity using different chemometric techniques.

| | Accuracy (%) | Specificity (%) | Sensitivity (%) |
|-----------------------------------|--------------|-----------------|-----------------|
| LDA | 83 | 89 | 78 |
| PLS-DA | 78 | 78 | 78 |
| SVM-DA | 78 | 56 | 100 |
| RF | 83 | 89 | 78 |
| k-NN (all variables) ^a | 94 | 89 | 100 |
| k-NN (using K and P) ^b | 83 | 89 | 78 |

^a $k = 5$.

^b $k = 7$.

rate of 94.4% ($k = 5$) in the test set and a better specificity of 100%. The order of successful identification rates was as follows: k-NN > RF > LDA > SVM-DA > PLS-DA (Table 4). As such, this method is accurate enough to employ this technique as a screening method for the discrimination of olive fruits according to their system of production.

In addition, the receiver operating characteristic (ROC) curves were used to evaluate the best three classification models, k-NN, SVM-DA and RF. The ROC curve is a useful statistical tool to assess classifier performance. Accuracy is measured by the area under the ROC curve (AUC) [16]. An area of 1 represents a perfect test; an area of 0.5 represents a worthless test. The examination of the AUCs of the different classifiers for organic and conventional samples was performed. In our study, the techniques whose AUC was > 0.7 were considered to play an

Target class: CNV
 Costs: FP = 500, FN = 500
 Target probability: 50.0 %

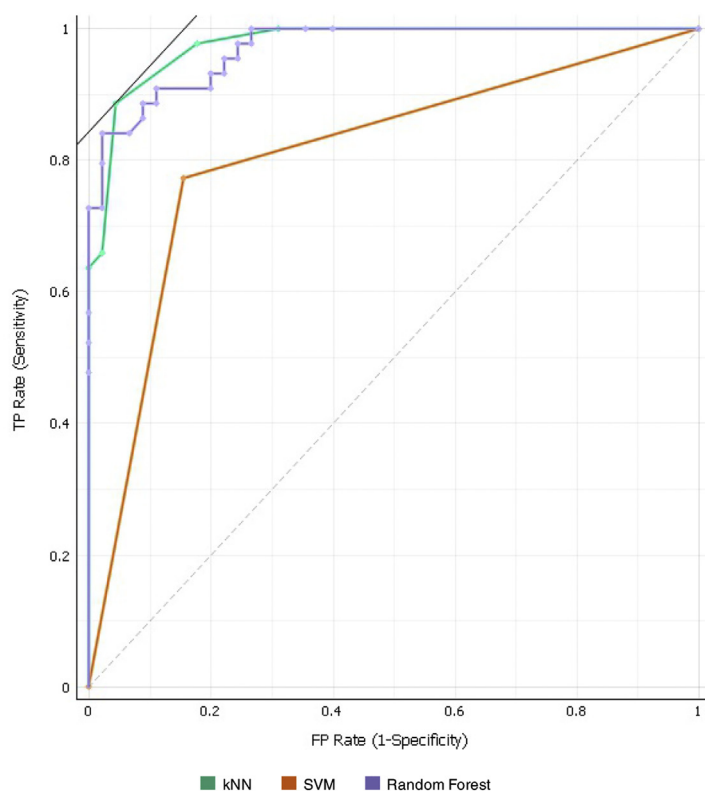


Fig. 2. ROC curve for comparison the performance of k-NN, SVM-DA and RF.

important role in olive authenticity. Fig. 2 show that k-NN (AUC = 0.984) and RF (AUC = 0.983) present better performance for authenticity of samples according to the production system.

Finally, the variable importance scores were computed in order to identify the key important parameters used by the RF classifier. After application of the RF to the data, most of the samples (83%) were correctly classified selecting the following variables: K and P. These results further confirm that the mayor element contents in olive fruit samples make their classification possible according to the system of production (organic and conventional) reasonably well (above 80%) by RF.

4. Conclusions

This paper describes an application of ICP-OES data to discriminate organic and conventional olive fruit samples. The concentrations of ten chemical elements (Ca, Cu, Fe, K, Mg, Na, P, S, Se and Zn) were analyzed using chemometric techniques such as PCA, LDA, PLS-DA, k-NN, SVM and RF. In particular, k-NN provided a robust approach for the authenticity evaluation of organic olive samples. The proposed model predicted the authenticity of organic olive samples with an accuracy of 94% when using the ten original elements. An accuracy of 83% was found when only the levels of elements K and P were selected. The use of a fingerprint based on major and trace elements levels associated with chemometric techniques may be used as a simple alternative for authenticity evaluation of organic olive samples.

Acknowledgements

This research was supported by Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) (PIF013/2017) and Secretaría General de Ciencia y Técnica of UNNE, Argentina.

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